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Ethanol to Ethyl Acetate

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# Ethanol to Ethyl Acetate

Abstract

Ethyl acetate is a specialty chemical with dominant use as a solvent, and total production exceeding 3.7MMT annually in 2017. Current production methods mainly utilize petrochemical-derived feedstocks of ethanol and acetic acid that undergo Fischer Esterification to produce ethyl acetate. This is traditionally considered to be an unsustainable process. A new startup company, Greenyug, based out of Santa Barbara, CA, has proposed a new design that solely utilizes fermentation ethanol, and, as a result, is considered sustainable. Greenyug describes (in accordance to US Patents US8562921B2, US9079851B2, and US9447018B2) a two-step reaction pathway that first partially dehydrogenates ethanol to acetaldehyde, then utilizes nucleophilic addition of ethanol to acetaldehyde to form ethyl acetate. This novel process makes use of reactive distillation to achieve both high conversion and selectivity in one reaction vessel, which is difficult to achieve with the current production methods. Technical and economic feasibility of Greenyug's process is investigated in this report.

A plant is designed to replicate Greenyug's newly constructed 50kT/year Columbus, NE facility. The process is composed of three main segments; one in which the main chemistry takes places through reactive distillation, and two in which separations occur. The final product is 99.8% ethyl acetate by mass and meets market purity specifications. The design requires an initial capital investment of $16.9MM, yields a fifteen year net present value (NPV) of $23.08MM, and has an estimated investor's rate of return (IRR) of 38.73%. The proposed process is expected to break even in Q1 2023. This investigation concludes that Greenyug poses a competitive threat to the ethyl acetate industry, from both a technical and economic standpoint.

Disciplines
Biochemical and Biomolecular Engineering | Chemical Engineering | Engineering
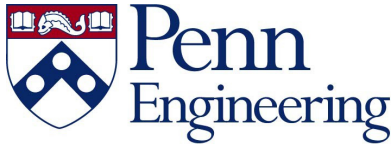
University of Pennsylvania, School of Engineering and Applied Science
Department of Chemical & Biomolecular Engineering
220 South 33rd Street
Philadelphia, PA 19104

23 April 2019

Dear Dr. Daeyeon Lee and Professor Bruce Vrana,

Enclosed is an analysis into the technical and economic feasibility of the Greenyug process: the sustainable conversion of ethanol to ethyl acetate. The following proposed process produces 50kT of ethyl acetate per year. The plant will be located in Columbus, NE, and in close proximity to the ADM corn plant. This allows for advantageous operation as the ethanol feedstock arrives at this plant via direct pipeline. The ethyl acetate produced has a weight purity of 99.8%, meeting market specifications.

This process makes use of three main unit operations, where the innovative technology stems from the reactive distillation. The ethanol is fed into the reactive distillation column, where it undergoes dehydrogenation, in the reactive zone located at the feed tray of the column. The ethyl acetate produced, along with the aldehyde/ketone byproducts, is fed into a hydrogenation reactor, modelled as a packed bed. This is required to convert the aldehyde/ketone byproducts into alcohol byproducts, as this would allow the byproducts to have a greater boiling point difference from ethyl acetate. This is important to ensure optimal separation of ethyl acetate from the byproducts. A distillation column is used to achieve this separation. One day's supply of ethanol is maintained and one week's supply of ethyl acetate remains on site before shipment to customers.

The plant will operate for 24 hours, 330 days a year, with ethanol available at a market price of $0.21/lb and ethyl acetate sold at a market price of $0.42/lb. Our team investigated the economic feasibility of this process by assuming conservative estimates for equipment costs and operating costs. The base case economic model suggests that this process yields a NPV of $23.08MM and an investor's rate of return (IRR) of 38.73%. This analysis is conservative in its approach as it does not assume the need for a green premium, even though the ethyl acetate produced is sustainable and could warrant the premium. We conclude that this process allows Greenyug to be a viable competitor and threat to the ethyl acetate market, both from an economic and technical standpoint.

Sincerely,

—————————————   —————————————   —————————————
Kerri Heuser   Vinson Liao   Neha Narain

Ethanol to Ethyl Acetate

Kerri Heuser, Vinson Liao, Neha Narain

Faculty Advisor: Dr. Daeyeon Lee
Project Author: Bruce Vrana

Contents

List of Tables

List of Figures

1 Abstract

Ethyl acetate is a specialty chemical with dominant use as a solvent, and total production exceeding 3.7MMT annually in 2017. Current production methods mainly utilize petrochemical-derived feedstocks of ethanol and acetic acid that undergo Fischer Esterification to produce ethyl acetate. This is traditionally considered to be an unsustainable process. A new startup company, Greenyug, based out of Santa Barbara, CA, has proposed a new design that solely utilizes fermentation ethanol, and, as a result, is considered sustainable. Greenyug describes (in accordance to US Patents US8562921B2, US9079851B2, and US9447018B2) a two-step reaction pathway that first partially dehydrogenates ethanol to acetaldehyde, then utilizes nucleophilic addition of ethanol to acetaldehyde to form ethyl acetate. This novel process makes use of reactive distillation to achieve both high conversion and selectivity in one reaction vessel, which is difficult to achieve with the current production methods. Technical and economic feasibility of Greenyug's process is investigated in this report.

A plant is designed to replicate Greenyug's newly constructed 50kT/year Columbus, NE facility. The process is composed of three main segments; one in which the main chemistry takes places through reactive distillation, and two in which separations occur. The final product is 99.8% ethyl acetate by mass and meets market purity specifications. The design requires an initial capital investment of $16.9MM, yields a fifteen year net present value (NPV) of $23.08MM, and has an estimated investor's rate of return (IRR) of 38.73%. The proposed process is expected to break even in Q1 2023. This investigation concludes that Greenyug poses a competitive threat to the ethyl acetate industry, from both a technical and economic standpoint.

2 Introduction

2.1 Background

Ethyl Acetate is a moderately polar solvent with volatile, non-toxic, and non-hygroscopic properties that make it a desirable product. It is commonly used as a solvent or a diluting agent, and can be found in several consumer products, including nail polish remover, paints, adhesives, wines, coffee, and tea.[1] Current global sales of ethyl acetate exceed \$4bn/year and are growing at a rate faster than that of global GDP. As of 2016, global demand for this product was 3.7MMT. A degree of excess capacity exists in the ethyl acetate market and is concentrated in the Asia-Pacific.

The current industry standard for the production of ethyl acetate revolves around the Fischer Esterification pathway. One feed material for this process is usually a variation or combination of synthetic and fermented ethanol. The other feed material is synthetic acetic acid, made from carbon monoxide and methanol. Therefore, at this time, the standard production process is not considered to be sustainable. The Fisher Esterification reaction takes place in a reactor, and its products are separated using distillation. An existing challenge is the ternary azeotrope that exists between ethanol, ethyl acetate, and water. To reach market standards, the final ethyl acetate product must meet a specification of 99.8% purity.

2.2 Motivation and Goals

Recent media reports of a company called Greenyug have captured the attention of several well-established companies in the ethyl acetate market. Greenyug is a small, privately-held startup company based in Santa Barbara. This company is commercializing a newly developed ethyl acetate production process that uses fermentation ethanol as its sole feedstock. Using 100% renewable resources makes this process more sustainable than the current in-

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[1] Statista [2018]

dustry standard. Greenyug claims that the process will be cost competitive, or even more economical than the current standard for ethyl acetate production. Though claims from startups are often far-fetched, Greenyug has already demonstrated its technology at a pilot plant in Pune, India, by building and starting up a commercial scale facility at ADMs corn processing plant in Columbus, NE that will produce 50 kT of ethyl acetate per year. The proximity to the ADM corn plant provides a logistical and economical benefit of ethanol supply; Greenyug is able to gain direct access through pipeline and could see a discounted ethanol price. These factors make Greenyugs claims feasible and could prove to be a concern for companies and jobs in this market.

Given the private nature of the company, there is virtually no public information about Greenyug and its process. The basis and majority of the data available is presented in three patents that Greenyug filed in 2012, 2013, and 2014 (Section 27.3). The overall main chemical reaction of this process is available and occurs as follows:

$$2CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + 2H_2$$
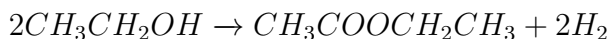
The patents also indicate the process uses reactive distillation technology to drive this reaction and make ethyl acetate in a simple, low-cost process. The patents also discuss the use of hydrogenation reactions to hydrogenate existing liquid co-products. The patents offer a good starting point for data and engineering design of the production plant, but the available public information is far from complete; this project thus makes a large number of assumptions to model this process.

The goal of this design project is to investigate the feasibility of Greenyugs process from both engineering and economic perspectives. The engineering aspects revolve around using the available information supplemented with several assumptions to reverse engineer the production process that Greenyug is using. From an economic viewpoint, this design project estimates Greenyugs operating and capital costs and estimates what green premium (if any)

Greenyug will need to receive to achieve at least a 15% IRR on their investment. Several other considerations are included, such as side reactions, the possibility of selling produced hydrogen, fluctuating market prices, and start-up, maintenance, and operational costs. The overall aim of this report is to determine if Greenyug will become a viable competitor to an already established company in the ethyl acetate industry.

3   Objective Time Chart

	Task Name	Start	ETA	January				February				March				April			
				Wk 1	Wk 2	Wk3	Wk4	Wk 1	Wk 2	Wk3	Wk4	Wk 1	Wk 2	Wk3	Wk4	Wk 1	Wk 2	Wk3	Wk4
1.0	**Preliminary Process Design**	1/15/2019	3/21/2019																
1.1	Mass Balance and Basic Block Flow Diagram	1/15/2019	1/20/2019																
1.2	Research Detailed Chemical Processes	1/18/2019	1/25/2019																
1.3	Preliminary ASPEN Simulation	1/22/2019	2/26/2019																
1.3	Finalize ASPEN Simulation	2/26/2019	3/21/2019																
2.0	**Equipment Design & Costing**	3/20/2019	4/18/2019																
2.1	Equipment Sizing and Design Calculations	3/20/2019	3/29/2019																
2.2	Preliminary Equipment Costing	3/25/2019	4/6/2019																
2.3	Finalize Equipment Costing	4/7/2019	4/21/2019																
3.0	**Profitability Analysis**	3/20/2019	4/18/2019																
3.1	Raw Material and Product Costing	3/20/2019	3/29/2019																
3.2	Profitability Measures	3/25/2019	4/6/2019																
3.3	Sensitivity Analyses	4/7/2019	4/21/2019																
4.0	**Report & Final Presesntation**	4/16/2019	4/30/2019																
4.1	First Draft Due April 16th	4/16/2019	4/16/2019																
4.2	Final Draft Due April 23rd	4/23/2019	4/23/2019																
4.3	Final Presentation Due April 30th	4/30/2019	4/30/2019																

Figure 1: Objective Time Chart for Ethanol to Ethyl Acetate Project

14

4 Innovation Map

N/A

5 Market and Competitive Assessment

5.1 Market Sizing and Applications

The global market consumption for ethyl acetate is currently 2,019,000 tonnes, set to grow at a CAGR of 5.75% between 2019 and 2023. On a global scale, Asia-Pacific is set to lead the market both in production and consumption of ethyl acetate.

The food and beverage segment accounts for the largest market share of ethyl acetate consumption, commonly using the chemical as synthetic flavoring. The widespread use of ethyl acetate across a diversity of flavorings, allows for ethyl acetate to be used in a versatile manner across regions. Analysts expect the general growth of the food and beverage sector to be the most significant driver of the growth of the ethyl acetate market[2]. The food and beverage sector in the US, for example, is set to see revenues increase at a CAGR of 11.0% between 2019 and 2023, resulting in a market volume of $27,300 MM by 2023[3]. Driving significant growth in the food and beverage sector is the increased prevalence of e-retail businesses and online food delivery patterns.

Looking specifically at the North American region, ethyl acetate is increasingly used in the decaffeination process to reduce caffeine in coffee, tea leaves, and cocoa. There has been increased investment in this application, and this points to the increased growth in the market, specifically in the North American region[4].

Ethyl acetate is also commonly used as a solvent for high-resolution printing inks and laminated adhesives in flexible packaging. Ethyl acetate is used in this application due to its fast evaporating properties. This application of ethyl acetate is significant in pointing towards a continued growth of the market as the manufacturing industry now looks to shift towards the class of flexible packaging. For example, flexible packaging allows for a greater ease of recycling, in comparison to rigid packaging. E-commerce plays a significant role here

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[2]Barnes [2018]
[3]Statista [2018]
[4]Anand, Koshy, and Arora [2018]

once again, as logistics companies and online businesses turn to flexible packaging options for shipment and delivery of products across the region.

Considering the variety of industries that rely on ethyl acetate and the growing regional demand for the product, the production of ethyl acetate is seen as a strong prospect for a business venture. Although it is without a doubt that the commodity already holds important clout with its customers, existing market leaders have already captured strong market share for ethyl acetate. The most attractive aspect of this process lies in its ability to yield sustainably produced ethyl acetate. The demand for green ethyl acetate is clear, whether the demand stems from regulations that require a sustainable approach, or from consumers who demand a sustainable chemical product. One example where sustainable ethyl acetate may be highly desirable is within the fragrances and perfume industry. This industry has seen consumers continuously search for sustainably produced products that limit environmental damage. The food and beverage industry is no different, with consumers often looking for sustainable ingredients and healthier alternatives[5].

5.2   Competitive Assessment

The specialty chemicals industry is usually dominated by large players, often those that have been established in the industry as a whole. Successful players in this industry are categorized by their ability to produce a suite of products that have interrelated economies of scale and cost benefits, rather than producing one specific chemical. The barriers of entry to the specialty chemicals industry are often high, limited by the significant capital requirements. For any new business in the industry, a unique value proposition is required, even if the business is able to bypass the capital requirements. In the case of Greenyug, the ability to be a first mover in the industry is key. For Greenyug, the unique value proposition lies in their ability to sustainably produce ethyl acetate. As mentioned above, this is the first commercialized process to produce green ethyl acetate.

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[5]Barnes [2018]

As the sustainably produced ethyl acetate product does not quite have an established market, it falls within the bounds of the current ethyl acetate market, and may have to face competitive forces that exist within this product market. This puts Greenyug at somewhat of a disadvantage, as they attempt to define a new market segment whilst continuously competing against existing giants in the field.

On a global scale, some of the most well known ethyl acetate competitors are INEOS (Switzerland), Celanese (USA), Carbohim (USA) and PT. IndoAcidatama Tbk (Indonesia)[6]. As mentioned previously, it is most likely that Greenyug's main competitors will be large and well-established chemical companies. As ethyl acetate is a relatively homogeneous product, it is likely that the main competitive metric will be the price.

5.3   Green Premium

As this process produces an ethyl acetate product that is considered to be more sustainable than the norm, the process may warrant the application of a green premium for the product. This green premium may bring a competitive edge for Greenyug, and could allow Greenyug to effectively compete against some of the larger players.

Based on a comprehensive study completed by the Nova-Institute, most participants (42%) indicated that the green premium for sustainable and bio-based products lies between 10-20%[7]. Participants of this study include major sustainable chemical producers located in the EU. It is therefore expected that Greenyug can apply a 15% green premium to the product price.

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[6]Anand, Koshy, and Arora [2018]
[7]Carus

6   Customer Requirements

The project objective requires 50kT of ethyl acetate to be produced per year. To compete with industry incumbents, a significantly high purity is required. From considering patent information and industry specifications, the goal purity for the green ethyl acetate product is 99.8%. The hydrogen byproduct in this process is burned for fuel value and this fuel value is assumed to be estimated at the current market price of natural gas. All other byproducts are considered to be waste products.

As mentioned in Section 5.2, Celanese is a major competitor and player in the ethyl acetate market. The purity specification for the ethyl acetate sold by Celanese is 99.7% , with a ethanol wt.% of 0.05% on the higher end. The sales specification sheet for Celanese (Section 27.5) indicates that the odor of the ethyl acetate product is nonresidual. The product is colorless, with a maximum of 10 Pt-Co Units.

The proposed process meets all of these customer requirements, and a detailed product composition can be seen in the ASPEN simulation output in Section 27.7.

7 Presented Innovation Edge

The proposed design provides an efficient process to produce cost-competitive, green ethyl acetate, compared to the traditional production process, outlined in Section 12.1. The traditional design relies heavily on product recycle to both increase conversion and yield, as well as improve separation efficiency in the process. Tweaking this recycle ratio has proven to be the major factor in determining the economics of the traditional process.

Greenyug's design solely utilizes fermentation ethanol as the feedstock for the process. The plant location has been strategically chosen to be within the vicinity of a corn facility, allowing for a reliable and potentially discounted source for feedstock material.

The process utilizes three major unit operations that can be easily scaled to meet customer demands. The first major unit operation mitigates the issue of low production conversion and selectivity. Reactive distillation shifts the equilibrium by continuously removing products from the reaction zone. The system can easily be scaled up past the current proposed 50kT production as both reaction equilibrium and column separation specifications are well understood for the process. To scale up the process, the column diameter can be increased and the appropriate heating and cooling equipment can be adjusted to account for additional feedstock. The other two major units accomplish the final separation to meet the desired 99.8% purity specification. These processes have been designed to avoid the issues that the traditional production process encounters. These two major unit operations have been designed such that independent scale up for a desired production output can be achieved. For example, there is no longer a need to include a recycle stream. This novel process allows for the creation of a high conversion, flexible, and profitable process that can easily be adapted to meet a variety of customer demands.

8 Critical-to-Quality Variables

N/A

9 Product Concepts

N/A

10 Superior Product Concepts

N/A

11 Competitive Patent Analysis

N/A

12 Preliminary Process Synthesis

12.1 Traditional Chemistry

Ethyl acetate is a specialty chemical product traditionally synthesized via acid-catalyzed Fischer Esterification of acetic acid and ethanol through the following overall reaction:

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$$
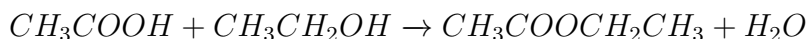
The conventional method uses acetic acid manufactured from syn-gas derived methanol and either petrochemical-derived or fermentation ethanol. The process can be considered "slightly green" due to the partial usage of fermentation ethanol. An example of the reaction schematic to produce ethyl acetate from raw materials is shown below, in Figure 2:
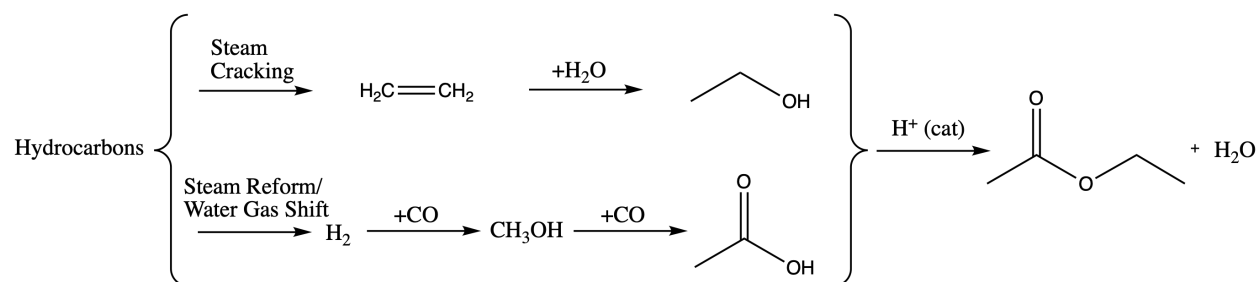
Figure 2: Overall reaction pathway to form ethyl acetate from raw materials.
Ethanol is synthesized from hydration of ethylene derived from steam cracking of hydrocarbons. Production of acetic acid is a two step process, which first requires the creation of syn-gas from hydrocarbons through Steam Reforming/Water Gas Shift, followed by methanol production. Finally, methanol undergoes carbonylation to form acetic acid. Ethanol and acetic acid react through acid-catalyzed Fischer Esterification to form the desired ethyl acetate and water.

The Dow Chemical Company[8] (formerly Union Carbide) and Celanese [9] have published patents on the process design to manufacture ethyl acetate using the Fischer Esterification reaction pathway. Ethyl acetate is produced by reaction over a strong sulfuric acid catalyst in a reaction vessel. The resulting vapors are passed through the bottom of a distillation

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[8]Papa and Bryant [1993]
[9]Horan, Murphy, Stephens, Warner, and Windhorst [2004]

column. A second distillation is performed to accomplish the desired separation for high purity ethyl acetate. A portion of the product is sent to the reaction vessel for usage as an azeotropic separation agent. For every mole of ester produced, a mole of water is also produced. Unfortunately, there is an excess of water in the system that exceeds the azeotrope between water and ethyl acetate and the desired separation cannot be achieved through distillation. Product is recycled into the distillation column to optimize the molar ratio between the ester and water in the system to allow for separation past the azeotrope. Adjusting this molar ratio in the distillation column is important for economic production of ethyl acetate.

12.2   Novel Chemistry

The novel reaction chemistry is a two-step reaction that utilizes ethanol as the initial feedstock as proposed by Gaspar et al.[10]. The first step, as shown below, involves a partial dehydrogenation of ethanol to acetaldehyde over a copper catalyst at elevated pressures and elevated temperatures below 250 °C.

$$CH_3OH \rightarrow CH_3COH + H_2$$

Acetaldehyde can be converted to ethanol through two possible mechanisms over a ZnO/Al_2O_3 catalyst via: (1) dimerization of acetaldehyde (Tischenko Reaction) or (2) nucleophilic addition of ethanol to acetaldehyde.

$$2CH_3COH \rightarrow CH_3COOCH_2CH_3 \tag{1}$$

$$CH_3COH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2 \tag{2}$$
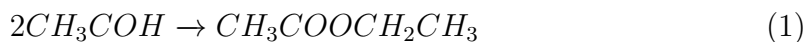
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[10]Gaspar, Esteves, Mendes, Barbosa, and Appel [2009]

Acetaldehyde can undergo various side reactions during the dimerization process through the mechanism[11] shown in Figure 3.
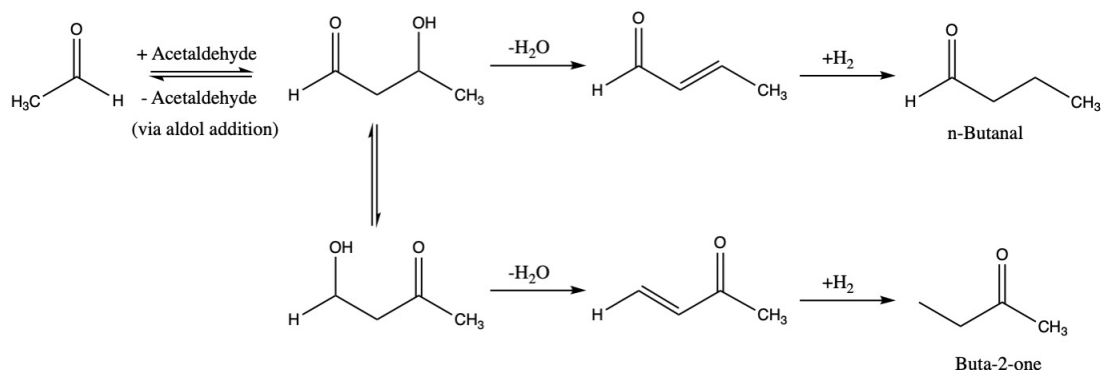
Figure 3: Byproduct Reactions in Novel Reaction Pathway. Acetaldehyde can undergo self-aldol addition, followed by dehydration, and then hydrogenation to form aldehyde and ketone byproducts.

Lab scale product selectivities and conversion data have been reported by Gaspar et. al [12], Gadewar [13], and Santacesaria et. al[14]. Equilibrium and kinetics of the two step process over $CuO/ZnO/Al_2O_3$ (40:40:20%, BASF K-310) have been reported by Carotenuto et. al[15] for (1) dehydrogenation of ethanol and (2) nucleophillic addition of ethanol to acetaldehyde. The temperature dependence of the equilibrium constant is shown below:

$$\ln(K_{eq}) = A + \frac{B}{T}$$

$$(1): A = 16.5, B = -9136.4$$

$$(2): A = -4.79, B = 4386.0$$

In a one pot synthesis, it is reasonable to assume that the dimerization reaction is outcompeted by the nucleophilic addition reaction, as excess ethanol is present. Therefore, the kinetics and equilibrium were not reported for the Tischenko reaction. At 200°C, where the reactions are reported to occur, the equilibrium constants are $K_{eq1} = 0.0599$ and $K_{eq2} = 88.476$,

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[11] Santacesaria, Carotenuto, Tesser, and Di Serio [2012]
[12] Gaspar, Esteves, Mendes, Barbosa, and Appel [2009]
[13] Gadewar [2013]
[14] Santacesaria, Carotenuto, Tesser, and Di Serio [2012]
[15] Carotenuto, Tesser, Di Serio, and Santacesaria [2013]

respectively. The nucleophilic addition of ethanol to acetaldehyde severely favors the products. Dehydrogenation of ethanol is reported to be the rate limiting step[16] in the process and can be seen from the relative ratio of the equilibrium constants.

Separation of the final product (ethyl acetate) from the resultant byproducts (namely, but-2-one and n-butanal) is difficult due to similarities in boiling point and volatility. Selective reduction of the ketone and aldehyde byproducts can allow for easier separation due to elevated boiling points from hydrogen bonding of the produced alcohols. The reactions are shown below:

$$HCOCH_2CH_2CH_3 + H_2 \xrightarrow{RaneyNi} CH_3CH_2CH_2CH_2OH$$

$$CH_3COCH_2CH_3 + H_2 \xrightarrow{RaneyNi} CH_3CH_2CHOHCH_3$$
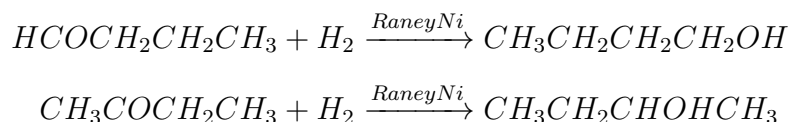
Oldenburg et. al [17] reports reaction conditions and kinetics of vapor phase hydrogenation of C4 ketones and aldehydes over Raney Nickel in a packed bed reactor using a simple power law expression. The rate constant was found to be 1st order in aldehyde/ketone partial pressure and $\frac{1}{2}$ order in hydrogen partial pressure.

In addition, separation between the reactants and desired products also proves to be a challenge in this process. Figure 4 shows the residue curves[18] at various pressures of the main reactants and products: hydrogen, acetaldehyde, ethanol, and ethyl acetate.

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[16] Carotenuto, Tesser, Di Serio, and Santacesaria [2013]
[17] Oldenburg and Rase [1957]
[18] Gadewar [2013]
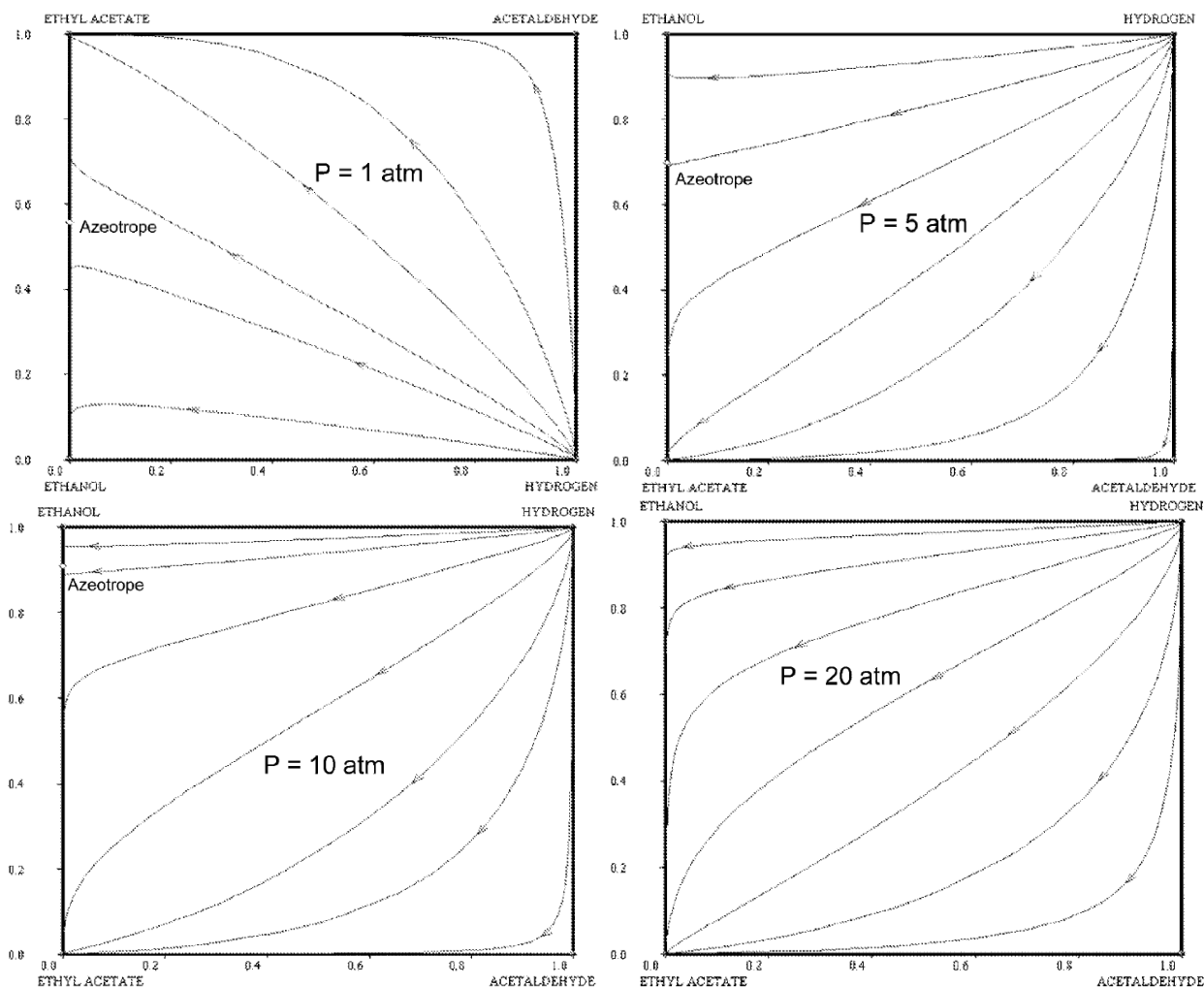
Figure 4: Residue curves between ethanol, acetaldehyde, hydrogen, and ethyl acetate. An azeotrope exists between ethyl acetate and ethanol at pressures below 13atm and makes separation difficult. At 20 atm (bottom right), residue curves show no evidence of azeotropes and all curves traverse towards the heaviest component, ethyl acetate.

12.3 Process Overview

Based on the patents and researched information, two possible configurations were proposed for the modeling of the ethyl acetate plant. The first configuration, shown in Figure 5, begins with a single feed of ethanol entering a reactive distillation column. A dehydrogenation zone exists within the column where the main reactions of the process, and associated side reactions, take place. Hydrogen exits from the top of this column. The bottoms products

include ethyl acetate and the byproducts that are produced in the reactive zone. The bottoms products are fed to a hydrogenation reactor that converts the byproducts to alcohols. The final step of the first configuration process consists of a separation process to isolate the ethyl acetate and achieve the 99.8% purity requirement. The second configuration, shown in Figure 6, differs from that of the first because the former includes the hydrogenation step inside the reactive distillation column. There are two feed streams entering the column, one of ethanol and one of hydrogen. The column then includes a hydrogenation zone below the dehydrogenation reactive zone. The bottoms products from this column are then sent directly to a separation process.
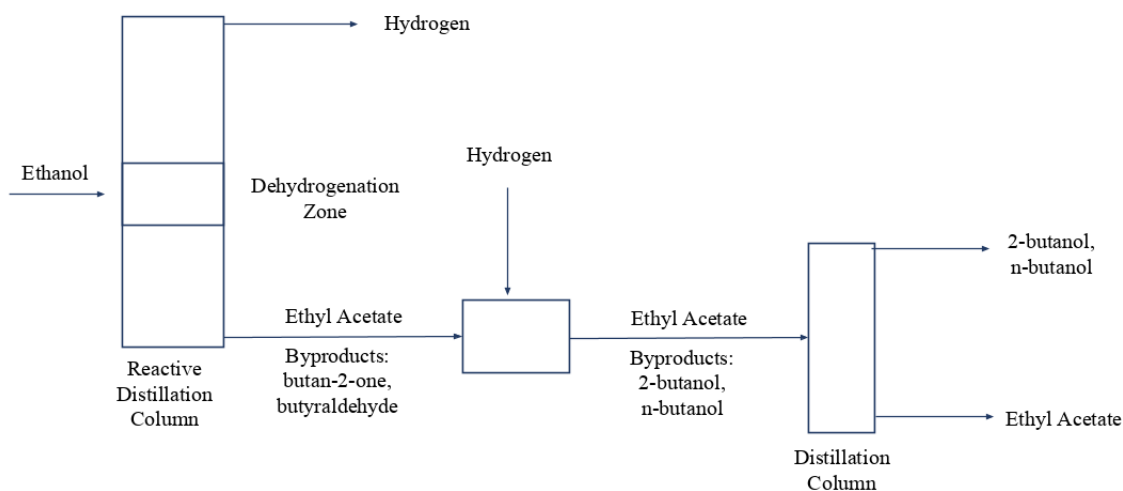
Figure 5: First proposed plant schematic based on initial patent information.
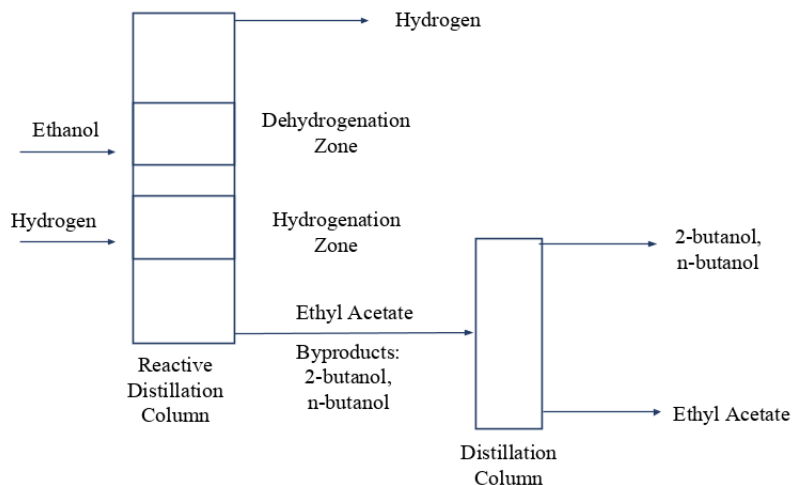
Figure 6: Second proposed plant schematic based on initial patent information

Taking into account both engineering and economic considerations, the first configuration was selected as the basis for this design project. This decision was made for several reasons. First, choosing the first proposed configuration avoids the complexity of embedding the hydrogenation reactor section into the reactive distillation column. This allows for a more simple model of the reactive distillation column itself. Additionally, guidance from industrial consultants points to the fact that combining the two reactions in this way would be more expensive than having two separate units. In addition to the cost of the reactive distillation column, this design choice also took into account the cost of the final separation process. Insight from industrial consultants also led to the belief that using the first proposed configuration would lead to a higher purity ethyl acetate stream entering the final separation process than that of the second configuration. In turn, this would lead to a lower cost for the final separation process because the separation would be achieved with a fewer number of stages. From an engineering standpoint, another important consideration came from the limited available patent information. The patents included data for a lab scale

model of the reactive distillation column. The data was provided for a reactive distillation column that included only a dehydrogenation reactive zone; i.e the column present in the first proposed configuration. Given that this lab scale information was the starting point for the modelling of the plant, this availability of lab-scale information greatly influenced the decision to choose the first configuration.

The chosen process can be viewed in three main unit operations: reactive distillation (C-101), hydrogenation (R-100), and separation processes (C-102). Several intermediate blocks are required to connect the three main unit operations. Figure 7 illustrates the overall process flow diagram, components of which are described in subsequent sections.
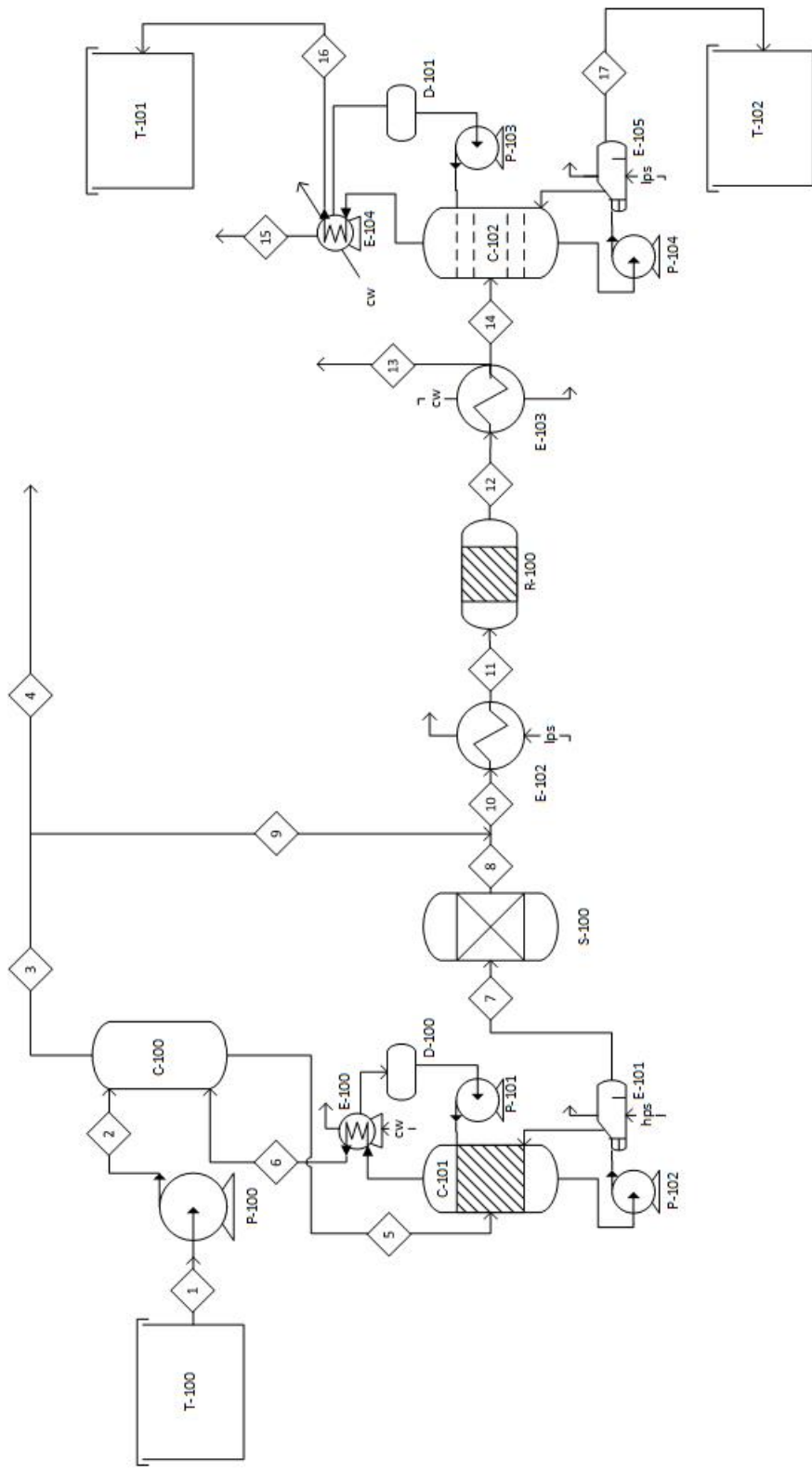
Figure 7: Overall Proposed Process Flow Diagram for Greenyug's Ethyl Acetate Plant

12.4 Reactive Distillation (C-101)

In the chosen configuration, a single stream of ethanol is fed to the reactive distillation column. Lab-scale data is available in the patents for the basis of modelling this column. Reactive distillation drives the chemical reaction by continuously removing its products.

The feed was chosen to be 200 proof liquid ethanol. This feed is provided from the neighboring ADM corn processing plant; the feed ethanol is assumed to arrive at Greenyug's plant through a direct pipeline. The liquid feed will be fed above the reactive zone of the column. The decision to use 200 proof ethanol was made to avoid introducing more water to the system than is already produced in the existent side reactions. The decision was also impacted by the proximity of Greenyugs commercial plant to ADMs corn processing plant. This will likely give Greenyug direct access as well as a possible discount to the ethanol needed for the process.

A key design consideration is the existence of the azeotrope between ethyl acetate, ethanol, and water, as discussed in Section 12.2. Available patent data shows that the binary azeotrope between ethyl acetate and ethanol disappears at pressures above 13 bar. This information, in addition to other research, led to the decision of operating the reactive distillation column at 20 bar.

The feed tray is assumed to be the reactive zone of the column. The entirety of the stage is packed with catalyst with a packing efficiency of 0.60[19]. The catalyst chosen was a physical mixture of Cuo/Al2O3 and ZnO/Al2O3. A list of potential catalysts studied by Gadewar[20] are shown in Table 1.

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[19]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]

[20]Gadewar [2013]

Table 1: Conversion and Selectivity for Catalysts in a Fixed Bed Reactor at 220°C, 1 atm
$CuO/ZnO/Al_2O_3$ provides the best conversion and selectivity

	As prepared/received		Reduced in H_2	
Catalyst Sample	Conversion	Selectivity	Convesion	Selectivity
$CuO/ZnO/Al_2O_3$	18.9	92.4	35.0	89.7
$CuO/Cr_2O_3/BaO$	43.5	89.4	36.0	74.6
CuO/SiO_2	19.6	96.2	22.5	80.9
CuO/Al_2O_3	50.2	47.3	-	-
CuO/ZnO	19.7	65.5	-	-
CuO/ZrO_2	41.5	63.4	-	-
$CuO/MgO/SiO_2$	37.9	70.0	32.1	65.7
$CuO/CaO/SiO_2$	33.3	73.4	29.0	42.7
$CuO/ZrO_2/SiO_2$	39.1	58.7	54.0	61.6

In the reducing conditions of the reaction, where two moles of hydrogen are produced for every mole of product, $CuO/ZnO/Al_2O_3$ provides the best selectivity for the desired products. Conversion is also relatively high; however, this is less of an issue as reactive distillation is being employed. High conversions can be achieved as product is being continually removed from the reaction zone to shift the equilibrium forward. In addtion, $CuO/ZnO/Al_2O_3$ is easily sourced, as it is the catalyst used for methanol synthesis.

Hydrogen and small amounts of acetaldehyde exit from the top of this reactive distillation column. The bottoms products include ethyl acetate, n-butanal, butan-2-one, and water.

12.5   Hydrogenation Reactor (R-100)

The boiling points at atmospheric pressure of ethyl acetate, n-butanal, and butan-2-one are 77°C, 79°C, and 74.8°C, respectively. These are much too similar to easily isolate ethyl acetate. Therefore, the bottoms products are fed to a hydrogenation reactor to convert the

byproducts to n-butanol and 2-butanol. These have boiling points at atmospheric pressure of 117°C and 100°C, respectively, allowing for a much easier separation of the byproducts from ethyl acetate.

This reactor also requires a hydrogen feed. As hydrogen is produced from the reactive distillation column, a fraction of the hydrogen can be used as a feed to this reactor. The reactor is a packed bed with Raney Nickel catalyst and is modelled using kinetics reported in literature, referred to in Section 12.2.

12.6 Distillation Column (C-102)

The patents pointed to the possibility that the final separation process would be liquid-liquid extraction (LLE). However, following industrial consultants' guidance, a distillation column is used instead. This decision was reached based on the belief that the relative difference in boiling points would allow for a cleaner split than the relative difference in solubilities. Thus, having a distillation column would be a more effective method of final separation.

The feed to this column consists of ethyl acetate, n-butanol, 2-butanol, and some hydrogen. The difference in boiling points allow for a relatively easy separation; ethyl acetate and hydrogen go to the top of the column while the heavier alcohols fall to the bottom. By adding a vent to the column's condenser, enough of the remaining hydrogen is released to allow for the final ethyl acetate product stream to reach the desired purity of 99.8%.

12.7 Intermediate Blocks

12.7.1 Stripper (C-100)

The output from the top of the reactive distillation column is a stream that consists mainly of hydrogen. As a hydrogen feed is needed later in the process, part of this stream is recycled. However, it was found that the stream was not quite pure enough to be a

successful feed to the hydrogenation reactor, as it contained a small yet significant amount of acetaldehyde. A stripper was added as an intermediate block. The pure ethanol feed to the process enters the stripper. Acetaldehyde is transferred from the hydrogen stream into the ethanol stream due to solubility differences. The hydrogen stream reaches a purity that is now acceptable for the hydrogenation reaction. A splitter is in place to send the desired amount of hydrogen back to the reactor and allows the rest of the hydrogen stream to be combusted to provide fuel value. The ethanol stream then enters the reactive distillation column. Acetaldehyde is the reaction intermediate, so it is more useful being present in the reactive distillation column than being vented.

12.7.2   Molecular Sieve (S-100)

Unfortunately, the side reactions that occur introduce water into the system. The water exits the reactive distillation column as part of the bottoms products stream. To resolve this issue, a molecular sieve is present in the process following the reactive distillation column. The bottoms products are fed in and the water is absorbed and removed from the stream. The resulting stream is then ready to be heated and sent to the hydrogenation reactor.

12.7.3   Flash Heat Exchanger (E-103)

Initially, the stream exiting the hydrogenation reactor was sent directly to the final distillation column. The amount of hydrogen present in the final column introduced a new problem. In order to obtain the desired purity of ethyl acetate, a significant amount of the product was also being lost through the vent of the column's condenser. To minimize the amount of product lost, a heat exchanger was added to the process before the final distillation column. This works to cool the stream to flash off a majority of the hydrogen from the stream before it enters the column. Less hydrogen then needs to exit through the vent of the condenser, and thus less ethyl acetate, allowing for the desired purity of the product stream with minimal product loss.

13   Assembly of Database

To produce ethyl acetate using the Greenyug process[21], ethanol is required as the sole feedstock. Spot prices from Bloomberg as of 16 April 2019 are used, with an ethanol purchase price of $0.21/lb and ethyl acetate selling price of $0.42/lb. Utility costs for cooling water, 150psig steam, 450psig steam, and electricity are sourced from Seider et. al[22]. To meet safety standards and improve heat integration, a flare system is employed and fuel value for the vented hydrogen co-product is accounted for. The monetary value of the combusted hydrogen is assumed to be equivalent to that of natural gas, taken from current market prices.

ASPEN Plus is utilized to design, simulate, and optimize the entire process. Initially, a non-random two-liquid model (NRTL) was chosen to account for azeotropes in the system. Residue curves produced in literature were compared to those created in ASPEN Plus to verify the thermodynamics of the model. Hydrogen was specified as a Henry Component and binary parameters were retrieved from associated databases.

The design process utilized RADFRAC blocks to model all columns and RPLUG to model packed bed reactors as plug flow reactors. HEATX blocks were used for heating and cooling of streams for heat integration. Initial parameters for distillation columns were estimated using either existing patent data or DSTWU. Kinetics for the relevant chemistry and reactions are described in Section 12.2 and are taken from reported expressions and values in literature.

Ethyl acetate is a Category 2 flammable liquid, and is toxic when ingested or inhaled. OSHA regulations limit exposure to concentrations below 400ppm 8-hour total weight average (TWA). Ethanol is a Category 3 flammable liquid and can cause severe eye and skin irritation. OSHA regulations limit exposure to concentrations below 1000ppm TWA. Both substances are stored in floating head storage tanks to account for volatility and flamma-

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[21]Gadewar [2013]
[22]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

bility concerns. Hydrogen is categorized as a Category 1 gas and is highly flammable. See Section 27.4 for all MSDS specification sheets. Trace amounts of vented hydrogen that are not used for fuel value motivated the inclusion of a flare system to combust the stream prior to release.

14 Process Flow Diagram and Material Balances
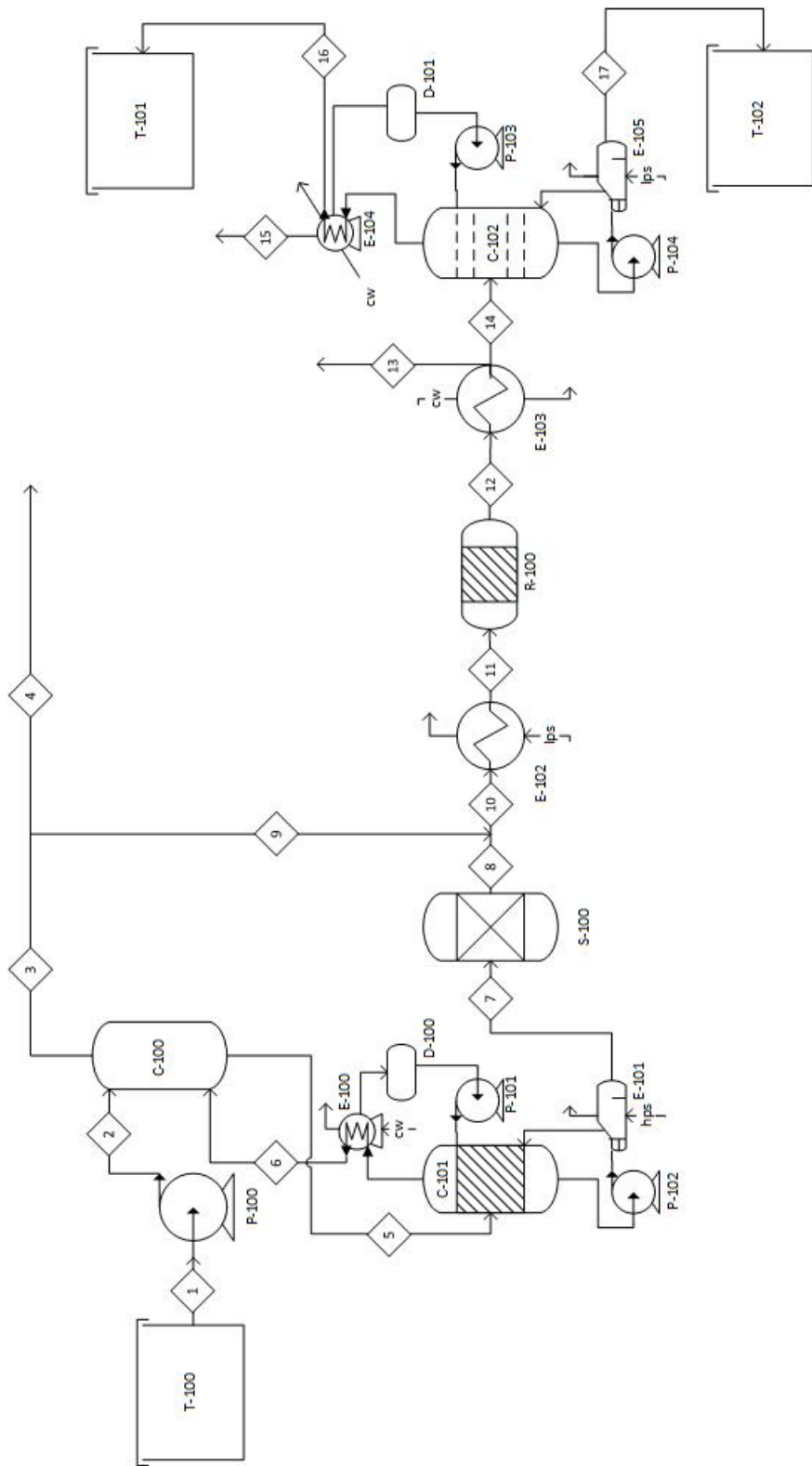
Figure 8: Overall Proposed Process Flow Diagram for Greenyug's Ethyl Acetate Plant

Table 2: Equipment Block List for Segment 001 of the Process Flow Diagram

Block Number	Block Type	Block Description
T-100	Tank	Feed Storage Tank
P-100	Pump	Feed Pump
C-100	Column	Stripping Column
C-101	Column	Reactive Distillation Column
E-100	Heat Exchanger	Reactive Distillation Column Condenser
D-100	Reflux Drum	Reactive Distillation Column Reflux Drum
P-101	Pump	Reactive Distillation Column Reflux Pump
P-102	Pump	Reactive Distillation Column Reboiler Pump
E-101	Heat Exchanger	Reactive Distillation Column Reboiler
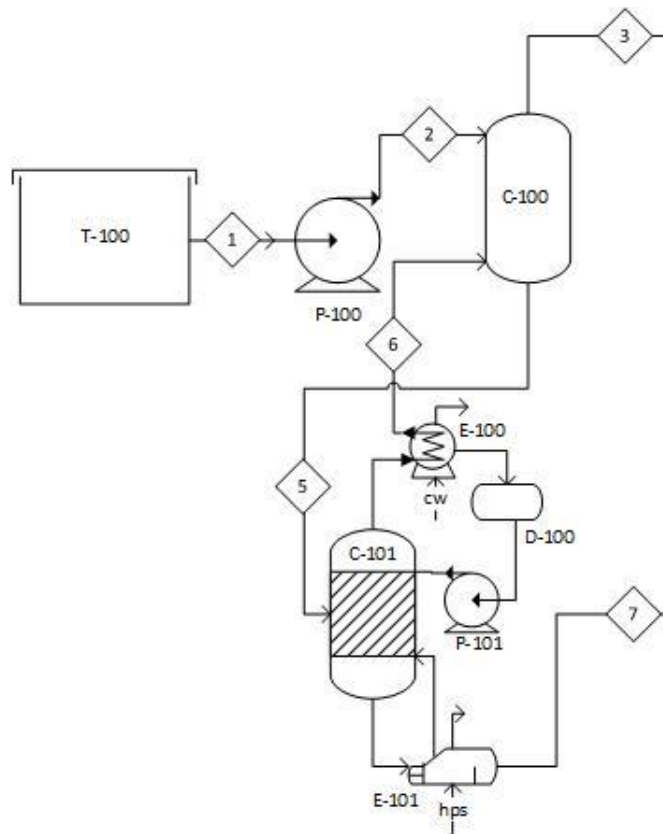
Figure 9: Segment 001 of the Process Flow Diagram

Table 3: Material Balance for Segment 001 of the Process Flow Diagram

Stream Number	1	2	3	5	6	7
Temperature (° F)	95.0	99.2	103.3	189.8	206.8	405.0
Pressure (bar)	1.0	20.0	20.0	20.0	20.0	20.0
Mass Flow (lb/hr)	13729	13729	710.5	16202	3184	13019
Component Mass Flow (lb/hr)						
Hydrogen	-	-	591.0	4.23	595.3	trace
Water	-	-	trace	331.0	331.0	40.2
Ethanol	13729	13729	119.5	13613	3.5	0.1
Ethyl Acetate	-	-	trace	1796	1796	12818
Acetaldehyde	-	-	0.0	454.8	454.8	0.0
Buta-2-one	-	-	trace	2.29	2.29	80.4
n-Butanal	-	-	trace	0.57	0.57	80.4
n-Butanol	-	-	-	-	-	-
2-Butanol	-	-	-	-	-	-
Molar Flow (lbmol/hr)	298.0	298.0	295.8	346.7	344.5	149.4
Volume Flow (cuft/hr)	279.5	280.5	6160	356.2	8494	348.3

Table 4: Equipment Block List for Segment 002 of the Process Flow Diagram

Block Number	Block Type	Block Description
S-100	Molecular Sieve	13X Molecular Sieve
E-102	Heat Exchanger	Double Piped Heat Exchanger
R-100	Reactor	Hydrogenation Reactor
E-103	Heat Exchanger	Double Piped Heat Exchanger
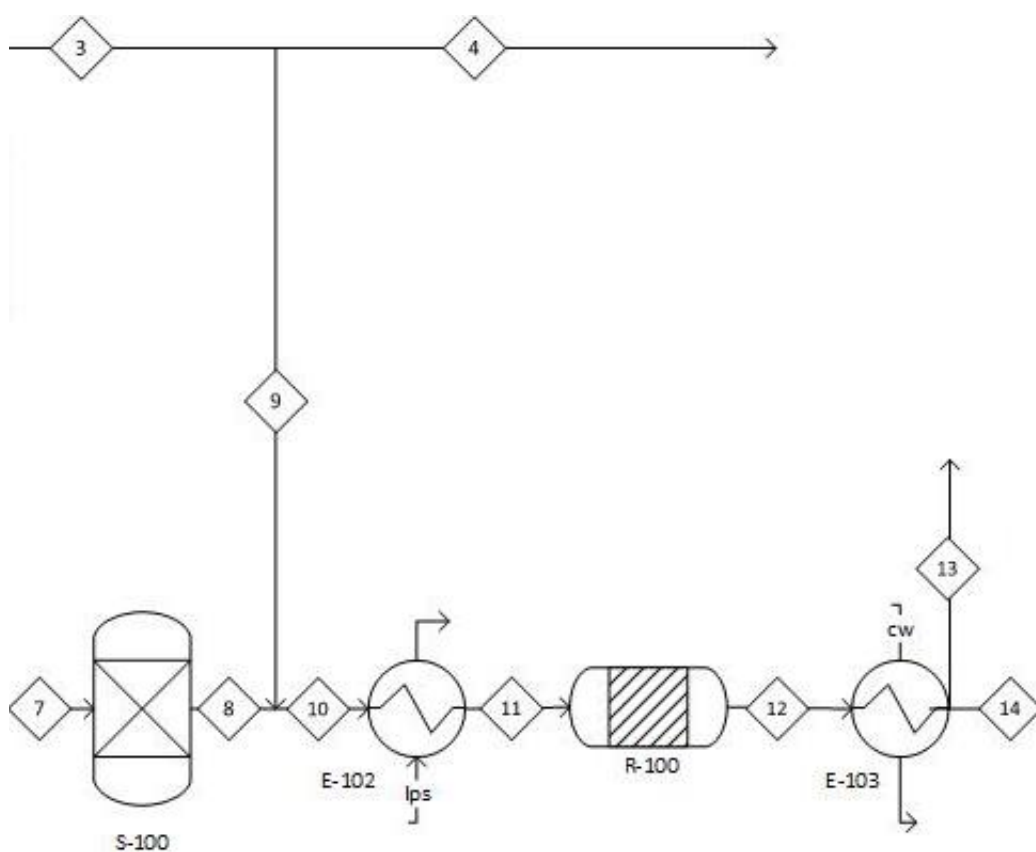
Figure 10: Segment 002 of the Process Flow Diagram

Table 5: Material Balance for Segment 002 of the Process Flow Diagram

Stream Number	3	4	7	8	9	10	11	12	13	14
Temperature (°F)	103.3	103.3	405.0	405.0	103.3	242.1	302.0	313.7	122.0	122.0
Pressure (bar)	20.0	20.0	20.0	20.0	20.0	4.0	4.0	4.0	4.0	4.0
Mass Flow (lb/hr)	710.5	639.5	13019	12979	71.1	13050	13050	13050	296.8	12753
Component Mass Flow (lb/hr)										
Hydrogen	591.0	531.9	trace		59.1	59.1	59.1	54.6	54.1	0.43
Water	trace	trace	40.2	-	trace	trace	trace	trace	trace	trace
Ethanol	119.5	107.5	0.08	0.08	11.9	12.0	12.0	12.0	0.48	11.5
Ethyl Acetate	trace	trace	12818	12818	trace	12818	12818	12818	241.0	12577
Acetaldehyde	0.02	0.02	0.01	0.01	trace	0.01	0.01	0.01	trace	0.01
Buta-2-one	trace	trace	80.4	80.40	trace	80.4	80.4	-	-	-
n-Butanal	trace	trace	80.4	80.40	trace	80.4	80.4	-	-	-
n-Butanol	-	-	-		-	-	-	83.0	0.38	82.6
2-Butanol	-	-	-		-	-	-	83.0	0.81	82.1
Molar Flow (lbmol/hr)	295.8	266.2	149.9	147.7	29.6	177.3	177.3	175.1	29.6	145.4
Volume Flow (cuft/hr)	6160	5544	348.3	347.5	616.0	18886	24979	25043	3188	236.6

41

Table 6: Equipment Block List for Segment 003 of the Process Flow Diagram

Block Number	Block Type	Block Description
C-102	Column	Distillation Column
E-104	Heat Exchanger	Distillation Column Condenser
D-101	Reflux Drum	Distillation Column Reflux Drum
P-103	Pump	Distillation Column Reflux Pump
P-104	Pump	Distillation Column Reboiler Pump
E-105	Heat Exchanger	Distillation Column Reboiler
T-101	Tank	Ethyl Acetate Storage Tank
T-102	Tank	Waste (Byproducts) Storage Tank
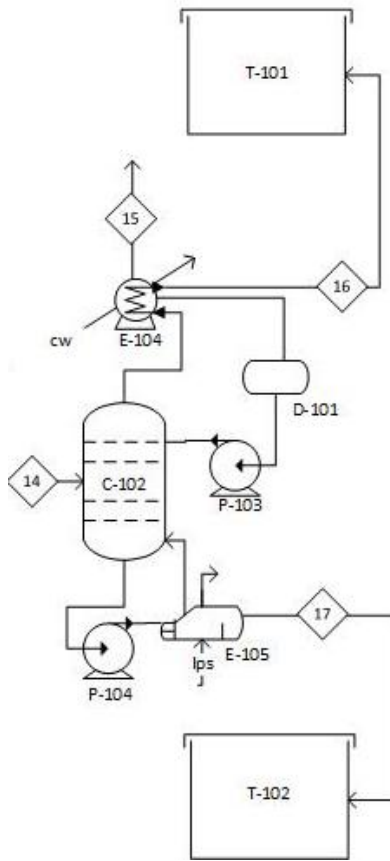
Figure 11: Segment 003 of the Process Flow Diagram

Table 7: Material Balance for Segment 003 of the Process Flow Diagram

Stream Number	14	15	16	17
Temperature (° F)	122.0	102.2	102.2	263.2
Pressure (bar)	4.0	2.0	2.0	2.0
Mass Flow (lb/hr)	12753	1.63	12573	178.5
Component Mass Flow (lb/hr)				
Hydrogen	0.43	0.24	0.20	trace
Water	trace	trace	trace	trace
Ethanol	11.5	trace	11.5	trace
Ethyl Acetate	12577	1.39	12550	25.1
Acetaldehyde	0.01	trace	0.01	trace
Buta-2-one	-	-	-	-
n-Butanal	-	-	-	-
n-Butanol	82.6	trace	0.02	82.6
5mm2-Butanol	82.1	trace	11.3	70.8
Molar Flow (lbmol/hr)	145.4	0.13	142.9	2.35
Volume Flow (cuft/hr)	236.6	27.7	229.1	4.08

15 Process Descriptions

15.1 Segment 001 - Reactive Distillation

Segment 001 is outlined in Figure 9 and Tables 2 and 3. An ethanol storage tank (T-100) is employed to hold one day's worth of feedstock inventory to prevent production halt due to possible site pipeline malfunctions. Stream 1 feeds ethanol from the storage tank into a pump (P-100) at a rate of 13,729 lb/hr at ambient conditions to pressurize the stream to 20 bar. A liquid, compressed ethanol stream (Stream 2) enters the top of a stripping column to remove acetaldehyde from Stream 6. The resultant stripping liquid (Stream 5) enters a 20 ideal stage reactive distillation column (C-101) on stage 8.

Stage 8 is packed with catalyst ($CuO/ZnO/Al_2O_3$, cylindrical pellets) with an estimated packing density of 0.60[23]. Both main reactions discussed in Section 12.2 occur in this reactive zone. A partial condenser, E-100, is used due to the presence of hydrogen in the stage 1 vapor stream. Stream 6, the vapor distillate stream from the the partial condenser (E-100), enters the stripping column mentioned previously. Stream 6 contains acetaldehyde that can be recovered in the stripping column using the feed ethanol (Stream 2). The resultant stripped gas (Stream 3) is a hydrogen product stream (with small amounts of ethanol) with a mass flow rate of 710.5 lb/hr.

The liquid distillate is sent to a reflux accumulator (D-100) and a reflux pump (P-101) at a molar reflux ratio of 1.6. The bottoms products (Stream 7) from the reactive distillation column is 98.5% purity ethyl acetate with 2:1:1 molar ratio of water:buta-2-one:n-butanal byproducts, with a total mass flow rate of 13,019 lb/hr. The reboiler (E-101) runs at 211°C and 20 bar.

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[23]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]

15.1.1 Process Optimization

The initial design challenge in Segment 001 was the modeling and scaling up of the reactive distillation column. Lab scale data for a single ethanol feed reactive distillation column is given in patent data and summarized below[24]:

A 200 proof feed of ethanol is fed into a 20 stage reactive distillation column with 8 stages in the rectifying section and 12 stages in the stripping section. The molar reflux ratio is 0.8 and the molar reboiler ratio is 4. A partial condenser operates at 20 bar. A vapor distillate product with a mass flow rate of 4g/hr is achieved. A bottoms products with a mass flow rate of 170g/hr is achieved with 98.5% purity of ethyl acetate. The column has a diameter of 10cm and a height of 3.5m.

Initial modeling was performed using ASPEN Plus to attempt to replicate the results from the lab scale data. The goal of the model was to generate a column that meets the criteria given the following priorities:

1. Has a bottoms flow rate and purity of ethyl acetate identical to that of the lab scale

2. Has 8 rectifying stages and 12 stripping stages

3. Operates at a condenser pressure of 20 bar

4. Has comparable dimensions

5. Has a molar reflux ratio of 0.8

6. Has a molar reboiler ratio of 4

Lower priority objects had their constraints relaxed until a satisfactory model was generated. To model the reactive section of the column, equilibrium data described in Section 12.2 was used[25]. An equilibrium relationship was used rather than a kinetic relationship due

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[24]Gadewar [2013]
[25]Carotenuto, Tesser, Di Serio, and Santacesaria [2013]

to the fact that tray spacing was unknown in the lab scale specifications. Kinetics would depend highly on the residence time of the reactants in the reactive zone of the column. It was assumed that the final column would have a sufficiently large tray spacing, and therefore residence time, to allow the reactions to reach equilibrium. In addition, the kinetic rate expression reported was not fit to a simple power law, but rather followed a more complicated functional form. While the equilibrium expression did not account for formation of byproducts, they must be included to successfully model the separation within the column. A stoichiometric amount of byproducts was added to the reaction based on the purity given from the data. A 0th order dependence with respect to these byproducts was used for the calculation of the equilibrium constant. The byproducts all have similar volatilities to that of ethyl acetate, so accumulation within the column was not a concern and the stoichiometric coefficients could be determined with a mass balance.

A column was designed using RADFRAC that met the strict criteria of 1 through 4, with relaxed constraints on criteria 5 and 6. A RADFRAC was modeled as a 20 ideal stage column with a partial vapor condenser operating at 20 bar. The column intervals were specified using the given lab scale dimensions. A feed stream of ethanol enters the column on stage 8 as a liquid stream. Stage 8 was specified as the sole stage where reaction occurs. The stage was assumed to be packed with pelleted catalysts with a particle packing efficiency of 0.60. Once these design choices were finalized, there were two independent variables that corresponded to operating conditions that could be specified to determine the entirety of the system. The mass flow rate of the bottoms was forced to the desired value to satisfy criteria 1. The other free variable could be specified to be either the reflux ratio, boilup ratio, or reboiler duty. The reflux ratio is traditionally made the free variable due to it being

an operating condition that can easily be changed by an operator in a plant environment to reach the desired purity. The boilup ratio and reboiler duty can also be manipulated if convergence becomes an issue to achieve a similar effect. Using a design specification, the reflux ratio was varied to achieve a purity of 98.5% ethyl acetate in the bottoms stream. A final converged value of 1.2 was achieved for the reflux ratio, with a corresponding boilup ratio of 6.3.

However, despite generating a model that was similar to that of the reported data, using this column would lead to extreme operating conditions with respect to the condenser. The flow rate of the bottoms was specified to be within 10% of the stoichiometrically calculated value, which means the vapor distillate product would be highly concentrated in hydrogen. With the partial condenser running at 20 bar, an operating temperature of -256°F would be required, leading to the usage of cryogenic cooling. Therefore, criteria 1 must be relaxed with respect to the product flow rate to allow the vapor distillate to condense at a higher temperature that can be ideally achieved with either a cooling water or chilled water loop.

A sensitivity analysis was performed to determine the bottoms rate that would lead to a more ideal condenser temperature. The reflux ratio design specification was still in place to ensure the desired bottoms purity was met. Table 8 shows the condenser temperature as a function of the ratio between the bottoms and distillate mass flow rates.

Table 8: Dependence of Condenser Temperature on the Bottoms to Feed Molar Ratio. A molar ratio of 0.50 corresponds to an ideal stoichiometric amount of ethyl acetate produced without byproducts. A higher ratio corresponds to a higher purity hydrogen stream in the vapor distillate.

Bottom to Feed Molar Ratio	Condenser Temperature(°F)
0.404	102.3
0.406	85.6
0.409	60.1
0.411	52.1
0.414	45.9
0.416	40.1
0.417	1.5
0.419	-53.2
0.421	-103.9
0.424	-189.4
0.426	-256.1
0.490	-300.6
0.500	-356.9

As the molar ratio between bottom and feed flow rates increases, the mole fraction of hydrogen in the vapor distillate increases and the condenser temperature monotonically decreases as a result. The ideal molar ratio range is between 0.40 and 0.416, where a cooling and chilled water loop can be used to partially condenser the vapor distillate. The design specification of the molar reflux ratio converged to a value of 0.95.

However, the trade-off with increasing the condenser temperature is that the composition in the vapor distillate changes. The composition of the vapor distillate was mainly hydrogen and acetaldehyde with trace amounts of ethanol. At the chosen bottoms to feed molar ratio

of 0.415, the composition of the vapor distillate is 0.68 hydrogen and 0.32 acetaldehyde by mass fraction. To mitigate the lose of intermediates, a vapor liquid stripping column was introduced to recover some acetaldehyde. The ethanol fed originally to the reactive distillation column was re-routed and introduced into the stripping column as the stripping liquid. Then, the stripped liquid, now containing ethanol and acetaldehyde, is sent to the reactive distillation column as the feed source to complete the loop.

The stripping column was modeled using a RADFRAC block without a condenser or reboiler. The stripping liquid is fed above stage 1 and the vapor distillate from the reactive distillation column is fed on the bottom stage. The most important design choice of the stripping column that dictated the separation was the number of stages. To determine the number of stages, a case study sensitivity analysis was conducted to analyze the composition and flow rate of the product gas as a function of stages. However, it was found that the separation only required 2 ideal stages to achieve the maximum separation; any additional stages provided no separation advantage.

15.2   Segment 002 - Conversion of Byproducts

Segment 002 is outlined in Figure 10 and Tables 4 and 5. Stream 3 (710.5 lb/hr) contains a hydrogen and ethanol vapor stream and Stream 7 (13,019 lb/hr) contains the 98.5% purity ethyl acetate liquid stream with n-butanal, buta-2-one, and water impurities. There are two main goals in Segment 002:

1. Removal of water from the product stream

2. Reduction of reaction byproduct aldehydes and ketones into alcohols

The removal of water is achieved through the use of a molecular sieve. Stream 8 enters a 13X molecular sieve vessel (S-100) to remove water from the product stream. The spherical 13X molecular sieve has a static adsorption of 25 wt% and is assumed to have a 0.60 packing

efficiency in the vessel[26]. A regeneration cycle of one day is assumed and an additional bed is accounted for. The regeneration of the bed requires heating the bed up to 572°F to allow for the desorption of adsorbed water molecules.

Stream 3, containing the hydrogen distillate, is split in a 9:1 mass ratio into Stream 4 and Stream 9. Stream 4 (639.5 lb/hr) is combusted for fuel value. Stream 9 is used as the hydrogen source for the reduction of the byproduct aldehydes and ketones in the bottoms products (Stream 7 and Stream 8). The split fraction was chosen to achieve a 20:1 molar ratio of hydrogen to aldehyde/ketone in the hydrogenation reactor. Stream 8 and Stream 9 are mixed at a pressure of 4 bar (from 20 bar) and enter a heat exchanger, E-102, to be heated to 302°F. A vapor, Stream 10, enters a packed bed reactor packed with Raney Nickel catalyst with a 0.60 packing efficiency[27]. With a high hydrogen partial pressure due to the 20:1 hydrogen to ketone/aldehyde molar ratio, a 100% selective reduction to alcohols is achieved. The reaction conditions and catalyst combination are too mild to reduce ethyl acetate.

15.2.1 Process Optimization

The bottoms stream from the reactive distillation column, Stream 7, enters a molecular sieve that is modeled as a FSPLIT block in ASPEN. All water is removed from the stream for modeling purposes only. A regeneration cycle of one day is assumed for the operation. The distillate stream containing predominantly hydrogen is split in a 9:1 mass ratio and the smaller of the split streams is mixed with the dried bottoms stream. The 9:1 split was determined to allow for a 20:1 molar ratio of hydrogen to ketone/aldehyde in the hydrogenation reactor for kinetic purposes.

The subsequent mixed stream is dropped to a pressure of 4 bar and heated to a temperature of 302°F prior to entering the hydrogenation reactor. A heat exchanger is used to

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[26]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]
[27]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]

heat the stream to the desired temperature. To determine the area of the heat exchanger, a sensitivity analysis was performed to calculate the steam requirement as a function of effective heat transfer area, shown below in Table 9. Low pressure (150 psig) steam is used to achieve a temperature of 302°F.

Table 9: Required Utilities Versus Heat Exchanger Area
As the heat transfer area decreases, the required utilities to achieve the desired temperature change increases. Heat transfer area requirements above 820lb/hr of steam asymptotically approaches 44.50 ft^2 and have diminishing returns in reduction of area which are not shown in the table.

Heat Transfer Area (ft^2)	Steam (150psig) Flow Rate (lb/hr)
63.2	704.0
52.7	712.8
49.8	721.6
48.1	730.4
47.1	739.2
46.4	748.0
45.9	756.8
45.5	765.6
45.2	774.4
45.0	783.2
44.8	792.0
44.7	800.8
44.6	809.6
44.6	818.4

As the heat transfer area of the heat exchanger increases, the amount of steam requirement decreases, as shown in Table 9. Steam flow rates higher than 818.4 lb/hr are not shown due to diminishing returns in heat exchanger area reduction; further increases in utilities were

found to asymptotically approach a constant value of heat exchanger area. The final area of 63 ft² minimized utility usage and was chosen solely on an economic basis, which is further explained in Section 20.1.2.

The heated hydrogen and bottoms stream enter a packed bed hydrogenation reactor modeled as a plug flow reactor using a RPLUG module. Kinetics for the reaction are reported by Oldenburg and Rase[28] and are described in detail in Section 12.2. The plug flow reactor (PFR) was designed to meet the following criteria:

1. Adiabatic operation to remove design of cooling the reactor

2. 100% conversion and reduction of aldehyde and ketone byproducts to alcohols

The reactor was chosen to run adiabatically due to the amount of inerts in the stream that can act as a heat sink for the process. The adiabatic temperature rise was 12°F in the final optimized system. Full conversion of the byproducts was desired in this process to allow for easier separation in Segment 003. The aldehyde and ketone byproducts have almost identical boiling points compared to that of ethyl acetate, making separation difficult. However, the converted alcohols have larger boiling point disparities relative to the aldehyde and ketone byproducts, making separation less costly. Using the power law expressions given by Oldenburg and Rase, a residence time can be calculated given a 20:1 molar ratio of hydrogen to aldehyde/ketone (Section 27.1.2). A high hydrogen partial pressure was chosen to allow for faster conversions and lower residence times, thus reducing the size and price of the reactor. However, the residence time of a PFR is dependent on the reactor length. The length, however, depends on the volume, which is a function of vessel diameter. With two free variables, the system could not be fully determined. To mitigate this issue, an aspect ratio of $L/D = 5$ was chosen to mimic the reactor used by Oldenburg and Rase. Reactor dimensions of $D = 2.91 ft$ and $L = 14.60 ft$ were determined, using the aforementioned relationships. Using these preliminary dimensions, RPLUG was used as a model in ASPEN.

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[28] Oldenburg and Rase [1957]

A catalyst packing efficiency of 0.60[29] was assumed to account for pressure drop. The reactor dimensions were optimized by analyzing the final conversion and conversion profile as a function of position through the reactor. Final dimensions were found to be $D = 3.28ft$ and $L = 16.40ft$.

The effluent from the hydrogenation reactor contains excess hydrogen that must be removed from the process. A heat exchanger is employed to cool the stream to a given temperature to flash off a majority of the hydrogen from the stream. However, the flash temperature determines a few variables:

1. Vapor mass split fraction

2. Purity of the liquid streams

3. Utility requirement

The optimal flash temperature is one that (1) minimizes the loss of product in the vapor stream and (2) maximizes the purge of hydrogen from the liquid stream while minimizing utilities is desired. The determination of the flash temperature was conducted via a sensitivity analysis of split fraction and mass fraction of hydrogen in the liquid stream as a function of flash temperature, shown below in Table 10. A FLASH block was used rather than a heat exchanger to simplify the computations.

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[29]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]

Table 10: Dependence of Split Fraction and Liquid Purity on Flash Temperature
As the flash temperature decreases, the vapor mass split fraction decreases and the mass fraction of hydrogen present in the liquid stream increases.

Flash Temperature (F)	Vapor Mass Split Fraction	Mass Fraction of Hydrogen in Liquid Stream
90.0	0.0124	3.14E-05
106.3	0.0167	3.27E-05
122.0	0.0227	3.38E-05
133.5	0.0288	3.44E-05
149.8	0.0406	3.48E-05
166.1	0.0581	3.44E-05
182.4	0.0851	3.30E-05
198.7	0.1290	3.02E-05
215.0	0.2088	2.56E-05
231.3	0.3876	1.87E-05
242.2	0.7016	1.26E-05

The sensitivity analysis was performed between the temperatures of 90°F to the bubble point of the effluent from the hydrogenation reactor. The lower bound was chosen due to it being the minimum temperature that can be achieved with a cooling water loop. As the flash temperature decreases, the vapor split fraction (and subsequent product lost in the vapor) decreases. The mass fraction of hydrogen in the liquid stream increases as the flash temperature decreases. Flash temperatures between 90°F and 150°F were able to reduce the split fraction to less than 5%. A final temperature was chosen to be 122°F due to diminishing returns in vapor split fraction as utilities increased.

After the flash temperature was chosen, a heat exchanger was employed and sized to accomplish the temperature drop. Similar to the design of the previous heat exchanger in

this section, a sensitivity analysis of the utility requirements versus the area was conducted, shown below in Table 11. An additional column specifying the exit stream of the cooling water was added to ensure the temperature did not exceed 120°F.

Table 11: Required Utilities and Exit Temperature for a Given Area
As the heat transfer area increases, the utility requirement decreases. The exit temperature of the cooling water was also accounted for to ensure the temperature did not exceed 120 °F

Heat Transfer Area (ft^2)	Cooling Water Flow Rate (lb/hr)	Exit Cooling Water Temperature(°F)
274.02	102294	120.0
270.68	113317	117.1
268.00	124341	114.7
265.80	135364	112.7
263.96	146387	111.0
262.41	157410	109.6
261.07	168433	108.3
259.91	179456	107.2
258.90	190479	106.2
258.00	201502	105.3

The upper and lower bound for the area and utility requirement, respectively, were determined by the maximum allowed exit temperature of the cooling water. The final area that minimized utilities was chosen on an economic basis; details are described in Section 20.1.2.

15.3   Segment 003 - Product Separation

Segment 003 is outlined in Figure 11 and Tables 6 and 7. Stream 14 enters a distillation column, C-102, with a mass flow rate of 12,753 lb/hr to complete the final product separation. The distillation column operates with a partial condenser (E-104) at 2 bar with a vapor

distillate (Stream 15) and a liquid distillate (Stream 16). A partial condenser running at 102°F is used due to the trace amounts of non-condensable hydrogen still present in Stream 14. The vapor distillate contains hydrogen and is vented out the top of the column. The liquid distillate containing 99.8% purity ethyl acetate is sent to a storage tank (T-101) to hold up to seven days of product for shipment purposes. The bottoms products, Stream 17, contains the converted alcohol byproducts, 2-butanol and n-butanol, from the hydrogenation reactor in Segment 002. Stream 17 enters a storage tank (T-102) to hold up to 30 days of waste for waste disposal purposes.

15.3.1 Process Optimization

The distillation column was designed to achieve 99.8% purity ethyl acetate in the distillate product. To get initial column specifications, calculations shown in Section 27.1.3 and the DSTWU shortcut method were employed to determine the number of stages and corresponding reflux ratio. The relative volatilities and separation specifications state ethyl acetate and 2-butanol to be the light and heavy keys, respectively. A partial condenser was employed with a conservative split fraction that would recover the greatest amount of product as well as allow the condenser to be cooled using a traditional cooling water loop (an in depth analysis on the split fraction was conducted, as described later in this section in Table 13). A sensitivity analysis was performed to determine the optimal conditions to design the column and is shown in Table 12.

Table 12: Estimated Number of Theoretical Stages and Reflux Ratio Required
The minimum number of stages needed to accomplish the desired separation is 19. As the number of stages increases, the reflux ratio monotonically decreases. There are diminishing returns in the reflux ratio as the number of stages increase.

Theoretical Stages	Reflux Ratio
19	170.7
20	9.6
21	6.4
22	4.9
23	3.8
24	2.8
25	2.3
26	2.1
27	1.9
28	1.8
29	1.7
30	1.6

The minimum number of theoretical stages needed to achieve the desired separation is 19. As the number of theoretical stages increases, the reflux ratio monotonically decreases with diminishing returns. The optimal number of stages is between 20 and 24 stages, where the required reflux ratio decreases significantly. A column with 20 ideal stages was used as the initial specification for a more detailed model using a RADFRAC block.

A RADFRAC block with 20 ideal stages was designed to meet the following criteria:

1. Has a liquid distillate purity of the desired 99.8% of ethyl acetate

2. Meets the 50kT/year ethyl acetate production specification

3. Has a partial condenser temperature that can be cooled using cooling water

4. Minimizes the lose of product in the vented vapor stream

To reach the desired ethyl acetate purity, a design specification was used that varied the molar reflux ratio to a 0.998 mass fraction of ethyl acetate. A similar technique was used in the reactive distillation column to achieve a purity result as well. The partial condenser temperature and product recovery are coupled in that the vapor liquid distillate split is dependent on the condenser temperature. A sensitivity analysis was performed that determined the relationship between mass split fraction and the condenser temperature, as shown in Table 13.

Table 13: Effect of Condenser Temperature on the Vapor Split Fraction and Product Purity
As the condenser temperature is lowered, more product is recovered. The minimum split fraction that can be achieved using cooling water is about 0.0001. The purity of ethyl acetate was found to not be sensitive to changes in the condenser temperature.

Condenser Temperature(°F)	Vapor Mass Split Fraction	Ethyl Acetate Purity
-423.3	1.00E-05	0.9983
-365.7	2.02E-05	0.9983
6.1	4.09E-05	0.9982
77.9	8.29E-05	0.9982
104.4	1.46E-04	0.9982
127.5	2.56E-04	0.9981
147.1	4.50E-04	0.9981
167.1	9.10E-04	0.9981
182.2	1.84E-03	0.9981
193.2	3.73E-03	0.9981
199.4	6.55E-03	0.9981
202.8	1.00E-02	0.9981

As the condenser temperature drops, the vapor split fraction decreases and more product is recovered in the liquid distillate stream. The ethyl acetate purity was found to be insensitive to changes in the condenser temperature. The range of split fractions corresponded to temperatures between 90 and 120°F was found to be compatible with a cooling water loop. The final vapor mass fraction was set to 1.3E-04 with a corresponding condenser temperature of 102°F. The corresponding design specified molar reflux ratio was found to converge at 10. The corresponding bottoms reboiler operates at 263°F and contains the byproducts of the reaction with the optimized distillate conditions.

16   Energy Balance

16.1   Energy Integration Method

The process produces several streams of almost pure hydrogen. However, the purity is not quite high enough to be able to sell this as a byproduct. The decision was made to burn these streams as a way to gain fuel value. To account for this, the amount of energy that would be released from the combustion of the hydrogen stream was calculated. An efficiency of 70% was assumed when this calculation was performed. From the calculated Btu/hr, a value of Btu/lb ethyl acetate was calculated. This was then included as a byproduct from the process to be sold. This is discussed further in the Section 23.

There are a total of 6 heat exchangers in this process, 4 of which are condensers and reboilers associated with columns. The temperature changes required are shown below in Table 14:

Table 14: Incoming and Target Temperature Changes for Specified Heat Exchangers
The only heat exchangers can that be networked are E-102 and E-103. However, the heating and cooling requirements for these are negligible compared to the heat duties of the condensers and reboilers.

Block	Description	Incoming Temperature (F)	Target Temperature (F)
E-100	Condenser of reactive distillation column, C-100	206.8 (vapor)	206.8 (partial vapor-liquid)
E-101	Reboiler of reactive distillation column, C-100	411.8 (liquid)	411.8 (vapor)
E-102	Preheat feed for hydrogenation reactor, R-100	242.1	302.0
E-103	Flash products post-hydrogenation, R-100	313.7	122.0
E-104	Condenser of distillation column, C-101	210.8 (vapor)	101.4 (partial vapor-liquid)
E-105	Reboiler of distillation column, C-101	263.2 (liquid)	263.2 (vapor)

The only heat exchangers that can be networked are E-102 and E-103. However, the heating and cooling requirements for these units are negligible, being 1.5 orders of magnitude lower compared to those of the condensers and reboiler exchangers. As a cost saving measure,

it was decided to be uneconomical to add an integrated heat exchanger design.

16.2 Energy Requirements

The heat exchangers, column condensers, column reboilers, and molecular sieve all contribute significantly to the energy requirements for this process. In addition, the feed, reflux, and reboiler pumps contribute to the electricity needed. Table 15 below summarizes the heat duties, energy, and power requirements of each aforementioned block. These values were all obtained from the ASPEN model.

Table 15: Heat Duties, Energy, and Power Requirements for Each Block

Block ID	Requirement Description	Quantity
E-100	Reactive Distillation Column Condenser Heat Duty (Btu/hr)	-9621280
E-101	Reactive Distillation Column Reboiler Heat Duty (Btu/hr)	16858600
E-102	Heat Exchanger 1 Heat Duty (Btu/hr)	708965
E-103	Heat Exchanger 2 Heat Duty (Btu/hr)	-3063260
E-104	Distillation Column Condenser Heat Duty (Btu/hr)	-28594700
E-105	Distillation Column Reboiler Heat Duty (Btu/hr)	28486200
S-100	Molecular Sieve Regeneration Energy Requirement (Btu/hr)	33177
P-100	Feed Pump Power Requirement (kW)	10.8
P-101	Reactive Distillation Reflux Pump Power Requirement (kW)	2.53
P-102	Reactive Distillation Reboiler Pump Power Requirement (kW)	1.89
P-103	Distillation Reflux Pump Power Requirement (kW)	1.25
P-104	Distillation Reboiler Pump Energy Power (kW)	0.0220

17   Utility Demands

The energy requirements listed in Table 15 above are all fulfilled by adding purchased cooling water, high pressure (450 psig) steam, low pressure (150 psig) steam, or electricity to the system. Using those values along with standard industry process for calculating amounts of water and steam, the necessary quantities of each utility were determined. Table 16 summarizes the utilities needed for each equipment block. Table 17 then summarizes the utility inputs as ratios per pound of ethyl acetate produced.

Table 16: Utility Requirements per Hour for Each Process Unit

Utility	Equipment Item	Quantity (per hr)
Cooling Water (lb)	E-100	282696
	E-103	90006
	E-104	840180
	Total (lb)	*1212882*
High Pressure Steam (450 psig) (lb)	E-101	22057
	S-100	43.41
	Total (lb)	*22101*
Low Pressure Steam (150 psig) (lb)	E-102	826
	E-105	33217
	Total (lb)	*34044*
Electricity (kW)	P-100	10.8
	P-101	2.53
	P-102	1.89
	P-103	1.25
	P-104	0.022
	Total (kW)	*16.48*

Table 17: Total Utility Requirements per Pound of Ethyl Acetate Produced

Utility	Unit	Ratio (per lb ethyl acetate)
Cooling Water	lb	96.64
High Pressure Steam (450 psig)	lb	1.76
Low Pressure Steam (150 psig)	lb	2.71
Electricity	kWh	0.0013
Process Water	lb	0

17.1   Cooling Water

Cooling water is used in this process in units E-100, E-103, and E-104. These are the reactive distillation column condenser, the heat exchanger prior to the final distillation column, and the distillation column condenser, respectively.

The heat capacity of the cooling water used was 1.001 Btu/(lb°F)[30]. The cooling water used was assumed to have a temperature change from 86°F to 120°F. These values were used to calculate the necessary flow rate of cooling water needed for the process. The 86°F starting temperature was chosen after taking into consideration the location of the plant and discussing the most likely temperature value of available cooling water with industry consultants. The total required cooling water for the process is 1,212,882 lb/hr.

17.2   High Pressure Steam

Following heuristics provided in Chapter 17 of *Seider et. al, 2017*, high pressure steam at 450 psig was used for the process. This steam is used in blocks E-101, the reactive distillation column reboiler, and S-100, the molecular sieve. A value of 764.305 Btu/lb was used as the latent heat of this high pressure steam to calculate the necessary mass flow rate of steam

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[30]Seider, Lewin, Seader, Widagdo, Gani, and Ng, [2017]

needed[31]. The utility requirement for high pressure steam is 22,101 lb/hr.

17.3   Low Pressure Steam

Similar to the rationale followed for high pressure steam, it was determined that low pressure steam at 150 psig would be used for the process. This steam is used in block E-102, the heat exchanger prior to the hydrogenation reactor, and E-105, the distillation column reboiler. The latent heat of the low pressure steam used in the calculations was 857.571 Btu/lb[32]. The calculated total value for low pressure steam is 34,044 lb/hr.

17.4   Electricity

The final utility requirement comes from the electricity required to run each of the five pumps in the process. The total required electricity for the process is 16.48 kW.

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[31]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]
[32]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

18 Equipment List & Unit Description

This section describes the major process equipment units. For each unit described in this section, the associated specification sheets can be found in Section 19.

18.1 Pumps

Feed Pump

Unit ID: P-100	Outlet Temperature: 97.5°F
Type: Centrifugal Pump	Pressure: 20 bar
Material: Stainless Steel 316	Work: 10.8382 kW
Specification Sheet: Page 77	Bare Module Cost: $30,815

The feed pump was designed with the aid of ASPEN, allowing a pressure rise of 19 bar and maintaining a flow rate of 279.5 ft^3/hr. The inlet pressure is 1 bar and the head necessary to accommodate the pressure rise is 384 ft. This calculation was carried out on the basis of equations detailed in Section 27.1.1. Based on the head calculated, guidelines [33] suggest that the feed pump be modelled as a standard centrifugal pump with Vertical Split Case (VSC) orientation with 1 stage, shaft rpm of 3600 and a maximum motor hp of 75. Stainless Steel 316 is used as the construction material for this pump, as this material is able to withstand corrosion. This is an important consideration as the end use of ethyl acetate is often a solvent, and therefore it is important that considerations be made to avoid material corrosion through the process.

18.2 Process Heat Exchangers

With the assistance of ASPEN Exchanger Design and rating (EDR) capabilities, both heat exchangers in this process were designed in accordance to TEMA[34] (Tubular Exchanger Manufacturers Association) standards.

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[33]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]
[34]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Heat Exchanger One: Flow to Hydrogenation Reactor

Unit ID: E-102
Type: Double Pipe Heat Exchanger
Material: Stainless Steel 316
Heat Duty: 708,965 Btu/hr
Pressure: 4 bar
Specification Sheet: Page 78

Inlet Hot Stream Temperature: 366.0°F
Outlet Hot Stream Temperature: 244.8°F
Inlet Cold Stream Temperature: 242.1°F
Outlet Cold Stream Temperature: 302.0°F
Area: 5.65 ft^2
Bare Module Cost: $11,138

Low pressure steam is used as the heat transfer media for this heat exchanger. E-102 was optimized on the basis of cost by specifying the inlet steam flow rates (See section 20.1.2). Using the specified inlet steam flow rate of 320 kg/hr, the heat exchanger surface area required is 5.65 ft^2, as determined from ASPEN outputs. For heat exchange surface areas of less than 200 ft^2, double pipe heat exchangers are selected over shell and tube heat exchangers[35]. Both the inner and outer pipe materials were chosen to be stainless steel. This design choice yields a material construction factor of 3. This heat exchanger has an average heat transfer coefficient of 149.7 $Btu/hr - ft^2 -° F$ and a log-mean-temperature-difference (LMTD) of 77.9°F.

Heat Exchanger Two: Flow to Distillation Column

Unit ID: E-103
Type: Double Pipe Heat Exchanger
Material: Stainless Steel 316
Heat Duty: -3,063,260 Btu/hr
Pressure: 1 bar
Specification Sheet: Page 79

Inlet Hot Stream Temperature: 313.7°F
Outlet Hot Stream Temperature: 122.0°F
Inlet Cold Stream Temperature: 86.0°F
Outlet Cold Stream Temperature: 120.0°F
Area: 25.5 ft^2
Bare Module Cost: $14,176

Low pressure steam is used as the heat transfer media for this heat exchanger. E-103 was optimized on the basis of cost by specifying the inlet steam flow rates (see Section 20.1.2). Using the specified inlet steam flow rate of 46,400 kg/hr, the heat exchanger surface area required is 25.5 ft^2, as determined from ASPEN outputs. As discussed above, this surface area falls within the decision criteria to design this heat exchanger as a double pipe heat

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[35]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

exchanger. Stainless Steel 316 was the material construction choice This heat exchanger has an average heat transfer coefficient of 149.2 $Btu/hr - ft^2 - ^oF$ and a log-mean-temperature-difference (LMTD) of 74.7°F.

18.3   Reactors

Reactive Distillation Column

Unit ID: C-101   Pressure: 20 bar
Type: Reactive Distillation Column   Height: 73 ft
Material: Stainless Steel 316   Diameter: 5.74 ft
Number of Theoretical Stages: 20   Condenser Temperature: 206.8°F
Number of Actual Trays: 31   Reboiler Temperature: 404.9°F
Specification Sheet: Page 80   Bare Module Cost: $2,425,977

The reactive distillation column was simulated in ASPEN and used to optimize the separation of the newly created ethyl acetate and byproducts from the hydrogen byproduct. This process required 20 theoretical stages, a condenser pressure of 20 bar, a molar reflux ratio of 1.6 and a molar bottoms rate of 68.01 kmol/hr. Sieve trays were used and hydraulic data generated indicated a stripping section diameter of 5.74 ft and an enriching section diameter of 2.66 ft. Following guidance from industrial consultants, it was proposed that this column be costed as a singular section column, with the larger diameter of 5.74 ft. O'Connell correlations account for tray efficiencies, and were used to determine the total number of actual trays required for this unit. These calculations are outlined in Section 27.1.2. The number of actual trays required is 31, with one tray accounting for the reboiler. The feed tray location is the 12th ideal tray, which corresponds to the 20th real tray. The feed tray is assumed to be packed with catalyst, with a packing efficiency of 0.6. The assumed tray spacing was 2 ft and was used to calculate the total height of the column. The tray spacing was multiplied by the total number of actual trays, and an additional skirt length of 4 ft for the enriching section and 7 ft for the stripping section were added. These values follow the guidance provided in Chapter 16 of *Seider et. al, 2017*. The reactive distillation

column is constructed out of Stainless Steel 316 to ensure that the column can withstand higher temperatures.

Following guidance from industrial consultants, a residence time of 10 minutes was used to design the reflux accumulator. The L/D ratio was set at 2, and the reflux accumulator was modelled as a horizontal pressure vessel. Using the design equations described in Section 27.1.2, the reflux accumulator was designed to have a diameter of 6.1 ft and a length of 12.2 ft. The reflux accumulator is constructed of Stainless Steel 316.

The partial condenser is modelled as a fixed head, shell and tube heat exchanger and operates at 206.7°F. These conditions will be maintained using 282,696 lb/hr of cooling water in a 824 ft^2 area exchanger with a heat duty of -9.62×10^6 Btu/hr. The LMTD for this exchanger is 119°F. The area for this exchanger was calculated on the basis of design equations detailed in Section 27.1.2, as described in *Seider et. al, 2017*.[36] The condensor is constructed of Stainless Steel 316 and has a tube length of 20 ft.

The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger with 20 ft tube length and operates at 404.9°F. A heat flux of $12,000\ Btu/hr - ft^2$ is assumed to avoid film boiling. The reboiler area was determined to be 1421 ft^2 and was calculated by using the equations outlined in Section 27.1.2. Again, for corrosion purposes, the reboiler was constructed out of Stainless Steel 316.

The reboiler and reflux pump for the reactive distillation column are each constructed entirely of stainless steel, to avoid concerns of high temperature and possible corrosion due to chemical products created. Both pumps were designed by considering the liquid flow through the pump, using output available from the ASPEN simulation. The reboiler pump was designed to have a head of 385 ft and the reflux pump was designed to have a head of 280 ft. Calculations for these pumps followed equivalent calculations for the feed pump, as described in Section 27.1.1.

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[36]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Hydrogenation Reactor

Unit ID: R-100   Pressure: 4 bar
Type: Packed Column   Length: 16.4 ft
Material: Stainless Steel 316   Diameter: 3.2 ft
Bare Module Cost: $300,602   Heat Duty: Adiabatic
Specification Sheet: Page 81

The hydrogenation reactor was modelled as a packed column. The catalyst packing chosen was Raney Nickel, with a packing efficiency of 0.60. The catalyst is assumed to be dumped packing for costing purposes. The catalyst is replaced every three months, in accordance to its reported lifetime.[37] The reactor is run adiabatically, with a adiabatic temperature increase of 12°F due to the large amounts of inerts in the stream acting as heat sinks. The residence time required for this reactor is short (20 seconds) due to running at excess hydrogen partial pressures. Information for the optimization of the reactor dimensions can be found in Section 15.2.1. The hydrogenation reactor is constructed out of Stainless Steel 316 to ensure that the reactor can withstand elevated temperatures.

18.4   Distillation Column

Unit ID: C-102   Pressure: 2 bar
Type: Distillation Column   Height: 69 ft
Material: Stainless Steel 316   Diameter: 7.1 ft
Number of Theoretical Stages: 20   Condenser Temperature: 101.4°F
Number of Actual Trays: 29   Reboiler Temperature: 263.1°F
Specification Sheet: Page 82   Bare Module Cost: $893,539

As discussed previously, following guidance from industrial consultants, a distillation column was chosen as the optimal choice for the final separation of ethyl acetate from the alcohol byproducts. To estimate the base case for initial specifications in the ASPEN simulation, a series of design equations and algorithms were used. The distillation column operating conditions were initially chosen using *Figure 9.9 Seider et.al, 2017*. In initially

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[37]Oldenburg and Rase [1957]

designing this column, the distillate stream was assumed to be 100% ethyl acetate, thereby assuming perfect separation for the initial design basis. The bubble point pressure of ethyl acetate at 120°F was calculated as 4.35 psia, using ASPEN's chemical database. A total condenser was included in the design of this column, assuming no hydrogen was present. Following guidelines presented in *Seider et.al, 2017.*, the condenser outlet pressure was set to approximately 2 bar. Following guidance from the NIST Handbook, the condenser pressure drop was assumed to be between 0 and 2 psia and the tower pressure drop was assumed to be between 5 and 10 psia. Using these guidelines, it was expected that the bottoms pressure, P_B, would be in the range of 5-12 psia higher than the condenser, and therefore the bottoms pressure was estimated to be around 2.2 bar. To determine the reboiler temperature, the bubble point temperature was established using ASPEN's chemical database.

To estimate the number of theoretical stages and the reflux ratio for this distillation column, the Fenske-Underwood-Gilliand (FUG) shortcut method was used, which is a common chemical engineering method applicable to ordinary distillation[38]. It is noted that this method is often used for ideal mixtures, free of azeotropes. This limitation was considered, yet was debunked after considering the magnitude of liquid-phase activity coefficients in this mixture and after noting that the mixture is free of azeotropes at the chosen operating conditions. In this column, 2-butanol is the heavy key and ethyl acetate is the light key. The number of minimum stages was estimated as 8.375 stages (or otherwise, 9 stages), using Fenske equations[39]. The design equations used to estimate the minimum number of stages are outlined in Section 27.1.3. The minimum reflux ratio was then determined, by making the key assumption that the mixture in this column can be treated as pseudo binary. Using this assumption, the minimum reflux ratio was calculated as 2.065. The design equation used to calculate this ratio is outlined in Section 27.1.3. The overall column reflux ratio is typically 3.5 times the minimum reflux ratio. Therefore, the base case

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[38]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

[39]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

estimation of the column reflux ratio was 7.23. This estimation was used to determine the number of theoretical stages in the column, using the Gilliland correlation. The base case number of theoretical stage was estimated to approximately be 11 stages. The graphical correlation can be found in Section 27.1.3. The base case number of stripping and rectifying stages was found to be 6.68 stages and 3.48 stages, respectively. These values were obtained by following the Kirkbride equation, as outlined in Section 27.1.3.

As discussed in Section 15.3.1, the distillation column specifications were optimized using DSTWU to ensure maximum separation. This optimization was done by using the ASPEN program capabilities and sensitivity analyses. Using this optimization, the calculated number of theoretical stages is 20 stages, with a condenser pressure of 2 bar and a column reflux ratio of 10. Based on guidance from industrial consultants, sieve trays were used with a 2 ft spacing. Hydraulic data generated in ASPEN indicated a stripping section diameter of 7.1 ft and a rectifying section diameter of 7.0 ft. It is proposed that this column be costed as a singular section, with the larger diameter of 7.1 ft.

O'Connell correlations account for tray efficiencies, and were used to determine the total number of actual trays required for this unit. These calculations are outlined in Section 27.1.3. The number of actual trays required is 29, with one tray accounting for the reboiler. The feed tray location is 15. Making use of the assumed tray spacing of 2 ft, the total height was calculated by multiplying the total number of actual trays by the assumed tray spacing, and then including the additional skirt length of 4 ft for the enriching section and 7 ft for the stripping section[40]. To prevent against corrosion, the column is constructed out of Stainless Steel 316.

For this column's reflux accumulator, a residence time of 10 minutes was used once again in designing the required specifications. The L/D ratio was set at 2, and the reflux accumulator was modelled as a horizontal pressure vessel. Using the design equations described in Section 27.1.3, the reflux accumulator was designed to have a diameter of 8.11

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[40]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

71

ft and a length of 16.2 ft. The reflux accumulator is constructed of Stainless Steel 316.

The partial condenser is modelled as a fixed head, shell and tube heat exchanger and operates at 101.3°F. These conditions will be maintained using 840,180 lb/hr flow rate of cooling water in a 2193 ft^2 area exchanger with a heat duty of -2.62×10^7 Btu/hr. The LMTD for this exchanger is 120°F. The area for this exchanger was calculated on the basis of design equations detailed in Section 27.1.3, as described in *Seider et. al, 2017.* The condenser is constructed of Stainless Steel 316, and has a tube length of 20 ft.

The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger with 20 ft tube length and operates at 263.1°F. A heat flux of $12,000 Btu/hr - ft^2$ is assumed to avoid film boiling. The reboiler area was determined to be $2362 ft^2$ and was calculated by using the equations outlined in Section 27.1.3. Again, the reboiler is constructed entirely of Stainless Steel 316.

The reboiler and reflux pump for the reactive distillation column are each constructed entirely of stainless steel, to avoid concerns of high temperature and possible corrosion due to chemical products created. Both pumps were designed by considering the liquid flow through the pump, using output available from the ASPEN simulation. The reboiler pump was designed to have a head of 331 ft and the reflux pump was designed to have a head of 262 ft. Calculations for these pumps followed equivalent calculations for the feed pump, as described in Section 27.1.1.

18.5 Stripper

Unit ID: C-100   Pressure: 20 bar

Type: Vertical Pressure Vessel   Height: 6.0 ft

Material: Stainless Steel 316   Diameter: 10.0 ft

Number of Theoretical Stages: 5   Temperature: 103.2°F

Specification Sheet: Page 83   Bare Module Cost: $601,796

The stripper was optimized to allow for maximum removal of intermediates from the hydrogen stream, leaving the reactive distillation column. The ASPEN simulation output and convergence outputs were used to determine the ideal specifications for this column. To account for efficiency limits, the column was oversized in its diameter and height specifications. An approximate 50% efficiency assumption was used, and the column was oversized using this specification. The stripper is modelled as a vertical pressure vessel and is constructed out of 316 Stainless Steel to account for potential corrosion effects. More information on the optimization of the column can be found in Section 15.1.1.

18.6 Molecular Sieve

Unit ID: S-100   Pressure: 20 bar

Type: Molecular Sieve   Heat Duty: 33177 Btu/hr

Material: Stainless Steel 316   Diameter: 2.06 ft

Bare Module Cost: $130,754 (each)   Length: 12.4 ft

Specification Sheet: Page 84

The molecular sieve is comprised of the sieve packing and holding vessel. The molecular sieve is assumed to have one day-bed, and one regenerating-bed. The total mass of the sieve packing material was found to be 3840 kg, as explained in Section 27.1.4. The molecular

sieve is assumed to have a void fraction of 0.40 and a packing density of 0.60. Professor Leonard Fabiano was consulted for the design of this molecular sieve vessel, and the aspect ratio (L/D) was set to 3. As outlined in Section 27.1.4, the molecular sieve vessel was sized with a diameter of 4.1 ft and a length of 12.4 ft. The molecular sieve vessel was modelled as a horizontal pressure vessel for cost correlation purposes. The molecular sieve vessel is constructed from Stainless Steel 316, to account for potential corrosive issues and elevated temperature operation during the regeneration process.

18.7   Storage Tanks

Ethanol Feed Storage Tank

Unit ID: T-100	Pressure: 1 bar
Type: Storage Tank	Temperature: 95°F
Tank Type: Floating Roof	Volume: 75240 ft^3
Specification Sheet: Page 85	Bare Module Cost: $612,507

One day's worth of ethanol feed is stored as an excess raw material. Ethanol has a boiling point of 173.1°F and because of this, the ethanol feed will be liquid at ambient temperatures and be a liquid in this storage tank. Using a volumetric flow of 279 ft^3/hr, and a volumetric safety factor of 1.5[41], the ethanol feed storage tank was sized to have a volume of 75,240 ft^3. This volumetric safety factor is imperative to ensure that the tank never operates at full capacity, for pressure and control considerations. A floating tank was chosen for this storage tank as the roof dynamically moves along with the height of the fluid in the tank. This design feature eliminates oxygen interacting with the ethanol in the storage tank. As discussed in Section 12.3, the ethanol is fed to this storage tank via a pipeline from a nearby ADM corn plant. Stainless Steel 316 is used for this storage tank construction material to ensure limited pipeline impurities that may occur from corrosion.

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[41]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Ethyl Acetate Storage Tank

Unit ID: T-101	Pressure: 2 bar
Type: Storage Tank	Temperature: 101.3°F
Tank Type: Floating Roof	Volume: 432219 ft^3
Specification Sheet: Page 86	Bare Module Cost: $1,486,117

One week's worth of ethyl acetate product is stored on site. This assumption follows guidance from industrial consultants, as this storage tank is an intermediate storage before the ethyl acetate is delivered to customers. Ethanol has a boiling point of 170.8°F and because of this, the ethyl acetate will be liquid at ambient temperatures and be a liquid in this storage tank. Using a volumetric flow of 229 ft^3/hr, and a volumetric safety factor of 1.5, the ethanol feed storage tank was sized to have a volume of 432,219 ft^3. Following similar reasoning applied to the ethanol storage tank, the safety factor is imperative to ensure that the tank does not operate at full capacity. A floating tank is chosen for this storage tank, allowing for the elimination of oxygen from the ethyl acetate stored in the tank. The storage tank is constructed from Stainless Steel 316.

Waste Storage Tank

Unit ID: T-102	Pressure: 2 bar
Type: Storage Tank	Temperature: 263.1°F
Tank Type: Floating Roof	Volume: 33114 ft^3
Specification Sheet: Page 87	Bare Module Cost: $328,942

The primary waste products formed in this process are n-Butanol and 2-Butanol. As these byproducts comprise a relatively smaller volumetric flows produced from the separation in the final distillation column, it was decided that the byproducts would be sent to waste

disposal, rather than selling the byproducts. (The volumetric flow of the byproduct stream is 4.08 ft^3/hr.) Following guidance from industrial consultants, these waste byproducts will be stored on site for one month, assuming a monthly waste collection from the chemical plant site. Using this volumetric flow and assumption, the volume of the storage tank was calculated to be 33,114 ft^3. Note that this volume also assumes a volumetric safety factor of 1.5, as applied to the ethanol and ethyl acetate storage tanks. A floating tank is chosen for this tank to eliminate the interaction of oxygen with the alcohol byproducts. The storage tank is constructed from Stainless Steel 316.

18.8   Minor Equipment

As the hydrogen byproduct is burned for fuel value, a flare system is deemed necessary for safety and operation considerations. A series of control valves are also included in several equipment units for safety, especially in situations of emergency plant shutdown. These valves are all included in the bare modules for this process.

19 Specification Sheets

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SPECIFICATION SHEET
FEED PUMP

Identification: Item No: P-100   Date: 23 April 2019
                               No. Required: 1   By: KVN

Function: Pressurize initial ethanol feed

Operation: Continuous

Materials	Feed	Discharge
Temperature(°F):	95.0	99.2
Pressure (bar):	1.0	20.0
Mass Flow (lb/hr):	13729	13729
Component Mass Flow (lb/hr)		
Hydrogen	-	-
Water	-	-
Ethanol	13729	13729
Ethyl Acetate	-	-
Acetaldehyde	-	-
Buta-2-one	-	-
n-Butanal	-	-
n-Butanol	-	-
2-Butanol	-	-
Molar Flow (lbmol/hr):	298.0	298.0
Volume Flow (cuft/hr)	279.5	279.5

Design Data: Material: Stainless Steel 316   Pressure: 20 bar
                          No. Stages: 1
                          Shaft rpm: 3600
                          Type: Centrifugal Pump
                          Head: 384.0 ft
                          Temperature: 97.5°F

Utilities: Electricity at 10.83 kW

Comments & Drawings: See Section 18.1

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SPECIFICATION SHEET
HEAT EXCHANGER ONE: FLOW TO HYDROGENATION REACTOR

Identification:	Item No: E-102	Date: 23 April 2019
	No. Required: 1	By: KVN

Function: Heat effluent stream from molecular sieve

Operation: Continuous

Materials	Cold In Vapor	Cold In Liquid	Cold Out	Hot In	Hot Out
Temperature(°F)	242.1	242.1	302.0	366.0	244.8
Pressure (bar)	4.0	4.0	4.0	11.4	11.4
Mass Flow (lb/hr)	10218	2831	13050	705.7	705.7
Component Mass Flow (lb/hr)					
Hydrogen	59.1	0.04	59.1	-	-
Water	trace	trace	trace	705.7	705.7
Ethanol	10.7	1.28	12.0	-	-
Ethyl Acetate	10022	2796	12818	-	-
Acetaldehyde	0.01	trace	0.01	-	-
Buta-2-one	63.8	16.7	80.4	-	-
n-Butanal	63.3	17.2	80.5	-	-
n-Butanol	-	-	-	-	-
2-Butanol	-	-	-	-	-
Molar Flow (lbmol/hr)	145.1	32.2	177.3	39.2	39.2
Volume Flow (cuft/hr)	18886	18886	24979	2107	12.5

Design Data: Surface Area: 5.65 ft^2 Pressure: 4 bar
LMTD: 77.9°F
Heat Duty: 708965 Btu/hr
Transfer Coefficient: 149.7 Btu/hr-ft^2-°F
Type: Double Pipe Heat Exchanger
Material: Stainless Steel 316

Utilities: 150 psig steam at 826 lb/hr

Comments& Drawings: See Section 18.2

SPECIFICATION SHEET
HEAT EXCHANGER TWO: FLOW TO DISTILLATION COLUMN

Identification: Item No: E-103   Date: 23 April 2019

                          No. Required: 1   By: KVN

Function: Cool the hydrogenaion reactor effluent

Operation: Continuous

Materials	Cold In	Cold Out	Hot In	Hot Out	Hydrogen Out
Temperature(°F)	86.0	120.0	313.7	122.0	122.0
Pressure (bar)	1.0	1.0	4.0	4.0	4.0
Mass Flow (lb/hr)	102294	102294	13050	12753	296.8
Component Mass Flow (lb/hr)					
Hydrogen	-	-	54.6	0.43	54.1
Water	102294	102294	trace	trace	trace
Ethanol	-	-	12.0	11.5	0.48
Ethyl Acetate	-	-	1288	12577	241.0
Acetaldehyde	-	-	0.01	0.01	trace
Buta-2-one	-	-	-	-	-
n-Butanal	-	-	-	-	-
n-Butanol	-	-	83.0	82.6	0.38
2-Butanol	-	-	83.0	82.2	0.81
Molar Flow (lbmol/hr)	5678	5678	175.1	145.4	29.6
Volume Flow (cuft/hr)	1660	1688	25043	236.6	3188

Design Data: Surface Area: 25.5 ft^2 Pressure: 1 bar

LMTD: 74.7°F

Heat Duty: 3063260 Btu/hr

Transfer Coefficient: 149.2 Btu/hr-ft^2-°F

Type: Double Pipe Heat Exchanger

Material: Stainless Steel 316

Utilities: Cooling water at 90006 lb/hr

Comments & Drawings: See Section 18.2

SPECIFICATION SHEET
REACTIVE DISTILLATION COLUMN

Identification: Item No: C-101   Date: 23 April 2019
                        No. Required: 1   By: KVN

Function: Allow and drive the ethyl acetate production reactions

Operation: Continuous

Materials	Feed	Bottoms	Distillate
Temperature(°F)	189.8	405.0	206.8
Pressure (bar)	20.0	20.0	20.0
Mass Flow (lb/hr)	16202	13019	3183
Component Mass Flow (lb/hr)			
Hydrogen	4.23	-	595.3
Water	330.9	40.2	330.9
Ethanol	13613	0.08	3.49
Ethyl Acetate	1796	12818	1796
Acetaldehyde	454.8	0.01	454.8
Buta-2-one	2.29	80.4	2.29
n-Butanal	0.57	80.4	0.57
n-Butanol	-	-	-
2-Butanol	-	-	-
Molar Flow (lbmol/hr)	346.7	149.9	344.5
Volume Flow (cuft/hr)	356.1	348.3	8494

Design Data: Number of trays: 31   Material: Stainless Steel 316
                     Feed Tray: 20   Pressure: 20 bar
                     Tray Spacing: 2 ft
                     Molar reflux ratio: 1.6
                     Height: 73 ft
                     Diameter: 5.74 ft
                     Skirt Height: 11 ft

Utilities: Cooling water at 282696 lb/hr and 450 psig steam at 22057 lb/hr

Comments & Drawings: See Section 18.3

SPECIFICATION SHEET
HYDROGENATION REACTOR

Identification:	Item No: R-100	Date: 23 April 2019
	No. Required: 1	By: KVN

Function: Hydrogenate the aldehyde and ketone byproducts to form alcohols

Operation: Continuous

Materials	**Feed**	**Discharge**
Temperature(°F):	302.0	313.7
Pressure (bar):	4.0	4.0
Mass Flow (lb/hr):	13050	13050
Component Mass Flow (lb/hr)		
Hydrogen	59.1	54.6
Water	trace	trace
Ethanol	12.0	12.0
Ethyl Acetate	12818	12818
Acetaldehyde	0.01	0.01
Buta-2-one	80.5	-
n-Butanal	80.5	-
n-Butanol	-	83.0
2-Butanol	-	83.0
Molar Flow (lbmol/hr):	177.3	175.1
Volume Flow (cuft/hr)	24979	25043

Design Data: Type: Packed Bed Reactor
Catalyst: Raney Nickel
Length: 16.4 ft
Diameter: 3.2 ft
Residence Time: 0.332 min
Pressure: 4 bar
Material: Stainless Steel 316

Utilities: None

Comments & Drawings: See Section 18.3

SPECIFICATION SHEET
DISTILLATION COLUMN

Identification: Item No: C-102   Date: 23 April 2019
                            No. Required: 1   By: KVN

Function: Separate the ethyl acetate product stream from hydrogen and byproducts

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Operation: Continuous

Materials	Feed	Bottoms	Liquid Distillate	Vapor Distillate
Temperature(°F)	122.0	263.2	101.4	101.4
Pressure (bar)	4.0	2.0	2.0	2.0
Mass Flow (lb/hr)	12753	178.5	12573	1.63
Component Mass Flow (lb/hr)				
Hydrogen	0.43	trace	0.20	0.24
Water	trace	trace	trace	trace
Ethanol	11.5	trace	11.5	trace
Ethyl Acetate	12577	25.1	12550	1.39
Acetaldehyde	0.01	trace	0.01	trace
Buta-2-one	-	-	-	-
n-Butanal	-	-	-	-
n-Butanol	82.6	82.6	0.02	trace
2-Butanol	82.1	70.8	11.3	trace
Molar Flow (lbmol/hr)	145.4	2.35	142.9	0.13
Volumetric Flow (cuft/hr)	236.6	4.08	229.1	27.7

Design Data: Number of trays: 29   Material: Stainless Steel 316
                          Feed Tray: 15   Pressure: 2 bar
                          Tray Spacing: 2 ft
                          Molar reflux ratio: 10
                          Height: 69 ft
                          Diameter: 7.1 ft
                          Skirt Height: 11 ft

Utilities: Cooling water at 840180 lb/hr and 150 psig steam at 33217 lb/hr

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Comments & Drawings: See Section 18.4

SPECIFICATION SHEET
STRIPPER

Identification: Item No: C-100 Date: 23 April 2019

No. Required: 1 By: KVN

Function: Remove valuable reaction intermediates from the C-101 distillate stream

Operation: Continuous

Materials	Liquid Feed	Vapor Feed	Liquid Effluent	Vapor Effluent
Temperature(°F)	99.2	206.8	189.8	103.3
Pressure (bar)	20.0	20.0	20.0	20.0
Mass Flow (lb/hr)	13729	3183	16202	710.5
Component Mass Flow (lb/hr)				
Hydrogen	-	595.3	4.23	591.0
Water	-	330.9	331.0	trace
Ethanol	13729	3.49	13613	119.5
Ethyl Acetate	-	1796	1796	trace
Acetaldehyde	-	454.8	454.8	0.02
Buta-2-one	-	2.29	2.29	trace
n-Butanal	-	0.57	0.57	trace
n-Butanol	-	-	-	-
2-Butanol	-	-	-	-
Molar Flow (lbmol/hr)	298.0	344.5	346.7	295.8
Volumetric Flow (cuft/hr)	280.5	8494	356.1	6160

Design Data: Theoretical trays: 5

Height: 6.0 ft

Diameter: 10.0 ft

Material: Stainless Steel 316

Pressure: 20 bar

Utilities: None

Comments & Drawings: See Section 18.5

SPECIFICATION SHEET
MOLECULAR SIEVE

Identification: Item No: S-100 Date: 23 April 2019

No. Required: 1 By: KVN

Function: Remove the water from the reactive distillation bottoms stream

Operation: Continuous

Materials	Feed	Discharge
Temperature(°F):	405.0	405.0
Pressure (bar):	20.0	20.0
Mass Flow (lb/hr):	13019	12979
Component Mass Flow (lb/hr)		
Hydrogen	trace	-
Water	40.2	-
Ethanol	0.08	0.08
Ethyl Acetate	12818	12818
Acetaldehyde	0.01	0.01
Buta-2-one	80.5	80.5
n-Butanal	80.5	80.5
n-Butanol	-	-
2-Butanol	-	-
Molar Flow (lbmol/hr):	150.0	147.7
Volume Flow (cuft/hr)	348.3	347.5

Design Data: Sieve Packing: 13X Material: Stainless Steel 316

Packing Mass: 3840 kg

Void Fraction: 0.4

Packing Density: 0.6

Length: 12.4 ft

Diameter: 2.06 ft

Pressure: 20 bar

Utilities: 450 psig steam at 43.41 lb/hr

Comments & Drawings: See Section 18.6

SPECIFICATION SHEET
ETHANOL FEED STORAGE TANK

Identification:	Item No: T-100	Date: 23 April 2019
	No. Required: 1	By: KVN

Function: Store excess Ethanol for feed to production process

Operation: Continuous

Materials	**To Process**
Temperature(°F)	95.0
Pressure (bar)	1.0
Mass Flow (lb/hr)	13729
Component Mass Flow (lb/hr)	
Hydrogen	-
Water	-
Ethanol	13729
Ethyl Acetate	-
Acetaldehyde	-
Buta-2-one	-
n-Butanal	-
n-Butanol	-
2-Butanol	-
Molar Flow (lbmol/hr)	298.0
Volumetric Flow (cuft/hr)	4.70

Design Data: Amount Stored: 1 day
Tank Type: Floating Roof
Volume: 75240 ft^3
Temperature: 95.0°F
Pressure: 1 bar
Material: Stainless Steel 316

Utilities: None

Comments & Drawings: See Section 18.7

SPECIFICATION SHEET
ETHYL ACETATE STORAGE TANK

Identification:	Item No: T-101	Date: 23 April 2019
	No. Required: 1	By: KVN

Function: Store ethyl acetate product from production

Operation: Continuous

Materials	**From Process**
Temperature(°F)	101.4
Pressure (bar)	2.0
Mass Flow (lb/hr)	12573
Component Mass Flow (lb/hr)	
Hydrogen	0.19
Water	trace
Ethanol	11.5
Ethyl Acetate	12550
Acetaldehyde	0.01
Buta-2-one	-
n-Butanal	-
n-Butanol	0.02
2-Butanol	11.3
Molar Flow (lbmol/hr)	142.9
Volumetric Flow (cuft/hr)	228.9

Design Data:
Amount Stored: 1 week
Tank Type: Floating Roof
Volume: 432219 ft^3
Temperature: 101.3°F
Pressure: 2 bar
Material: Stainless Steel 316

Utilities: None

Comments & Drawings: See Section 18.7

SPECIFICATION SHEET
WASTE STORAGE TANK

Identification:	Item No: T-102	Date: 23 April 2019
	No. Required: 1	By: KVN

Function: Store waste from production until waste collection

Operation: Continuous

Materials	**From Process**
Temperature(°F)	263.2
Pressure (bar)	2.0
Mass Flow (lb/hr)	178.5
Component Mass Flow (lb/hr)	
Hydrogen	trace
Water	trace
Ethanol	trace
Ethyl Acetate	25.1
Acetaldehyde	trace
Buta-2-one	-
n-Butanal	-
n-Butanol	82.6
2-Butanol	70.8
Molar Flow (lbmol/hr)	2.40
Volumetric Flow (cuft/hr)	4.10

Design Data: Amount Stored: 1 month
Tank Type: Floating Roof
Volume: 33114 ft^3
Temperature: 263.1°F
Pressure: 1 bar
Material: Stainless Steel 316

Utilities: None

Comments & Drawings: See Section 18.7

20   Equipment Costing Summary

To begin plant operation, a total capital investment (TCI) of $ 16.9 MM is required. The TCI is comprised of the total equipment bare module costs, the cost of site preparations, the cost of service facilities, the cost of contingencies and contractor fees, the cost of land and plant start-up, and the working capital costs.

The total permanent investment (TPI) is equal to $ 14.7 MM. Of the TPI, $10.1 MM is equal to the total bare module cost for all equipment units in this process. Table 18 describes the purchase and bare module cost of each unit in this process. Note that bare module costs are inclusive of costs of installation materials, installation labor, freight, insurance, taxes, construction overhead and contractor engineering expenses. All bare module factors listed in Table 18 (page 90) are found in Chapter 17 of *Seider et. al, 2017*.[42] Figure 12 includes a breakdown of the total bare module equipment costs for this plant.
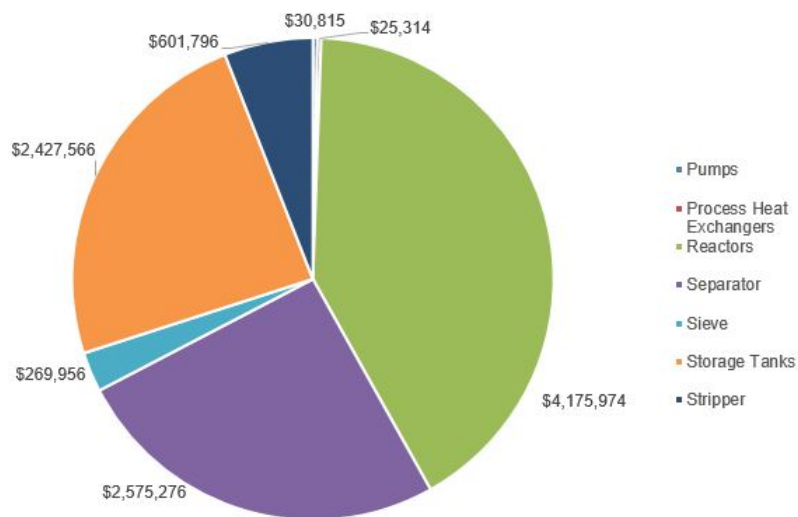
Figure 12: Breakdown of total bare module equipment costs for plant construction. The reactive distillation column, C-101, is classified as a reactor and represents 38.2% of the total bare module equipment cost. The distillation column, C-102, is the second most expensive unit, representing 25.5% of the total costs. The total bare module equipment cost is equal to $10.1 MM.

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[42]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

The reactors (reactive distillation column and hydrogenation reactor) constitute 41.3% of the total $10.1 MM required for all equipment. The reactive distillation column, specifically, is the most expensive equipment unit, costing approximately $3.9 MM, which is about 39% of the total bare module equipment costs. The distillation column constitutes 25.6% of the total equipment costs, approximated at a $2.6 MM bare module cost.

It is expected that the two distillation columns, the reactive distillation column (C-101) and distillation column (C-102), are the most expensive equipment units. Tray columns have a high bare module factor of 4.16, as installation costs and required installation materials are high for these units[43]. These columns are also large in size, requiring approximately 30 trays for each of the two columns. The two columns are also constructed entirely of Stainless Steel 316, yielding a construction material factor of 2.16. All of these factors point towards the strong likelihood that the C-101 and C-102 are the most expensive equipment units.

Note that C-101 and R-100 make use of catalysts that are replaced at distinctive time periods, as discussed in Section 18.3. The first purchase of the catalyst for these two units, at the start-up point, is capitalized. Therefore, the first purchase of catalyst is considered an equipment cost and all subsequent purchases of replacement catalyst material are considered operating costs. Further note that the sieve packing material is capitalized and accounted for in a similar manner to the catalyst material; the sieve packing material is replaced on a yearly basis. The catalyst costs and sieve packing material are included in the TCI estimate of $16.9 MM and the total bare module equipment cost estimate of $10.1 MM.

The molecular sieve is the only equipment unit that has a swinging design, and therefore two units of the molecular sieve vessel and sieve packing were included in the equipment cost summary. Inclusion of spare units of the reactive distillation column, C-101, and the distillation column, C-102, were not deemed necessary for the first iteration of the design of this plant.

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[43]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Table 18: Summary Table for all Process Units including purchase costs, bare module factor, and bare module costs; not inclusive of first purchase of catalyst material for C-101 and R-100.

Process Equipment ID	Equipment Type	Purchase Cost ($)	Bare Module Factor	Bare Module Cost ($)
T-100	Storage	153,127	4.00	612,507
P-100	Process Machinery	9,388	3.30	30,815
C-100	Fabricated Equipment	144,633	4.16	601,796
C-101	Fabricated Equipment	516,104	4.16	2,425,977
E-100	Fabricated Equipment	69,354	3.17	219,853
D-100	Fabricated Equipment	101,041	4.16	420,329
P-101	Process Machinery	9,375	3.30	30,938
E-101	Fabricated Equipment	207,986	3.17	659,317
P-102	Process Machinery	9,366	3.30	30,810
S-100A	Fabricated Equipment	31,431	4.16	130,754
S-100B	Spare	31,431	4.16	130,754
E-102	Fabricated Equipment	6,188	3.17	11,138
R-100	Fabricated Equipment	71,037	4.16	300,602
E-103	Fabricated Equipment	7,875	3.17	14,176
C-102	Fabricated Equipment	165,818	4.16	893,539
E-104	Fabricated Equipment	110,169	3.17	349,236
D-101	Fabricated Equipment	77,660	4.16	323,065
P-103	Process Machinery	9,532	3.30	31,456
E-105	Fabricated Equipment	256,601	3.17	813,424
P-104	Process Machinery	49,865	3.30	164,556
T-101	Storage	371,529	4.00	1,486,117
T-102	Storage	82,235	4.00	328,942

20.1   Unit Costing Considerations

20.1.1   Pumps

Cost estimates for all pumps in this process were determined by correlations available in *Seider et. al, 2017.* Purchase cost correlations for the pumps required the liquid flow rate, in gallons per minute, and the desired pump head, in feet. The liquid flow rate and the component values used to calculate the pump head was retrieved from ASPEN simulation results.

20.1.2   Process Heat Exchangers

Both heat exchangers were costed according to the required surface area and material construction. The correlation to cost both double pipe heat exchangers is outlined in Chapter 16 of *Seider et. al, 2017.*[44]. All input values for the cost correlation were determined from ASPEN output values. The heat exchangers were designed to minimize cost over an assumed 15 year useful life. Total equipment cost over 15 useful years was calculated as sum of the the upfront cost plus the utility costs over lifespan of the equipment. It was determined, for both heat exchangers (E-102 and E-103), that increased upfront equipment cost subsequently decreased utilities and minimized the cost of the equipment over 15 years. Therefore, the designs which minimized utility requirements led to the lowest overall cost. This is true for both E-102 and E-103. These cost optimizations are outlined in Table 19 and Table 20.

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[44]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Table 19: Total Equipment Cost Over a 15 Year Useful Lifespan of Heat Exchanger 1 (E-102) Increasing the area of the heat exchanger decreases the utility requirement. Initial upfront savings for a smaller heat exchanger is not warranted over the lifetime of the equipment.

Area (ft^2)	Steam (psig) Flow Rate (lb/hr)	Total Equipment Cost Over 15 Year Useful Life
47.2	815.7	$714,611
46.4	804.7	$705,563
46.0	793.7	$696,464
46.1	782.6	$687,311
46.5	771.6	$678,105
47.3	760.6	$668,848
48.6	749.6	$659,548
50.2	738.5	$650,212
52.2	727.5	$640,849
54.6	716.5	$631,471
57.4	705.5	$622,086

Table 20: Total Equipment Cost Over a 15 Year Useful Lifespan of Heat Exchanger 2 (E-103) Increasing the area of the heat exchanger decreases the utility requirement. Initial upfront savings for a smaller heat exchanger is not warranted over the lifetime of the equipment.

Area (ft^2)	Cooling Water Flow Rate (lb/hr)	Total Equipment Cost Over 15 Year Useful Life
173.7	215600	$377,498
262.1	187000	$339,362
288.8	167200	$312,037
293.8	151800	$290,207
293.7	138600	$271,329
293.4	127600	$255,590
293.7	121000	$246,163
294.6	112200	$233,615
295.6	105600	$224,214
296.5	99000	$214,813

20.1.3 Reactors

Reactive Distillation Column

As discussed in Section 15.1.1, patent literature provided lab scale data that was used to model the reactive distillation column. In modelling the column in ASPEN, an initial estimate of the required stage number was determined. In using Murphee Tray efficiencies and O'Connell correlations (see Section 27.1.2), the actual number of trays required were found. This value was then used to calculate the total height of the column, as described in section 18.3. The cost correlations for the reflux accumulator, reboiler and condenser were outlined in Chapter 16 of *Seider et. al, 2017.*, and the required input for these correlations were found from ASPEN simulation outputs[45].

The reflux accumulator was modelled as a horizontal pressure vessel, with a residence time of 10 minutes. This residence time was suggested at the guidance of industrial consultants. The reflux accumulator was assumed to have an aspect ratio of 2, and detailed design calculations can be found in Section 27.1.2.

The partial condenser is modelled as a fixed head, shell and tube heat exchanger. The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger. These assumptions follow the guidance of industrial consultants, and assumptions presented in Chapter 12 of *Seider et. al, 2017.*[46]

Hydrogenation Reactor

The hydrogenation reactor was modelled as a packed bed, with a residence time of 20 seconds. It was noted that the diameter of the hydrogenation reactor is out of the costing correlation limits, as it is smaller than the minimum diameter for this correlation. This rose concerns on whether a packed column is the most appropriate costing model for the hydrogenation reactor. This concern, however, was debunked based on two observations.

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[45]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

[46]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

First, the residence time is short and would therefore warrant the decision to use the packed column costing model. Second, the costing correlation's extrapolation is linear when extrapolating to this smaller diameter. The linear extrapolation is a valid indication that the packed column costing model can be applicable to the hydrogenation reactor.

20.1.4 Distillation Column

The distillation column was initially designed using the equations and calculations outlined in Section 27.1.3. These specifications were a base case, and were used as an initial input into the ASPEN simulation model. As described in Section 15.3.1, a series of sensitivity analyses were conducted to optimize the column to ensure maximum separation. The O'Connell relationships are used to determine the Murphee tray efficiencies, to gather the actual number of trays required for the column. This actual number of required trays is used in the costing correlations available in Chapter 16 of *Seider et. al, 2017*.[47] An example of these calculations can be found in Section 27.1.3. Using an assumed tray spacing of 2 ft, and an additional skirt length of 4 ft and 7 ft for the enriching and stripping sections, respectively. These values follow the guidance provided in Chapter 16 of *Seider et. al, 2017*. Stainless Steel 316 is the chosen construction material to avoid issues of product contamination due to corrosion. The cost correlations for the reflux accumulator, reboiler and condenser were outlined in Chapter 16 of *Seider et. al, 2017.*, and the required input for these correlations were found from ASPEN simulation outputs.

The reflux accumulator was modelled as a horizontal pressure vessel, with a residence time of 10 minutes. This residence time was suggested at the guidance of industrial consultants. The reflux accumulator was assumed to have an aspect ratio of 2, and detailed design calculations can be found in Section 27.1.3.

The partial condenser is modelled as a fixed head, shell and tube heat exchanger. The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger. These assumptions

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[47]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

follow the guidance of industrial consultants and assumptions presented in Chapter 12 of *Seider et. al, 2017.*

20.1.5 Stripper

The stripper was designed with the use of the ASPEN simulation model and made use of convergence outputs in the simulation. The stripper was modelled as a vertical pressure vessel, constructed of Stainless Steel 316 material. The stripper column was oversized to account for efficiency considerations, and was therefore sized to account for a 50% efficiency through the stripper. It is noted that this is a conservative estimate of the stripper efficiency. The number of theoretical stages in this column is 5. Cost correlations for the stripper were obtained from Chapter 16 of *Seider et. al, 2017.*[48]

20.1.6 Molecular Sieve

The molecular sieve vessel was modelled as a horizontal pressure vessel. The molecular sieve has one day-bed and one regenerating-bed. The molecular sieve vessel was designed with an aspect ratio (L/D) of 3, with a diameter of 2.06 ft and a length of 12.38 ft. The vessel is constructed of Stainless Steel 316, to account for potential corrosion limitations in the process. The cost correlations for the vessel were obtained from Chapter 16 of *Seider et. al, 2017.*

The molecular sieve has a spherical particle size and is assumed to pack with a packing efficiency of 0.60[49]. The sieve packing material cost estimates were obtained by calculating the amount of water that must be removed and determining the appropriate mass of sieve required to perform this process. The chosen 13X molecular sieve can hold 25 wt% of water. The volume of the sieve vessel was determined via the density of the chosen bead, 0.68 kg/L, coupled with the estimated packing efficiency.

A spare molecular sieve will be purchased as the packing material is regenerated on a

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[48]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]
[49]Donev, Cisse, Sachs, Variano, Stillinger, Connelly, Torquato, and Chaikin [2004]

daily basis. This swinging design of the molecular sieve accounts for the time required for the regeneration. In including this swinging design, we are ensuring that there will be no interruption in ethyl acetate production.

20.1.7 Storage Tanks

Storage tanks T-100, T-101, and T-102 were costed using costing correlations available from Chapter 16 of *Seider et. al, 2017*. All storage tanks make use of a volumetric safety factor of 1.5,[50] to ensure that the storage tanks never operate at full capacity. All three storage tanks in this process make use of a floating tank, which is considered as an additional safety consideration. Insulation costs for the byproduct storage tank, Tank-102, are considered unnecessary as this storage tank's temperature does not need to be maintained at a high temperature as all the byproducts are considered to be waste products. The ethanol and ethyl acetate storage tanks (T-100 and T-101, respectively) are at ambient conditions, and therefore no insulation costs were considered for these two storage tanks.

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[50]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

21 Fixed Capital Investment Summary

The TCI for this process is $ 16.9 MM, of which $14.7 MM is equal to the TPI. $10.1 MM is the total bare module cost for all equipment required in this process. As discussed in Section 20, note that the first purchase of the catalyst is capitalized and considered an equipment cost, included in the total bare module estimations with a bare module factor of 1.0[51]. The TCI for this process is estimated using the following accounting formula[52]:

$$C_{\text{TCI}} = C_{\text{TDC}} + C_{\text{start}} + C_{\text{land}} + C_{\text{WC}}$$

where C_{TDC} is the total depreciable capital cost and C_{WC} is the total working capital cost.

The total working capital costs is equal to approximately $2.2 MM. The working capital calculations follow standard accounting practices of assuming thirty days of cash reserves (excluding raw materials), thirty days of accounts receivable for product at the sales price and thirty days of accounts payable by the company for the feedstocks (in this case, ethanol) at the purchase price. As discussed in Section 12.3, this plant will be in close proximity to a corn plant, and therefore it is assumed that the raw material (ethanol) inventory will be for one day. For this process, the working capital comprises 13.1% of the TCI. Note that the cost of capital was approximated as 15% for working capital calculations, as the working capital estimate of $2.2 MM is the present value of the working capital requirements for this process. Table 21 includes a detailed breakdown of working capital calculations and estimations.

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[51]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]
[52]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Table 21: Breakdown of calculation of C_{WC}

The total working capital is the present value of the working capital over the first three years of this project, calculated at a cost of capital of 15%

	2019	2020	2021
Accounts Receivable ($)	1,724,587	862,293	862,293
Cash Reserves ($)	246,443	123,222	132,222
Accounts Payable ($)	(1,007,570)	(503,785)	(503,785)
Ethyl Acetate Inventory ($)	402,404	201,202	201,202
Raw Materials ($)	30,704	15,352	15,352
Total ($)	1,396,567	698,284	298,284
Present Value at 15%	1,214,406	528,003	459,133
Total Working Capital ($)	**2,201,542**		

The total permanent investment (TPI) for this process is \$14.7 MM. Table 22 describes the cost components for the calculation of TPI.

Table 22: Breakdown of Total Permanent Investment (TPI) Estimation.
Cost correlations and assumptions applicable in this summary are outlined in Table 23.

Bare Module Costs ($)	
Fabricated Equipment	7,293,960
Process Machinery	288,575
Spares	-
Storage	2,427,566
Other Equipment	-
Catalysts	96,596
Computer, Software, etc.	-
Total Bare Module Costs	**10,106,697**
Direct Permanent Investment ($)	
Cost of Site Preparations	505,335
Cost of Service Facilities	505,335
Allocate Costs for Utility Plants and Related	-
Total Direct Permanent Investment	**11,117,367**
Total Depreciable Capital ($)	
Cost of Contingencies & Contractor Fees	2,001,126
Total Depreciable Capital	**13,118,493**
Total Permanent Investment ($)	
Cost of Land	262,370
Cost of Royalties	-
Cost of Plant Start-Up	1,311,849
Total Permanent Investment - Unadjusted	**14,692,712**
Site Factor	1.00
Total Permanent Investment	**14,692,712**

In this process costing model, the cost correlations and assumptions are outlined in Table 23[53]. The cost of royalties for this plan are assumed to be zero.

Table 23: Outline of cost correlations and assumptions to calculate TPI

TPI Cost Component	Assumption
Cost of Site Preparations	5.00 % of Total Bare Module Costs
Cost of Service Facilities	5.00 % of Total Bare Module Costs
Cost of Contingencies and Contractor Fees	18.00% of Direct Permanent Investment
Cost of Land	2.00% of Total Depreciable Capital
Cost of Plant Start-Up	10.00% of Total Depreciable Capital

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[53]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

22 Operating Costs

22.1 Variable Operating Costs

22.1.1 Raw Materials

As discussed in Section 12.3, this plant will be located in close proximity to a corn plant, and therefore this economic analysis assumes that only a one day inventory of ethanol will be required. The ethanol feed arrives at this plant via a pipeline from this corn plant, as discussed in Section 12.3. Although it would be safe to assume that the ethanol could be purchased at a discount due to this plant's proximity to the corn plant, a conservative approach to the economic analysis was adopted and the purchase price of ethanol instead reflects no such discount. The ethanol purchase price used in this analysis is the market spot price of ethanol as of market close on 16 April 2019. The catalyst used in C-101 is Copper Oxide/Zinc Oxide on Alumina, and this catalyst is replaced four times a year. The cost for this catalyst was determined by obtaining a quotation from a local vendor. The catalyst used in R-100 is Raney Nickel, which is also replaced four times a year. The cost for this catalyst was also determined by obtaining a quotation from a local vendor. The sieve packing material is replaced on a yearly basis, and the quotation was obtained from a local vendor. As discussed in Section 20, the first purchase of each catalyst/sieve packing material is capitalized, and subsequent purchases are treated as variable operating costs. Table 24 outlines the relevant raw material costs. Note that these raw material costs are quoted on a yearly basis, using the goal basis of 50kT of ethyl acetate production per year. The total raw material cost is calculated as $0.27 per lb of Ethyl Acetate produced, or $24.9MM per year.

Table 24: Breakdown of Raw Material Costs and Requirements

Raw Material	Required Ratio (lb per lb of Ethyl Acetate)	Cost of Raw Material ($/lb of Ethyl Acetate)
Ethanol	1.109	0.20
CuO/ZnO on Aluminna Catalyst	1.65×10^{-6}	90.90
Molecular Sieve Packing	1.58×10^{-5}	1.00
Raney Nickel Catalyst	3.36×10^{-5}	13.64

22.1.2 Utility Costs

The utility requirements and relevant costs for the utilities are outlined in Table 25. The total utility cost is calculated as $0.021 per lb of ethyl acetate produced, or $2.34MM per year. Note that this process did not require any process water, at least for the first iteration of this plant design.

Table 25: Utility Requirements on a Yearly Basis and Cost Ratios

Utility	Required Ratio (per lb of Ethyl Acetate Produced)	Cost of Utility ($ per unit)
High Pressure Steam (450 psig)	1.76 lb	0.0050
Low Pressure Steam (150 psig)	2.71 lb	0.004
Cooling Water	11.59 gal	0.00005
Electricity	0.00131 kWh	0.07

22.1.3 Hydrogen Fuel Value

As discussed in Section 16.1, the hydrogen produced at this plant will be burnt to extract fuel value. The amount of energy released, assuming a 70% efficiency of combustion, was calculated as 1814 Btu/lb of ethyl acetate produced. Following guidance provided by industrial consultants, the hydrogen fuel value was determined by using the selling price of natural gas as a basis. The hydrogen fuel value is treated as a byproduct in this economic analysis. The

hydrogen fuel value was considered to be sold at 1.4×10^{-5}/Btu. The estimated fuel value of the hydrogen is therefore estimated to be $2.79 MM, per year.

22.1.4 General Expenses

General expense data estimations and assumptions are outlined in Chapter 17 of *Seider et. al, 2017*[54]. These assumptions and correlations are outlined in Table 26. General expenses, on a yearly basis, are estimated at $5.38 MM.

Table 26: Breakdown of General Expense Calculations and Assumed Correlations

General Expense	Relationship to Sales	Total Annual Cost ($)
Selling/Transfer Expenses	3.00% of Sales	1,398,831
Direct Research	4.80% of Sales	2,238,130
Allocated Research	0.50% of Sales	233,139
Administrative Expense	2.0% of Sales	932,554
Management Incentive Compensation	1.25% of Sales	582,846
Total	**11.55% of Sales**	**5,385,500**

22.1.5 Summary of Operating Variable Costs

Using the aforementioned assumptions and correlations, the total operating variable costs were estimated to be $29.8 MM per year and are shown in Table 27.

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[54]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Table 27: Summary of Total Operating Variable Costs on a Yearly Basis, assuming a target production of 50kT of Ethyl Acetate

General Expenses ($)	
Selling/Transfer Expenses	1,398,831
Direct Research	2,238,130
Allocated Research	233,139
Administrative Expense	932,554
Management Incentive Compensation	582,846
Total General Expenses	**5,385,501**
Raw Materials ($)	24,904,296
Byproducts ($)	(2,799,426)
Utilities ($)	2,337,415
Total Variable Costs	**29,827,785**

22.2 Fixed Operating Costs

22.2.1 Operations

To ensure successful and safe operation of the plant, five daily operator shifts were deemed necessary. Following guidance from industrial consultants, one operator was required for each main process unit, which yields three operators per shift for this process[55]. A standard wage of $40/operator hour was used. The control laboratory costs were set to a conservative minimum as few quality controls are required, other than the quality control tests of the final ethyl acetate product. Table 28 outlines further assumptions necessary in determining the operations component of the fixed operating cost. This was estimated as $2.21 MM.

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[55]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Table 28: Breakdown of costing assumptions applied in calculation of operations component of fixed operating costs

Fixed Operating Costs: Operations	Costing Details
Operators per Shift	3 (assuming 5 shifts)
Direct Wages and Benefits	$40/operator hour
Direct Salaries and Benefits	15% of Direct Wages and Benefits
Operating Supplies and Services	6% of Direct Wages and Benefits
Technical Assistance to Manufacturing	$13,333 per year, per operator
Control Laboratory	$33,333 per year, per operator

22.2.2 Maintenance

Table 29 indicates the assumptions applied in determining the total site maintenance fixed costs for this plant. These assumptions follow guidelines listed in Chapter 17 of *Seider et. al, 2017*[56]. The total maintenance fixed operating costs are estimated to be $1.36 MM.

Table 29: Breakdown of costing assumptions applied in calculation of maintainence component of fixed operating costs

Fixed Operating Costs: Maintenance	Costing Details
Wages and Benefits	4.50% of Total Depreciable Capital
Salaries and Benefits	25% of Maintenance Wages and Benefits
Materials and Services	100% of Maintenance Wages and Benefits
Maintenance Overhead	5% of Maintenance Wages and Benefits

22.2.3 Overhead

Table 30 outlines the assumptions applied in determining the overhead fixed operating costs for this plant. These guidelines follow those listed in Chapter 17 of *Seider et. al, 2017*[57].

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[56]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]
[57]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

The total operating overhead costs are estimated to be \$495M. Following standard accounting practices, property taxes and insurance is assumed to be 2.00% of total depreciable capital. The total property taxes and insurance costs are estimated to be \$262M. Note for this process, licensing and rental fees are assumed to be zero or negligible.

Table 30: Breakdown of costing assumptions applied in calculation of overhead component of fixed operating costs

Fixed Operating Costs: Overhead	Costing Details
General Plant Overhead	7.1% of Maintenance and Operations Wages and Benefits
Mechanical Department Services	2.4% of Maintenance and Operations Wages and Benefits
Employee Relations Department	5.9% of Maintenance and Operations Wages and Benefits
Business Services	7.4% of Maintenance and Operations Wages and Benefits

22.2.4 Summary of Fixed Operating Costs

Using the aforementioned assumptions and correlations, the total operating fixed costs were estimated to be \$4.3 MM, per year, as shown in Table 31.

Table 31: Fixed Operating Costs on a Yearly Basis

Operations ($)

Direct Wages and Benefits	1,248,000
Direct Salary and Benefits	187,200
Operating Supplies and Services	74,880
Technical Assistance to Manufacturing	199,995
Control Laboratory	499.995
Total Operations	**2,210,070**

Maintenance ($)

Wages and Benefits	590,332
Salaries and Benefits	147,583
Materials and Services	590,332
Maintenance Overhead	29,517
Total Total Maintenance	**1,357,764**

Operating Overhead ($)

General Plant Overhead	154,291
Mechanical Department Services	52,155
Employee Relations Department	128,214
Business Services	160,811
Total Operating Overhead	**495,470**

Property Taxes and Insurance ($)

Property Taxes and Insurance	262,370
Total Taxes and Insurance	**262,370**

Other Annual Expenses ($)

Rental Fees	-
Licensing Fees	-
Miscellaneous	-
Total Other Annual Expenses	**-**
Total Fixed Costs	**4,325,674**

23 Profitability Analysis

The novel process that Greenyug proposes to produce ethyl acetate from ethanol proves to be a profitable venture in the specialty chemicals industry, with a IRR of 38.73% and ROI of 43.2% for this project.

23.1 Cash Flow Model

Several key assumptions in costing correlations have been noted in previous sections. One important assumption in this cash flow model is that the plant will be operated for 330 days/year, which is equivalent to an operating factor of 0.904. Following standard industry practice, this plant is assumed to take one year to design and one year to construct. The TPI of $17.7MM is assumed to be paid up-front in the first year of construction. This cash flow model makes use of a start-up profile, a sensible and conservative assumption to include as chemical plants often need a period of time to achieve their full/desired operating capacity. This period of time is often used to ensure safety of the plant and scale production at an incremental level annually. This time is also taken for training purposes and to continuously improve the first iteration of the design[58]. For this cash flow model, the plant achieves 50% of production capacity in the first year, and achieves 90% of design capacity within two years. For safety reasons, the maximum operating capacity is set at 90% of design capacity.

As this project inherently looks to determine the technical and economic feasibility of the Greenyug process, a conservative approach was taken in developing this cash flow model. Therefore, aligning with this approach, the net present value (NPV) projections consider a fifteen year time horizon. This is a typical assumption made in project cash flow models.[59]

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[58]Lager [2012]
[59]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

A five year MACRS depreciation schedule was applied for this cash flow model. It is advantageous for a company to rapidly depreciate its capital investment early in the life of its process. Choosing a shorter (five year) MACRS depreciation schedule reduces tax liability and accelerates the rate of return[60].

This cash flow model assumes a weighted average capital cost (WACC) of 15% and cash flows are discounted at this rate in the model. As mentioned previously, it is assumed that the selling price of ethyl acetate is $0.42/lb, with no green premium. The selling price of ethyl acetate is assumed to be constant through the fifteen years of the project, assuming no inflation. The argument and analysis of the green premium is elaborated upon later in this section. The choice to include no green premium as the base case is, once again, aligns with the conservative approach to the analysis. This analysis assumes that 100% of the production is sold.

The detailed summary of the cash flow model can be found in Section 27.2. Table 32, however, outlines the undiscounted and discounted cash flows at a WACC of 15%, on a yearly basis. As seen in Table 32, the cumulative NPV at the end of 15 years, at a WACC of 15% is $23.08MM.

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[60]Prono [2019]

Table 32: Summary of Cash Flows Over Fifteen-Year Lifespan of Project

Year	Cash Flow ($)	Cumulative NPV at 15% ($)
2018	-	-
2019	(16,089,300)	(13,990,700)
2020	2,395,600	(12,179,300)
2021	5,668,200	(8,452,300)
2022	8,890,900	(3,368,900)
2023	8,659,200	936,200
2024	8,659,200	4,679,800
2025	8,485,400	7,869,800
2026	8,311,600	10,586,800
2027	8,311,600	12,949,500
2028	8,311,600	15,004,000
2029	8,311,600	16,790,500
2030	8,311,600	18,344,000
2031	8,311,600	19,694,900
2032	8,311,600	20,869,500
2033	8,311,600	21,891,000
2034	11,104,700	23,077,700

As seen below in Figure 13, cumulative discounted cash flows remain negative until year three of production. The process yields constant yearly revenues of $41.9MM. An explanation for the negative cumulative discounted cash flows lies in the fact that for the first two years of this project, there are no ethyl acetate sales. The capital costs are also paid up-front in year one of construction. The graphical representation of the cumulative discounted cash flows illustrates that the break-even point lies between 2022 and 2023.
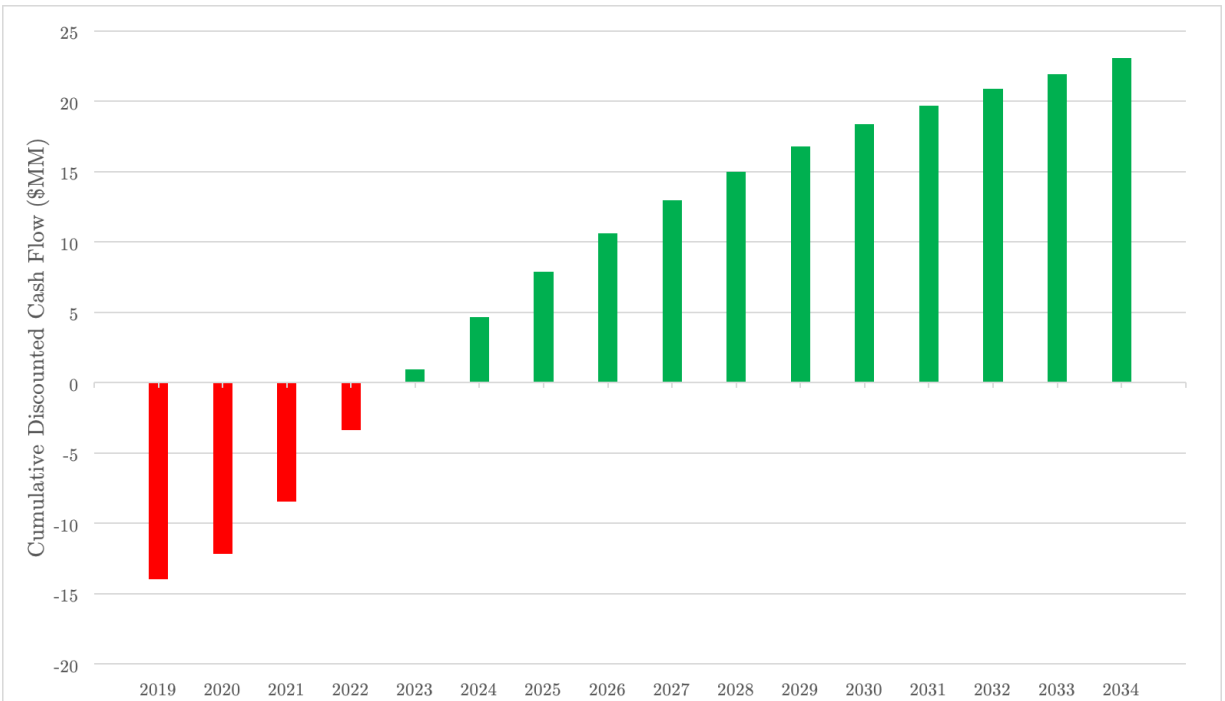
Figure 13: Cumulative discounted free cash flow ($MM) for project over fifteen-year lifespan assuming Ethyl Acetate selling price of $0.42/lb and Ethanol purchase of $0.20/lb. The process shows a break even point between years three and four of production. The production sees full operating capacity within two years of production.

23.2   Profitability Measures

23.2.1   Internal Rate of Return

Over the plant's first fifteen years of useful life, this model projects an internal rate of return (IRR) of 38.7%. This is greater than the WACC of 15%, signalling the potential of a profitable venture. The IRR is generally a strong measure of profitability, as it takes into account the timing of the project and its timeline, giving weight to the time value of money[61]. As discussed in Section 23.3, the WACC can be variable for each company and a sensitivity analysis is conducted on the WACC to illustrate how a variation in WACC can affect the company's profitability. The advantage with using IRR as a measure of profitability, is that the WACC and IRR are independent of each other. As Greenyug is a start-up company

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[61]Lanctot [2019]

and new to the industry, it is quite likely that the estimation of the WACC at 15% may be misleading and affect profitability measures. However, this is not the case for the IRR measure, which remains at 38.7%, regardless of the variation in WACC.

A major assumption of IRR is that it assumes all cash flows are re-invested at the same rate as the IRR. Given that the IRR for this project is 38.7%, it is unlikely that it is realistic and possible. This, therefore, overestimates the annual equivalent rate of return. The formula inherently assumes that the company has other projects with equally attractive prospects. As Greenyug is a new start-up, it is unlikely that this is the case. Often, to sidestep this issue, a modified IRR formula is used with reinvestment at the cost of capital. This goes beyond the initial scope of analysis for the first iteration of this process design.

23.2.2   Return on Investment

The return on investment (ROI) is a measure of the efficiency of an investment. A positive ROI is roughly indicative of a profitable venture. The ROI is a simple formula that accounts for the change in the current value of investment and the cost of investment, and compares this change against the cost of investment. The ROI is calculated at the third production year as this is the year that the process achieves full operating capacity. Table 33, shown below, outlines the ROI calculations conducted for this analysis. Note that often the ROI and the IRR are used in conjunction with each other to determine the profitability of a project. In this case, both the IRR and ROI are positive, indicating a profitable venture.

Table 33: Breakdown and Summary of ROI Calculation

ROI Analysis (Third Production Year)

Annual Sales ($)	41,964,942
Annual Costs ($)	(31,170,681)
Depreciation ($)	(980,004)
Income Tax ($)	(2,257,279)
Net Earnings ($)	7,556,978
Total Capital Investment ($)	17,485,846
ROI (%)	43.22

23.2.3 Working Capital Ratio

The working capital ratio is the ratio between current assets and current liabilities. The ratio is a measure of liquidity, illustrating a company's ability to pay off its obligations. According to general accounting guidelines, a working capital ratio of less than 1.0 indicates possible future liquidity problems, whereas a working capital ratio at around 2.0 is indicative of good short-term liquidity[62]. For this process, the working capital ratio is about 2.38, indicating that the process will allow the company to have a strong short-term liquidity to pay off its debt. This is yet another measure indicating a strong profitability narrative for this venture.

23.3 Sensitivity Analyses

Previous sections present the base case profitability analysis for this project, making use of several assumptions in the cash flow model, as outlined in Section 23.1. The following sensitivity analyses analyze the robustness of this project's profitability in response to variations in several key project factors. Note that although the base case makes use of a

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[62]Bragg [2019]

conservative and rigorous approach to determining the aforementioned profitability factors, this process is considered to only be in its first iteration of design. It is likely that as the process is continuously operated, further improvements are made which may increase capital or operating costs.

23.3.1   Sensitivity Analysis: IRR

A series of sensitivity analyses were carried out to further understand the effect of certain forces on the IRR for this project. As discussed in Section 22.1, the variable costs for this process are estimated to be \$29.8MM. Table 34, shown below, illustrates the variation of variable costs and product price $\pm$ 50% from the base case. As expected, the IRR decreases as variable costs increase and the IRR increases as the product price increases. The IRR is relatively more sensitive to product price, falling to a negative range if the product price reduces by only 20%, whereas the IRR falls to a negative range only when the variable cost increases by 50%. As ethyl acetate is a specialty chemical, it is likely to be exposed to market risks and forces that govern the price in the free market. This is an important managerial consideration and is something the management team should be aware of, as it is a likely risk exposure and the IRR is significantly sensitive to the product price. Although the variable cost is also inclusive of a commodity chemical exposed to significant market risk (ethanol), this cost also includes the costs of utilities and general expenses which are less likely to change quite as drastically. Even so, the variable costs would have to increase by 50% for the company to see a negative IRR.

Table 34: Sensitivity of IRR to Variations in Product Price and Variable Cost

						Variable Costs					
Product Price	$14,913,893	$17,896,671	$20,879,450	$23,862,228	$26,845,007	**$29,827,785**	$32,810,564	$35,793,342	$38,776,121	$41,758,900	$44,741,678
$ 0.21	11.94%	-7.07%	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.25	29.26%	18.64%	5.23%	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.30	43.22%	34.17%	24.38%	13.06%	-3.21%	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.34	55.75%	47.43%	38.75%	29.54%	19.35%	6.89%	-17.04%	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.38	67.39%	59.52%	51.43%	43.07%	34.28%	24.83%	14.05%	-0.44%	Negative IRR	Negative IRR	Negative IRR
$ 0.42	78.39%	70.84%	63.15%	55.27%	47.16%	**38.73%**	29.79%	20.00%	8.31%	-10.50%	Negative IRR
$ 0.47	88.87%	81.58%	74.17%	66.64%	58.96%	51.07%	42.92%	34.39%	25.25%	14.96%	1.74%
$ 0.51	98.93%	91.84%	84.67%	77.40%	70.02%	62.51%	54.82%	46.91%	38.70%	30.04%	20.60%
$ 0.55	108.62%	101.70%	94.72%	87.67%	80.53%	73.29%	65.93%	58.42%	50.73%	42.79%	34.49%
$ 0.59	117.98%	111.22%	104.40%	97.53%	90.59%	83.57%	76.46%	69.24%	61.90%	54.39%	46.68%
$ 0.63	127.06%	120.42%	113.75%	107.03%	100.26%	93.42%	86.52%	79.53%	72.45%	65.25%	57.92%

Table 35: Sensitivity of IRR to Variations in Green Premium and TPI

					Total Permanent Investment						
Green Premium	$11,019,534	$11,754,169	$12,488,805	$13,223,441	$13,958,076	**$14,692,712**	$15,427,347	$16,161,983	$16,896,619	$17,631,254	$18,365,890
0.00%	60.19%	54.81%	50.07%	45.85%	42.10%	**38.73%**	35.69%	32.93%	30.43%	28.13%	26.03%
2.50%	64.77%	59.03%	53.98%	49.50%	45.50%	41.92%	38.70%	35.78%	33.13%	30.70%	28.48%
5.00%	69.25%	63.17%	57.81%	53.06%	48.83%	45.04%	41.63%	38.55%	35.75%	33.20%	30.86%
7.50%	73.64%	67.21%	61.55%	56.54%	52.08%	48.09%	44.50%	41.25%	38.31%	35.62%	33.17%
10.00%	77.95%	71.19%	65.23%	59.96%	55.27%	51.07%	47.30%	43.90%	40.81%	37.99%	35.42%
12.50%	82.19%	75.09%	68.85%	63.32%	58.40%	54.00%	50.05%	46.49%	43.26%	40.32%	37.63%
15.00%	86.35%	78.93%	72.40%	66.62%	61.48%	56.88%	52.76%	49.03%	45.66%	42.59%	39.79%
17.50%	90.46%	82.71%	75.90%	69.87%	64.51%	59.72%	55.41%	51.53%	48.02%	44.83%	41.91%
20.00%	94.49%	86.44%	79.34%	73.07%	67.49%	62.51%	58.03%	54.00%	50.34%	47.02%	44.00%
22.50%	98.47%	90.11%	82.74%	76.23%	70.43%	65.26%	60.61%	56.42%	52.63%	49.19%	46.05%
25.00%	102.40%	93.73%	86.09%	79.34%	73.33%	67.97%	63.16%	58.82%	54.89%	51.32%	48.07%

The green premium is an important factor to consider for any sustainably produced chemical. For the base case economic analysis, a green premium was not applied to the ethyl acetate product in order to maintain a rigorous and conservative approach. As expected and seen in Table 35, shown above, the greater the green premium, the greater the IRR. Table 35 also illustrates the effect of variation in TPI on the IRR. In this sensitivity analysis, the TPI was varied by $\pm 50\%$ from the base value of \$14.8MM. It is expected that as TPI increases, the IRR decreases; however, even if the TPI increases by 50%, the IRR remains positive (albeit, is half the value). This illustrates that the IRR is relatively insensitive to variations in TPI.

As mentioned in Section 23.1, the base case cash flow model assumes that 100% of all ethyl acetate produced is sold to customers. For a start-up company like Greenyug, this may be unlikely, especially in the preliminary years of production as they are a new player in the market competing against large chemical companies. The reason for suspicion in a figure of 100% of production sold lies not in whether there remains to be enough demand, but rather lies in the fact that Greenyug is a new player and would have groundwork to do (just as any start-up) in establishing themselves in the industry. For this reason, a sensitivity analysis was conducted to determine the effect on the IRR in response to a variation in the percentage of production sold. As seen in Table 36, shown below, the IRR remains in the positive range if the percentage of production sold falls as low as 75%. However, this quickly changes if the product price falls by even 10%. As discussed above, the IRR is highly sensitive to the product price. However, this sensitivity is further accelerated when considering the percentage of production sold. This analysis therefore advocates for the important of a green premium for ethyl acetate, especially in the beginning years of the project when the percentage of production sold may not be 100%. As seen in Table 34, even a small increase in product price (and therefore an application of a modest green premium) will comfortably allow the project to see a positive IRR even as the percentage of production sold remains low in the preliminary years.

116

Table 36: Sensitivity of IRR to Variations in Product Price and % of Production Sold

Product Price		% of Production Sold					
	75.00%	80.00%	85.00%	90.00%	95.00%	100.00%
$ 0.21	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.25	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.30	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 0.34	Negative IRR	Negative IRR	Negative IRR	Negative IRR	-2.61%	6.89%
$ 0.38	Negative IRR	-12.75%	2.18%	11.23%	18.47%	24.83%
$ 0.42	1.01%	11.26%	19.27%	26.27%	32.68%	**38.73%**
$ 0.47	16.67%	24.65%	31.83%	38.54%	44.93%	51.07%
$ 0.51	28.12%	35.67%	42.77%	49.56%	56.12%	62.51%
$ 0.55	38.00%	45.55%	52.79%	59.80%	66.62%	73.29%
$ 0.59	47.01%	54.73%	62.19%	69.47%	76.58%	83.57%
$ 0.63	55.42%	63.37%	71.11%	78.68%	86.11%	93.42%

117

The following tornado chart illustrates the degree to which IRR is sensitive to the variations in product price, percentage of production sold, variable costs, TPI and fixed costs. The tornado chart illustrates the variations in IRR while holding all other independent variables constant. As seen in Figure 14, the IRR is most sensitive to the product price and least sensitive to fixed costs. Figure 14 also lends itself to the discussion that a green premium would be advantageous in offsetting any market shocks to the product price as this factor is significant to the profitability of the project.
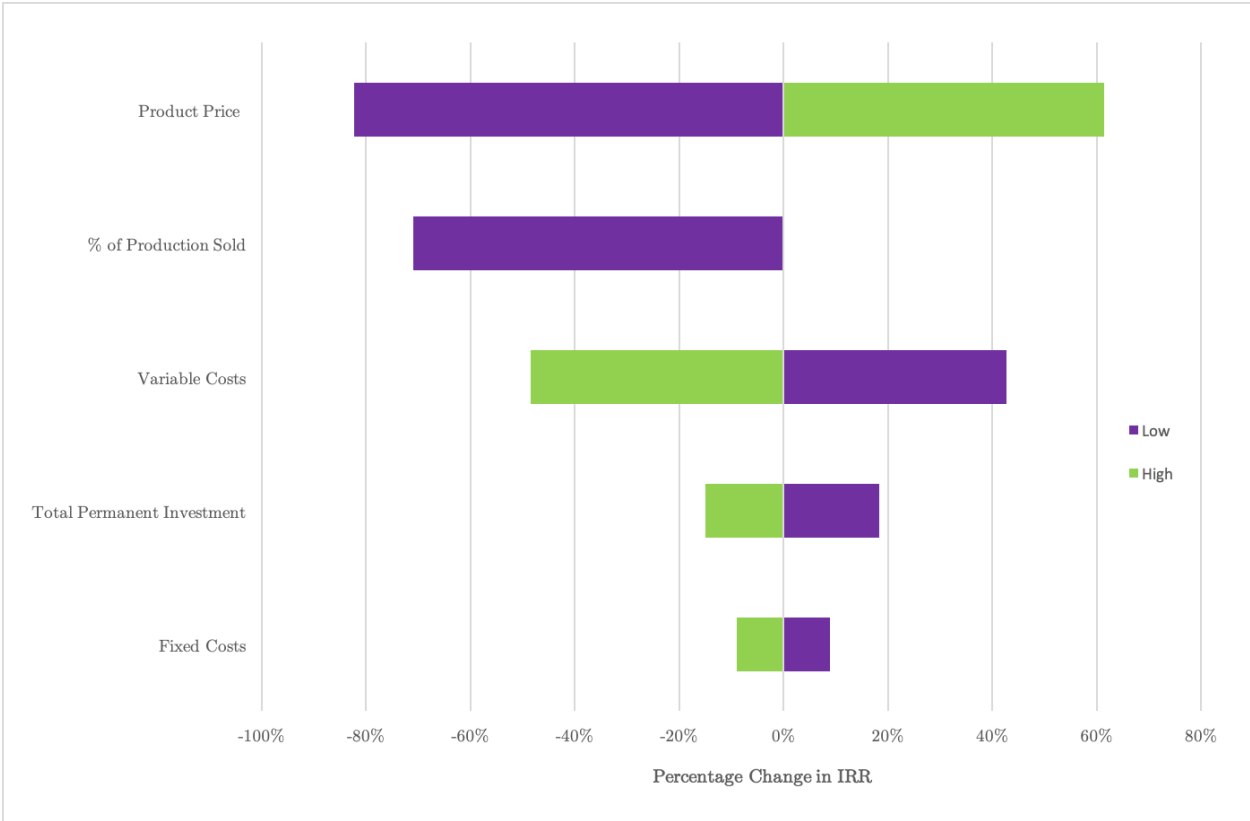
Figure 14: Tornado chart illustrating the variation in IRR to a change in the product price, % of production sold, variable costs, TPI and fixed costs. The base case IRR is equal to 38.73%. This chart shows a variation of the independent variable by $\pm$ 20% from their base case, where applicable.

23.3.2 Sensitivity Analysis: NPV

A series of sensitivity analyses were carried out to further understand the effect of certain forces on the NPV for this project. The WACC used for the base case economic analysis was

15%. Although this follows general capital budgeting models, often the WACC is above or below this estimation and can effect the profitability and NPV of the project. The WACC is the average rate of return a company expects to compensate all its investors. This discount rate typically increases the "riskier" the project, and it is likely that a smaller start-up company such as Greenyug may face higher discount rates. As the IRR is indifferent to the WACC, a series of sensitivity analyses were carried out on the basis of the cumulative NPV over the fifteen year useful life of the project.

Table 37, as shown below, illustrates the variation of WACC and the product price. As expected, the NPV falls as the WACC increases. Table 37 outlines that the NPV falls within a negative range if the WACC increases by 30%. The NPV is even more sensitive to the product price, as the NPV falls within the negative range if the product price falls by 20%.

Table 37: Sensitivity of NPV to Variations in Product Price and WACC

Product Price	WACC							
	12.00%	13.50%	**15.00%**	16.50%	18.00%	19.50%	21.00%	22.50%
$0.21	$ (34,182,606)	$ (42,465,668)	$ (49,133,652)	$ (54,494,858)	$ (58,794,887)	$ (62,230,189)	$ (64,958,526)	$ (67,107,085)
$0.25	$ (16,623,467)	$ (26,571,918)	$ (34,691,382)	$ (41,323,223)	$ (46,740,312)	$ (51,161,692)	$ (54,763,918)	$ (57,689,879)
$0.30	$ 935,673	$ (10,678,168)	$ (20,249,112)	$ (28,151,587)	$ (34,685,738)	$ (40,093,196)	$ (44,569,311)	$ (48,272,673)
$0.34	$ 18,494,812	$ 5,215,582	$ (5,806,841)	$ (14,979,952)	$ (22,631,164)	$ (29,024,699)	$ (34,374,703)	$ (38,855,467)
$0.38	$ 36,053,952	$ 21,109,332	$ 8,635,429	$ (1,808,316)	$ (10,576,589)	$ (17,956,203)	$ (24,180,096)	$ (29,438,261)
$0.42	$ 53,613,091	$ 37,003,082	**$ 23,077,699**	$ 11,363,319	$ 1,477,985	$ (6,887,706)	$ (13,985,488)	$ (20,021,055)
$0.47	$ 71,172,231	$ 52,896,832	$ 37,519,969	$ 24,534,954	$ 13,532,560	$ 4,180,790	$ (3,790,881)	$ (10,603,849)
$0.51	$ 88,731,370	$ 68,790,582	$ 51,962,240	$ 37,706,590	$ 25,587,134	$ 15,249,287	$ 6,403,727	$ (1,186,643)
$0.55	$ 106,290,510	$ 84,684,332	$ 66,404,510	$ 50,878,225	$ 37,641,709	$ 26,317,783	$ 16,598,334	$ 8,230,563
$0.59	$ 123,849,649	$ 100,578,082	$ 80,846,780	$ 64,049,861	$ 49,696,283	$ 37,386,280	$ 26,792,942	$ 17,647,769
$0.63	$ 141,408,789	$ 116,471,832	$ 95,289,051	$ 77,221,496	$ 61,750,857	$ 48,454,776	$ 36,987,549	$ 27,064,975

120

To account for the sensitivity of NPV to the product price, a green premium can be applied to the ethyl acetate product, as explained previously. This green premium allows for more flexibility in keeping the NPV positive for this project, even if the company faces a higher WACC. As seen below in Table 38, if a modest green premium of 7.5% is added to the ethyl acetate selling price, the WACC can increase to an even greater extent (as far as 40%) before seeing a negative NPV. This sensitivity analysis furthers the case to include and consider the green premium, especially given the fact that a higher WACC is highly probable for a smaller company.

As described in previous sections, it is unlikely that a small company will be able to sell 100% of their total production, at least in the preliminary years of production. This could be true of a start-up such as Greenyug, who yet needs to establish themselves in the industry. As seen below in Table 39, the NPV for this project is sensitive to this metric, and reducing the % of production sold to even 80% at a WACC of 15%, will yield a negative NPV. This is again an important managerial consideration to be aware of, especially in the beginning years of production.

Table 38: Sensitivity of NPV to Variations in Green Premium and WACC

		WACC						
	12.00%	13.50%	**15.00%**	16.50%	18.00%	19.50%	21.00%	22.50%
0.00%	$ 53,613,091	$ 37,003,082	**$ 23,077,699**	$ 11,363,319	$ 1,477,985	$ (6,887,706)	$ (13,985,488)	$ (20,021,055)
2.50%	$ 58,002,876	$ 40,976,520	$ 26,688,267	$ 14,656,228	$ 4,491,629	$ (4,120,582)	$ (11,436,836)	$ (17,666,753)
5.00%	$ 62,392,661	$ 44,949,957	$ 30,298,834	$ 17,949,137	$ 7,505,272	$ (1,353,458)	$ (8,888,185)	$ (15,312,452)
7.50%	$ 66,782,446	$ 48,923,395	$ 33,909,402	$ 21,242,046	$ 10,518,916	$ 1,413,666	$ (6,339,533)	$ (12,958,150)
10.00%	$ 71,172,231	$ 52,896,832	$ 37,519,969	$ 24,534,954	$ 13,532,560	$ 4,180,790	$ (3,790,881)	$ (10,603,849)
12.50%	$ 75,562,015	$ 56,870,270	$ 41,130,537	$ 27,827,863	$ 16,546,203	$ 6,947,914	$ (1,242,229)	$ (8,249,547)
15.00%	$ 79,951,800	$ 60,843,707	$ 44,741,105	$ 31,120,772	$ 19,559,847	$ 9,715,039	$ 1,306,423	$ (5,895,246)
17.50%	$ 84,341,585	$ 64,817,145	$ 48,351,672	$ 34,413,681	$ 22,573,490	$ 12,482,163	$ 3,855,075	$ (3,540,944)
20.00%	$ 88,731,370	$ 68,790,582	$ 51,962,240	$ 37,706,590	$ 25,587,134	$ 15,249,287	$ 6,403,727	$ (1,186,643)
22.50%	$ 93,121,155	$ 72,764,020	$ 55,572,807	$ 40,999,499	$ 28,600,778	$ 18,016,411	$ 8,952,379	$ 1,167,659
25.00%	$ 97,510,940	$ 76,737,457	$ 59,183,375	$ 44,292,407	$ 31,614,421	$ 20,783,535	$ 11,501,030	$ 3,521,960

Green Premium

Table 39: Sensitivity of NPV to Variations in % of Productino Sold and WACC

		WACC						
	12.00%	13.50%	**15.00%**	16.50%	18.00%	19.50%	21.00%	22.50%
75.00%	$ 14,209,363	$ 1,308,958	$ (9,381,520)	$ (18,262,584)	$ (25,655,845)	$ (31,820,683)	$ (36,967,187)	$ (41,266,234)
80.00%	$ 22,090,109	$ 8,447,783	$ (2,889,676)	$ (12,337,403)	$ (20,229,079)	$ (26,834,088)	$ (32,370,847)	$ (37,017,198)
85.00%	$ 29,970,854	$ 15,586,607	$ 3,602,168	$ (6,412,223)	$ (14,802,313)	$ (21,847,492)	$ (27,774,507)	$ (32,768,162)
90.00%	$ 37,851,600	$ 22,725,432	$ 10,094,011	$ (487,042)	$ (9,375,547)	$ (16,860,897)	$ (23,178,168)	$ (28,519,127)
95.00%	$ 45,732,346	$ 29,864,257	$ 16,585,855	$ 5,438,138	$ (3,948,781)	$ (11,874,302)	$ (18,581,828)	$ (24,270,091)
100.00%	$ 53,613,091	$ 37,003,082	$ 23,077,699	$ 11,363,319	$ 1,477,985	$ (6,887,706)	$ (13,985,488)	$ (20,021,055)

% of Production Sold

The following tornado chart illustrates the degree to which NPV is sensitive to the variations in product price, % of production sold, variable costs, TPI and fixed costs. The tornado chart illustrates the variations in NPV while holding all other independent variables constant. As seen in Figure 15, the NPV is most sensitive to the product price and least sensitive to fixed costs. It is important to note that the NPV is also significantly sensitive to the WACC. This follows a similar pattern to the variables that show significant sensitivity to IRR. Figure 15 lends itself to the discussion that a green premium would be advantageous in offsetting any market shocks to the product price and discount rate availabilities, as the product price is significant to the profitability of the project.
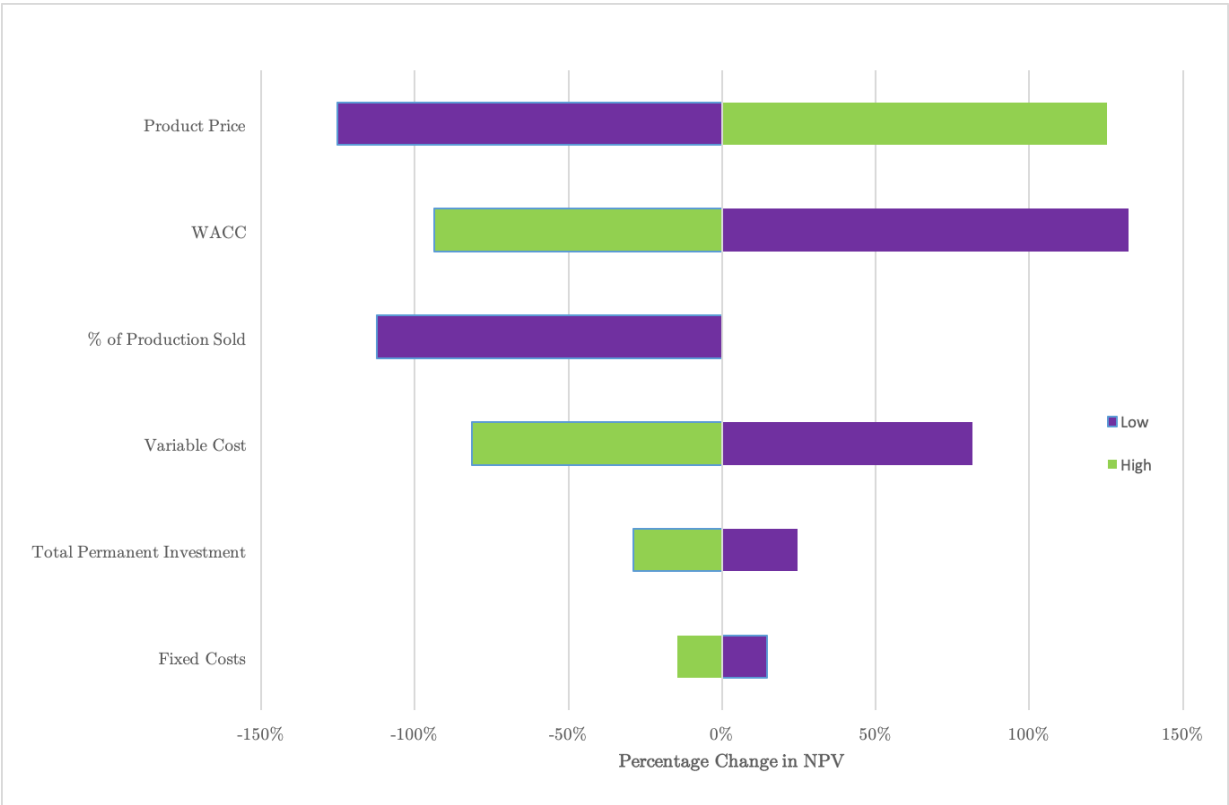
Figure 15: Tornado chart illustrating the variation in NPV to a change in the product price, % of production sold, variable costs, TPI and fixed costs. The base case NPV is equal to $23.07 MM. This chart shows a variation of the independent variable by ± 20% from their base case, where applicable.

24 Other Important Considerations

24.1 Health and Safety Considerations

Both ethanol and ethyl acetate are classified as hazardous materials by OSHA; they can cause harm from prolonged exposure or contact. The appropriate personal protective equipment must be worn by the workers in the plant to offer protection from the potential dangers. In addition, both of these chemicals are highly flammable in both the liquid and vapor forms. Floating head storage tanks were designed for each material to mitigate the risks associated with their high flammabilities. Explosion proof equipment and columns designed to accomodate the necessary high temperatures were also accounted for in the design of the plant. The MSDS sheets for both of these key materials as well as other intermediates in the process are included in Section 27.4.

In addition to explosion proof and fireproof equipment, the minor equipment detailed in Section 18 provides extra safety precautions for the process by accounting for necessary control valves and a flare system.

24.2 Environmental and Location Considerations

The overall Greenyug process presents a key environmental consideration. The use of fermentation ethanol as the single feed for the process gives Greenyug a sustainable edge. Compared to the current industry standard, the process Greenyug is implementing is decidedly more green.

The location of the plant in Columbus, NE also brings up key considerations and advantages for Greenyug. As previously mentioned, the proximity to ADM's corn processing plant gives Greenyug easy access to the needed fermentation ethanol. It is possible that Greenyug is getting a discounted price of ethanol for this reason. Additionally, though a single day ethanol feed storage tank was designed here for this process, it is likely that Greenyug is simply using a direct pipeline to supply the feed to the process.

A further consideration based on plant location was the temperature of available cooling water. Meetings with industry consultants led to a discussion of a study done on cooling water temperatures in Iowa. This led to the decision of accounting for an initial cooling water temperature of 86°F.

24.3   Start Up Considerations

Starting up a new plant entails land purchase, site preparation, contractor fees, service facilities, building inventory, and the loading of chemicals into the process equipment. All of these considerations contribute to the previously mentioned up front and start up costs. The $262,370 land cost and the $1,311,849 start up costs discussed in Section 21, are a significant consideration for Greenyug as compared to more established companies.

Plant start up is also associated with several business considerations. Important mentions for Greenyug are establishing the agreements with the neighboring corn plant and procuring funding. As previously discussed, it is also imperative to consider a start-up profile. As a start up, it is unlikely that Greenyug will be able to sell all of its product in the first few years of production. The company will have to acquire customers and gain prominence in the existing market. In addition to this, Greenyug looks to establish a new segment of the ethyl acetate market by introducing a unique value proposition.

24.4   Continuous Evaluation

For the purpose of this project, additional backup units for the reactive distillation column, hydrogenation reactor, and distillation column were not included in the costing analysis. The design presented is the first iteration of plant design. Throughout the operating year, the plant would be continuously evaluated for process development and subsequent capital and control mechanisms may be improved. Note that the profitability analysis conducted above is rigorous and conservative in its approach and as shown in Section 23.3, profitability measures are able to withstand some degree of TPI variation. However, should

the continuous evaluation of this process yield higher investment requirements, it will be necessary that these profitability measures be revisited.

25   Conclusion and Recommendations

An investigation into Greenyug's proposed process for the sustainable conversion of ethanol to ethyl acetate was conducted. This novel process makes use of three main unit operations, where the innovative technology stems from the reactive distillation component of the process. This proposed process yields a ethyl acetate purity of 99.8%, thereby satisfying customer and market demands. n-Butanol and 2-butanol are byproducts in this process and are treated as waste products. The hydrogen produced during this process is burned for fuel value.

As explained in previous sections, the Greenyug process was reverse engineered from limited patent information. The design of this process includes several optimizations on the basis of efficiency, separation, and cost. Following several assumptions on catalyst, kinetic and equilibrium operations, the investigation concludes that the Greenyug process is a feasible from a technical perspective.

The project yields a NPV of $23.08MM, and an IRR of 38.73%. Thes metrics suggest that the process is profitable and therefore it is deemed likely that Greenyug would be able to compete with large players in the industry effectively. However, as discussed in Section 23.3, these profitability measures are significantly sensitive to the product price (See Figure 14 and 15).

The ethanol is procured at a market price of $0.21/lb. Although the proposed plant is located in close proximity to the ADM corn plant and a discount on the feedstock could be seen, the economic analysis does not assume any discount, so to be rigorous in its approach.

This current economic model follows the base case that the ethyl acetate product can be sold at $0.42/lb. Note that this is the current market price, and assumes no green premium. As discussed throughout this report, the proposed process is sustainable and can therefore warrant the potential addition of a green premium. Economic analyses suggest that the green premium may be advantageous from a competitive standpoint for Greenyug as the green premium applied to the product price would be able to offset any other variations in

cost metrics (TPI, variable cost, etc.). Further note that the economic base case follows a WACC of 15%, which is standard of project modelling; however, given that Greenyug is a startup company, it is likely that the company may face a WACC greater than 15%. The profitability measures are sensitive to the WACC, however using a conservative approach, NPV and IRR still remain attractive even at a higher WACC.

This is the first iteration of the design, and therefore operating costs and TPI may vary after iterative improvements. Future evaluation may further account for design optimizations in the process. The investigation concludes that with the current proposed design, following all assumptions aforementioned, the process is feasible both from a technical and economic perspective, with no green premium necessary.

26 Acknowledgments

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28 Appendix

28.1 Equipment Design Calculations

28.1.1 Feed Pump

The head for the feed pump (P-xxx) was calculated on the basis of the pressure change and density, ρ, of the fluid flowing through the pump. The density of liquid flow through this pump, as reported by ASPEN, is 48.9 lb/ft^3 and the pressure rise required is 19 bar ($\simeq 130.5psi$).

$$\text{Head} \quad = \quad \frac{\text{Pressure Rise}}{\text{Liquid Flow Density}} \quad = \quad \frac{130.5 \ lb/ft^3 * 144 \ in^2/ft^2 * 32.2 \ ft/s^2}{48.9 \ lb/ft^3 * 32.2 \ lbft/lbfs^2} \quad \simeq \quad 383.6ft$$

28.1.2 Reactors

Reactive Distillation Column

The operating conditions for the reactive distillation column were initially provided by patent literature, describing a lab-scale model of this column. The number of stages required for the reaction and adequate separation of ethyl acetate and by products from the hydrogen byproduct were also determined, and appropriately specified, in the ASPEN simulation model. Tray profiles from the ASPEN simulation provided data on the viscosity of liquid on each stage. The O'Connell relationship was initially a graphical correlation, but over the years, industry have proposed the following empirical relationship, where E_{OC} represents the Murphee Tray Efficiency, α represents the relative volatility between key components and μ represents the viscosity in cP:

$$E_{OC} \quad = 0.492 * (\alpha * \mu)^{-0.245}$$

In this case, acetaldehyde is the light key and ethyl acetate is the heavy key. The relative volatility is calculated by taking the ratio of the K values for these two components, at each tray. A sample calculation to determine the relative volatility, and hence relevant efficiency

and real number of trays, is carried out below using data from tray 5 as an example:

$$\alpha = \frac{K_{1,5}}{K_{2,5}} = \frac{2.4732}{0.7308} = 3.384$$

$$E_{OC} = 0.492 * (\alpha * \mu)^{-0.226} = 0.492 * (\alpha * \mu)^{-0.226} = 0.586$$

$$\text{Number of Real Trays Required} = \frac{1}{E_{OC}} = 1.705$$

Table 40: Individual Stage Tray Efficiencies: Reactive Distillation

Theoretical Stage Number	Viscocity of Liquid (cP)	K1 Value (Acetaldehyde)	K2 Value (Ethyl Acetate)	Relative Viscocity (cP)	Stage Efficiency	Real Trays Required
1	-	-	-	-	-	-
2	0.140	2.320	0.665	3.489	0.579	1.728
3	0.136	2.460	0.722	3.407	0.585	1.710
4	0.136	2.474	0.729	3.393	0.586	1.707
5	0.136	2.473	0.731	3.384	0.586	1.706
6	0.136	2.477	0.731	3.388	0.586	1.706
7	0.136	2.479	0.732	3.389	0.586	1.706
8	0.136	2.482	0.732	3.393	0.586	1.707
9	0.136	2.485	0.732	3.396	0.586	1.707
10	0.136	2.488	0.732	3.398	0.586	1.707
11	0.135	2.462	0.732	3.364	0.588	1.702
12	0.132	2.306	0.618	3.729	0.578	1.731
13	0.121	2.863	0.762	3.757	0.588	1.700
14	0.115	2.840	0.734	3.867	0.591	1.691
15	0.106	2.950	0.772	3.819	0.604	1.657
16	0.098	3.130	0.846	3.699	0.619	1.616
17	0.093	3.270	0.909	3.597	0.631	1.586
18	0.090	3.360	0.949	3.541	0.638	1.568
19	0.088	3.408	0.973	3.504	0.642	1.557
20	-	-	-	-	-	-

$$Number\ of\ Real\ Trays = \sum_{i=20}^{n} Real\ Trays\ Required = 30.1$$

The number of actual trays is rounded up to a whole number, for practical sense. Therefore, the reactive distillation column requires 31 trays.

$$Total\ Number\ of\ Real\ Stages = (31\ trays * 2\ ft\ spacing) + 4 + 7\ ft = 73\ ft$$

Reflux Accumulator Design

The reflux accumulator is modelled as a horizontal pressure vessel. To determine the length and diameter of the reflux accumulator, the volumetric flow into the drum is first calculated. The reflux ratio and distillate volumetric flow rate were determined from ASPEN simulation results.

$$V_{\text{drum,in}} = (1 + R) * (D_{\text{volumetric}}) = (1 + 1.6) * (9136^3/hr) = 23754\ ft^3/hr$$

For a residence time of 10 minutes, assuming the reflux accumulator is half full, the total volume of the accumulator is calculated.

$$Volume = 23754\ ft^3/hr * 2 * \frac{10min}{60min/hr} = 7918 ft^3$$

$$D = \frac{2V^{\frac{1}{3}}}{\pi} = \frac{2 * 7918 ft^3{}^{\frac{1}{3}}}{\pi} = 17.1 ft$$

Using the L/D ratio equal to 2, the length of the reflux accumulator was calculated to be 34.2 ft.

Partial Condenser Design

The partial condenser is modelled as a fixed head, shell and tube heat exchanger. To

determine the area of the condenser, the heat duty and the LMTD was used.

$$A_c = \frac{-9.62 * 10^6 Btu/hr}{100 Btu/hr -^o F * 119^o F} = 824 ft^2$$

Reboiler Design

The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger. To determine the area of the reboiler, the heat flux and heat duty was used.

$$A_R = \frac{Q_R}{Flux} = \frac{1.701 * 10^7 \ Btu/hr}{12000 \ Btu/hr - ft^2} = 1420 ft^2$$

Catalyst Costing and Design The catalyst, $CuO/ZnO/Al_2O_3$ was chosen on a basis of selectivity and conversion from lab scale data. It is assumed that the entire tray spacing of the feed tray contains cylindrical pellets with a packing efficiency of 0.6 and corresponding void fraction of 0.4. The total mass of catalyst required can be found if the volume of the tray spacing and density of the catalyst is known. The former can be found from ASPEN Plus modeling, while the latter can be found from the catalyst specification sheet.

$$V_{cat} = (1 - \epsilon)V = (1 - \epsilon)\pi\frac{D^2}{4}H$$
$$= 0.307m^3 = 10.8cuft$$
$$m_{cat} = V_{cat} * \rho_{cat} = 400kg = 882lb$$

Hydrogenation Reactor

The hydrogenation reactor is assumed to be a plug flow reactor. A differential mass balance can be performed to achieve the following design equation:

$$\frac{V}{F} = \tau = \int_0^{x_{af}} \frac{dx_a}{-r_a}$$

The reaction kinetics are reported in literature and discussed in the Relevant Chemistry

section. The limiting reactant in the process in the aldehyde and ketone, denoted as "a".
The rate expression can be written in terms of partial pressures and fractional conversion,
then subsequently inputted into the design equation.

$$r_a = k[P_a][P_{H_2}]^{1/2}$$

$$= k[P_{a0}](1 - x_a)([P_{H_20}] - [P_{a0}]x_a)$$

$$\tau = \int_0^{x_{af}} \frac{dx_a}{-k[P_{a0}](1 - x_a)([P_{H_20}] - [P_{a0}]x_a)}$$

The rate constant changes as a function of temperature. However, the temperature will
be essentially linearly dependent on the fraction conversion and can be found by an energy
balance assuming complete conversion. This assumption is true if the heat capacity of the
system stays constant. Since there is a major amount of inerts in the system, the heat
capacity can be assumed to be constant.

$$k = k_0 \exp[\frac{-E_a}{RT}]$$

$$T = T_i + x_a(T_F - T_i)$$

$$\tau = \int_0^1 \frac{dx_a}{-k_0 \exp[\frac{-E_a}{R(T_i+x_a(T_F-T_i))}][P_{a0}](1 - x_a)([P_{H_20}] - [P_{a0}]x_a)}$$

$$= 10s$$

Initial sizing of the reactor column utilized the following residence time. To account for
pressure drop throughout the reactor due to a catalyst packing, modeling in ASPEN Plus
was utilized.

The catalyst is assumed to pack in the reactor vessel with a packing efficiency of 0.6
and void fraction of 0.4. The volume and mass of catalyst required can then be calculated
from the volume of the reactor (previously calculated) and density of the catalyst (from

specification sheets).

$$V_{cat} - (1 - \epsilon)V = 2.355m^3 = 86.2 cuft$$

$$m_{cat} = \rho_{cat} * V_{cat} = 8148kg = 17,963lb$$

28.1.3 Distillation Column

Algorithm Used for Choice of Operating Conditions

Note that this distillation column was designed using the Fenske Underwood Gillian (FUG) shortcut method[63]. A key assumption of this method is that the relative volatility of the light key to the heavy key remains constant through the column.

Determining The Minimum Number of Stages

Firstly, the relative volatility of the light key to the heavy key was calculated. The K values for n-butanol and ethyl acetate were determined from the ASPEN simulation output.

$$\alpha = \frac{K_{LK}}{K_{HK}} = \frac{0.79}{0.33} = 2.39$$

Next, the Fenske equation was used to determine the minimum number of stages. Specific values for the component distillate and bottoms product can be found in the block reports in Section 28.7.3. The following is the Fenske equation used:

$$N_{min} = \frac{\log[(\frac{d_{LK}}{b_{LK}})(\frac{b_{HK}}{d_{HK}})]}{\log(a_{LK,HK})} = 8.375 \ stages$$

where d is a component flow rate in the distillate and b is a component flow rate in the bottoms product.

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[63]Seider, Lewin, Seader, Widagdo, Gani, and Ng [2017]

Determining The Minimum Reflux Ratio

The minimum reflux ratio was determined by following the assumption that the mixture could be treated as a pseudo binary mixture. The following design equation was used:

$$\frac{L_{min}}{F} = \frac{(D * x_{D,LK}/F * x_{D,LK}) - \alpha_{LK,HK}(D * x_{D,HK}/F * x_{D,HK})}{\alpha_{LK,HK} - 1} = 2.065$$

Kirkbride Equation: Number of Stripping and Rectifying Stages

The Kirkbride equation was used do determine the number of stripping and rectifying stages. The equation provides us with the ratio of the rectifying to stripping stages. The total number of stages is equal to the number of rectifying stages plus the number of stripping stages.

$$\frac{N_R}{N_S} = \left[\left(\frac{x_{HK,F}}{x_{LK,F}}\right)\left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2\left(\frac{B}{D}\right)\right]^{0.206} = 0.5203$$

$$N_R = 3.48 stages$$

$$N_S = 6.68 stages$$

O'Connell Relationships: Determining Actual Number of Stages As outlined in Section 29.2.2, the O'Connell relationship provides information on the efficiency of each tray and thereby the total number of actual stages required. In this case, the 2-butanol is the heavy key and the ethyl acetate is the light key. Equivalent calculations to Section 29.2.2 were carried out for this column.

Table 41: Individual Stage Tray Efficiencies: Distillation Column

Theoretical Stage Number	Viscocity of Liquid (cP)	K1 Value (Ethyl Acetate)	K2 Value (2-Butanol)	Relative Viscocity (cP)	Stage Efficiency	Real Trays Required
1	-	-	-	-	-	-
2	0.205	0.998	0.706	1.413	0.651	1.536
3	0.205	1.000	0.708	1.413	0.651	1.536
4	0.260	1.000	0.708	1.413	0.617	1.621
5	0.206	1.000	0.707	1.414	0.650	1.537
6	0.206	1.001	0.707	1.416	0.650	1.538
7	0.251	1.002	0.706	1.419	0.621	1.609
8	0.206	1.003	0.705	1.422	0.649	1.540
9	0.207	1.004	0.704	1.426	0.649	1.542
10	0.207	1.005	0.702	1.432	0.648	1.544
11	0.207	1.008	0.701	1.437	0.647	1.545
12	0.209	1.011	0.698	1.448	0.645	1.551
13	0.210	1.016	0.696	1.460	0.643	1.556
14	0.212	1.023	0.690	1.483	0.639	1.565
15	0.216	1.036	0.683	1.517	0.633	1.579
16	0.221	1.060	0.671	1.580	0.624	1.602
17	0.231	1.120	0.655	1.710	0.607	1.648
18	0.250	1.330	0.660	2.015	0.574	1.741
19	0.262	1.875	0.790	2.373	0.548	1.826
20	-	-	-	-	-	-

The number of real trays is the sum of the number of real trays required for each stage. The number of actual trays is rounded up to a whole number, for practical sense. Therefore, the reactive distillation column requires 29 trays.

$$\text{Total Number of Real Stages} = (29\ trays * 2\ ft\ spacing) + 4 + 7\ ft = 69\ ft$$

Reflux Accumulator Design

The reflux accumulator is modelled as a horizontal pressure vessel. To determine the length and diameter of the reflux accumulator, the volumetric flow into the drum is first calculated. The reflux ratio and distillate volumetric flow rate were determined from ASPEN simulation results.

$$V_{\text{drum,in}} = (1+R)*(D_{\text{volumetric}}) = (1+10)*(229.2^3/hr) = 2522 \ ft^3/hr$$

For a residence time of 10 minutes, assuming the reflux accumulator is half full, the total volume of the accumulator is calculated.

$$\text{Volume} = 2522 \ ft^3/hr * 2 * \frac{10min}{60min/hr} = 840.7 ft^3$$

$$D = \frac{2V^{\frac{1}{3}}}{\pi} = \frac{2*840.7ft^{3\,\frac{1}{3}}}{\pi} = 8.11ft$$

Using the L/D ratio equal to 2, the length of the reflux accumulator was calculated to be 16.22 ft.

Partial Condenser Design

The partial condenser is modelled as a fixed head, shell and tube heat exchanger. To determine the area of the condenser, the heat duty and the LMTD was used.

$$A_c = \frac{-2.62*10^7 Btu/hr}{100Btu/hr -^o F * 120^o F} = 2193ft^2$$

Reboiler Design

The reboiler is modelled as a kettle vaporizer, shell and tube heat exchanger. To determine the area of the reboiler, the heat flux and heat duty was used.

$$A_R = \frac{Q_R}{Flux} = \frac{2.83*10^7 \ Btu/hr}{12000 \ Btu/hr - ft^2} = 2362ft^2$$

28.1.4 Molecular Sieve

The molecular sieve consists of the 13X sieve material and the vessel containing the sieve. The sieve material has a static adsorption of 25 wt%. The total amount of sieve material needed can be found from the total mass of water removal required, which can be obtained from ASPEN Plus modeling. The bed is assumed to be regenerated every day, so the mass removal is on a daily basis.

$$m_{sieve} = m_{water}/0.25 = 1920kg = 4233lb$$

The volume of the vessel can be calculated if the particle density is known (from the specification sheets) and assuming a packing efficiency of the spherical particles to be 0.6.

$$V_{sieve} = m_{sieve} * \rho_{sieve} = 2.82m^3 = 100cuft$$

$$V_{vessel} = V_{sieve}/(1 - \epsilon) = 4.7m^3 = 166cuft$$

Finally, the vessel can be sized. A general heuristic is to size a molecular sieve vessel with a ratio of $L/D = 3$. The following system of equations can be solved:

$$V_{vessel} = \pi \frac{D^2}{4} L = 166cuft$$

$$\frac{L}{D} = 3$$

$$L = 12.5ft$$

$$D = 4.12ft$$

28.2 Detailed Cash Flow Summary

Table 42: Detailed Cash Flow Summary Over 15 Years Useful Lifetime

Cash Flow Summary

Year	Percentage of Design Capacity	Product Unit Price	Sales	Capital Costs	Working Capital	Variable Costs	Fixed Costs	Depreciation	Allowance	Taxable Income	Taxes	Net Earnings	Cash Flow	Cumulative Net Present Value at 15%
2018	0%	-	-	-	-	-	-	-	-	-	-	-	-	-
2019	0%	-	-	(14,692,700)	(1,396,600)	-	-	-	-	-	-	-	(16,089,300)	(13,990,700)
2020	45%	$0.42	20,982,500	-	(698,300)	(13,422,500)	(4,325,700)	(2,623,700)	-	610,600	(140,400)	470,200	2,395,600	(12,179,300)
2021	68%	$0.42	31,473,700	-	(698,300)	(20,133,800)	(4,325,700)	(4,197,900)	-	2,816,400	(647,800)	2,168,600	5,668,200	(8,452,300)
2022	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	(2,518,800)	-	8,275,500	(1,903,400)	6,372,100	8,890,900	(3,368,900)
2023	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	(1,511,300)	-	9,283,000	(2,135,100)	7,147,900	8,659,200	936,200
2024	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	(1,511,300)	-	9,283,000	(2,135,100)	7,147,900	8,659,200	4,679,800
2025	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	(755,600)	-	10,038,600	(2,308,900)	7,729,700	8,485,400	7,869,800
2026	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	10,586,800
2027	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	12,949,500
2028	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	15,004,000
2029	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	16,790,500
2030	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	18,344,000
2031	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	19,694,900
2032	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	20,869,500
2033	90%	$0.42	41,964,900	-	-	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	8,311,600	21,891,000
2034	90%	$0.42	41,964,900	-	2,793,100	(26,845,000)	(4,325,700)	-	-	10,794,300	(2,482,700)	8,311,600	11,104,700	23,077,700

28.3 Greenyug's 2012, 2013, and 2014 Filed Patents

US 20120035390A1

(54) **ETHYL ACETATE PRODUCTION**

(76) Inventor: **Sagar B. Gadewar**, Goleta, CA (US)

(21) Appl. No.:   **12/925,460**

(22) Filed: **Oct. 20, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/253,349, filed on Oct. 20, 2009.

Publication Classification

(51) **Int. Cl.**
   C07C 67/40   (2006.01)
   B01J 19/00   (2006.01)

(52) **U.S. Cl.** **560/239**; 422/187

(57)   **ABSTRACT**

A process for the production of high purity ethyl acetate from ethanol is described. The process involves reacting ethanol over a suitable catalyst in a reactive distillation column. The reactive distillation setup allows overcoming the reaction equilibrium for increased conversion of ethanol. Hydrogen is removed as the distillate and ethyl acetate is obtained as a bottoms product from the reactive distillation column. A feed of hydrogen at the bottom of the column and a suitable hydrogenation catalyst placed at the bottom of the column allows for a significant reduction of impurities such as butan-2-one, butyraldehyde in the ethyl acetate product. Adding side reactors to the reactive distillation column allows additional catalyst holdup for improved reactant conversion.
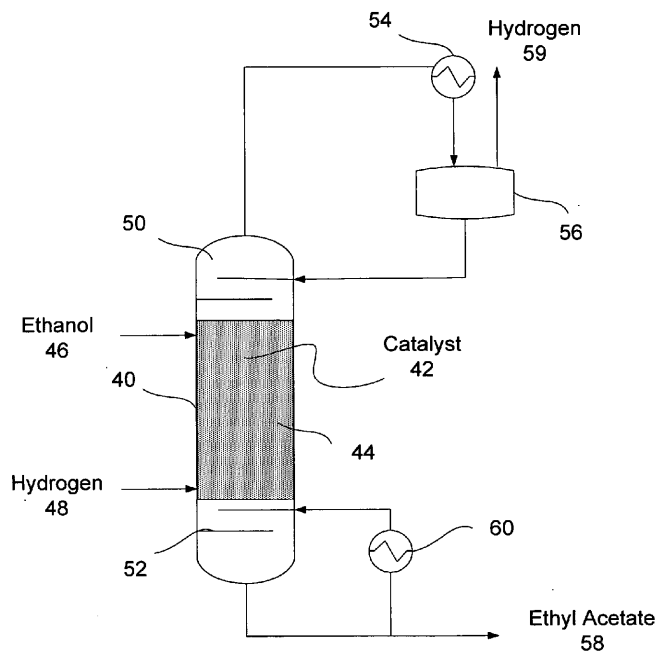
Double feed reactive distillation column schematic with an upper feed of ethanol and lower feed of hydrogen.

Figure 1: Reactive residue curve maps at pressures of 1 atm and 5 atm.
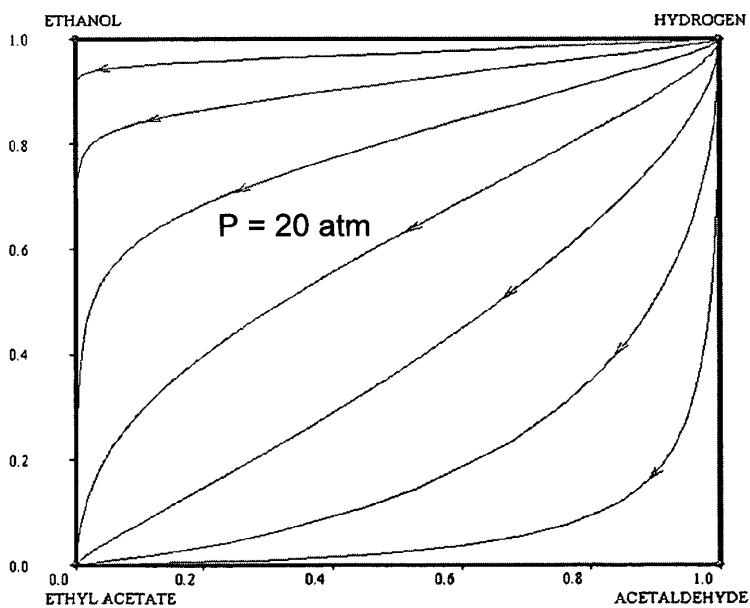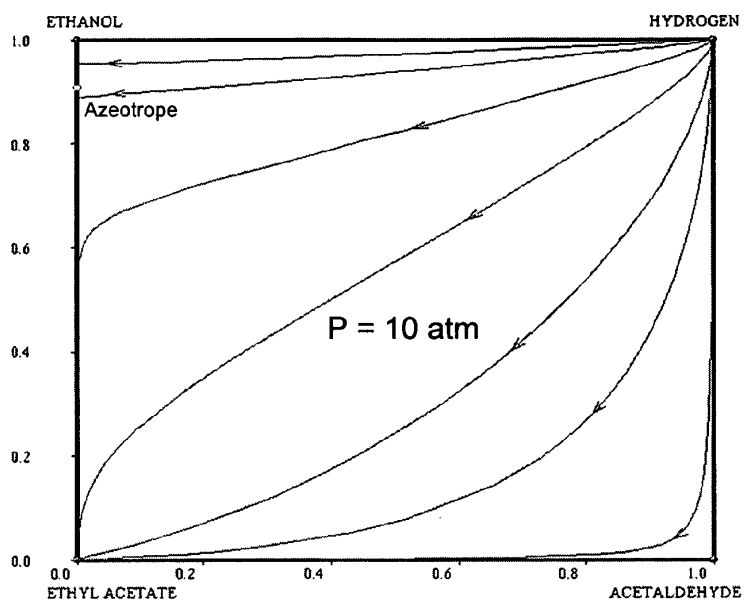
144

Figure 2: Reactive residue curve maps at pressures of 10 atm and 20 atm.

Figure 3: Single feed reactive distillation column schematic.
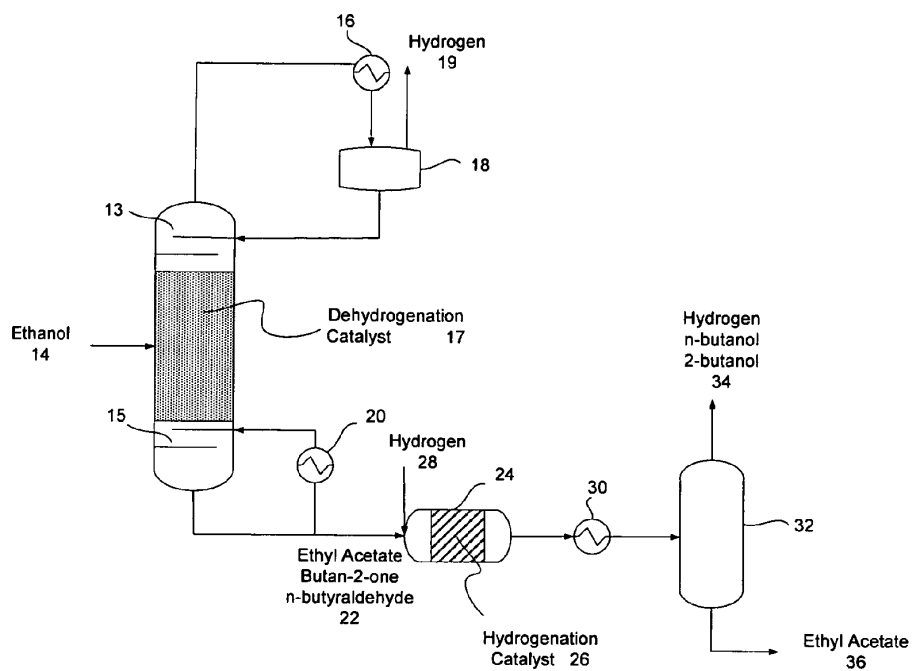
Figure 4: Schematic for a reactive distillation system with subsequent product hydrogenation.
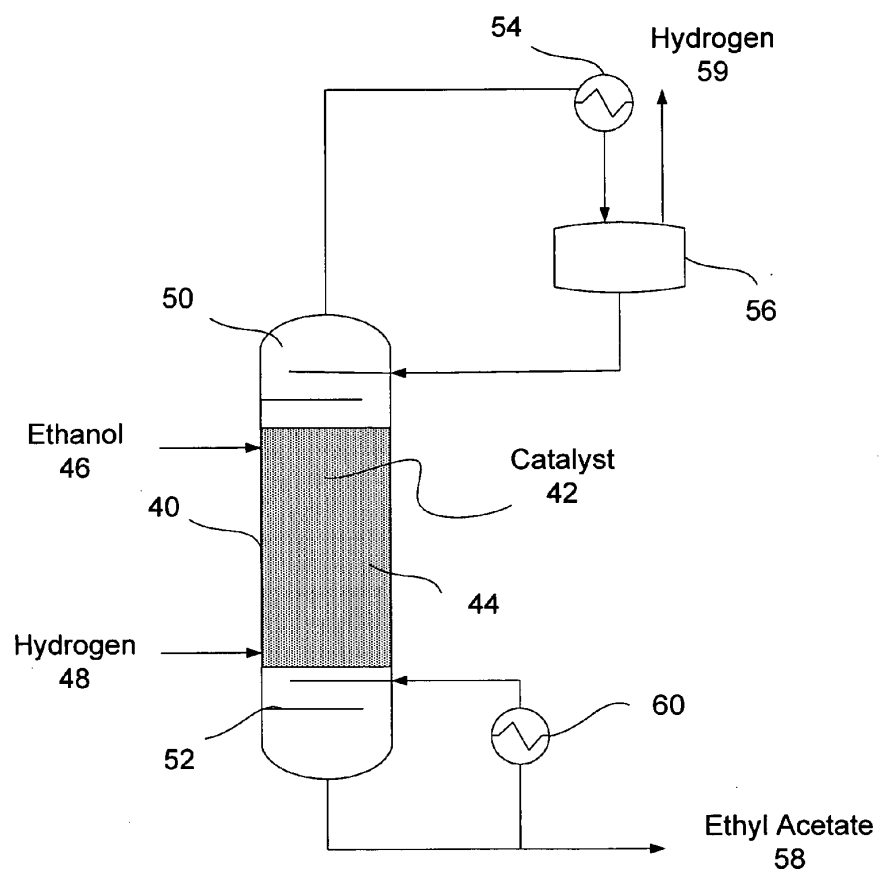
Figure 5: Double feed reactive distillation column schematic with an upper feed of ethanol and lower feed of hydrogen.

Figure 6: Double feed reactive distillation column schematic using dual catalyst beds with an upper feed of ethanol and lower feed of hydrogen.

Figure 7: Side reactor configuration (a) upward flow feed to side reactor (b) downward flow feed to side reactor.
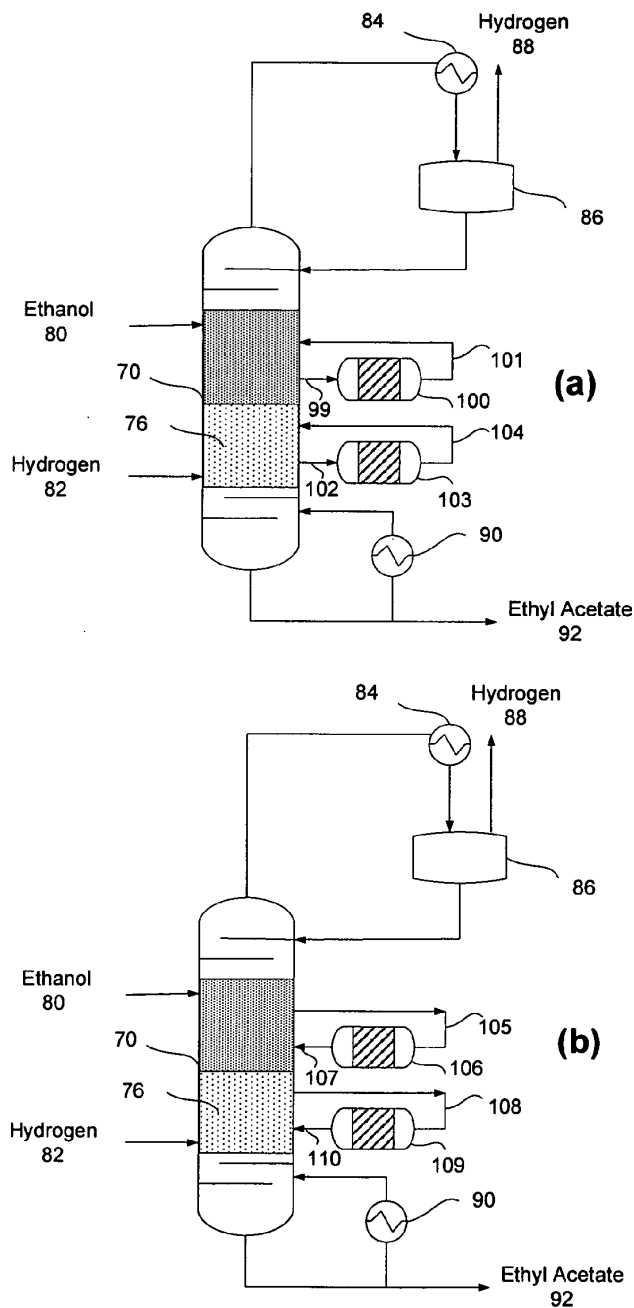
Figure 8: Double Side reactor configuration (a) upward flow feed to multiple side reactors (b) downward flow feed to multiple side reactors.

ETHYL ACETATE PRODUCTION

RELATED APPLICATIONS

[0001] This application claims the benefit of Gadewar, U.S. Prov Appl 61/253,349, filed Oct. 20, 2009, which is incorporated herein by reference in its entirety, including drawings.

FIELD OF THE INVENTION

[0002] The present invention relates to preparation of ethyl acetate by reactive distillation.

BACKGROUND OF THE INVENTION

[0003] The following discussion is provided solely to assist the understanding of the reader, and does not constitute an admission that any of the information discussed or references cited constitute prior art to the present invention.

[0004] Ethyl acetate can be produced from acetaldehyde according to the Tischenko reaction:

$$2CH_3CHO \leftarrow \rightarrow CH_3COOC_2H_5$$
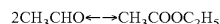
[0005] When acetaldehyde is produced from ethanol, ethyl acetate can be produced from ethanol according to the following reaction:

$$2C_2H_5OH \leftarrow \rightarrow CH_3COOC_2H_5 + 2H_2$$

[0006] Alternately, ethanol can react with acetaldehyde according to the following reaction:

$$C_2H_5OH + CH_3CHO \leftarrow \rightarrow CH_3COOC_2H_5 + H_2$$
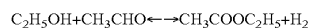
[0007] Conversion of primary alcohols into esters and ketones using copper catalyst is described by K. Takeshita in the Bulletin of the Chemical Society of Japan, (1978) vol. 51(9), pp 2622-2627.

[0008] U.S. Pat. No. 4,996,007 describes a process for the oxidation of primary alcohols to aldehydes, esters and acids. A primary alcohol is reacted with oxygen, with a catalyst selected from ruthenium, rhodium, platinum, palladium, rhenium and mixtures thereof, with the option of quaternary C1 to C20 alkyl ammonium co-catalyst, and dihydrodihydroxynaphthalene, dihydroxyanthracene or a mixture thereof as an oxygen activator.

[0009] In U.S. Pat. No. 4,220,803 catalytic dehydrogenation of ethanol for the production of acetaldehyde and acetic acid using a supported copper oxide essentially free of barium is proposed.

[0010] U.S. Pat. No. 4,052,424 suggested a silver-cadmium alloy catalyst for use in production of alkyl alkanoate esters, by contacting a primary alkanol in the vapor phase with the catalyst at a temperature of between about 250° C. and 600° C.

[0011] In U.S. Pat. No. 4,440,946 there is described a process for producing a carboxylate ester which comprises contacting a mixture of alcohol and aldehyde in the vapor phase with a co-precipitate composition comprising silver-cadmium-zinc-zirconium which is substantially in the free metal form.

[0012] Use of the Tischenko reaction for the production of mixed esters from aldehydes is described in U.S. Pat. No. 3,714,236.

[0013] U.S. Pat. No. 5,334,751 describes production of ethyl acetate by reaction of ethanol and oxygen in the presence of a solid catalyst that contains crystalline TiP_2O_7 and has the formula $Pd_aM_bTiPcO_7$, where M is Cd, Au, Zn, TI, or an alkali metal or alkaline earth metal, a is 0.0005-0.2, b is 0.3a, c is 0.5-2.5, x has a value to satisfy the valencies, and Ti and P of the crystalline TiP_2O_7 represent part of the crystalline TiP_2O_7.

[0014] BR-A-91/04652 describes pre-treatment of a palladium on a silica carrier catalyst for production of ethyl acetate by direct oxidation of ethanol with air.

[0015] Production of esters from primary alcohols by dehydrogenation using bromous acid or a salt thereof in acid medium is described in JP-A-59/025334.

[0016] In SU-A-362814 there is described a process for production of ethyl acetate by dehydrogenation of ethanol at 180° C. to 300° C. in the presence of a copper catalyst containing zinc as an activator with an ethanol feed rate of 250 to 700 liters per liter of catalyst per hour.

[0017] The dehydrogenation of ethanol to form ethyl acetate is described in GB-A-287846. This proposes use of a dehydrogenating agent, such as a copper catalyst, a temperature of from 250° C. to 500° C., and a pressure of more than 10 atmospheres (1.013×106 Pa).

[0018] Vapor phase contact of ethanol at a temperature above its critical temperature with a catalyst comprising copper and a difficultly reducible oxide, such as zinc oxide or manganese oxide, is proposed in GB-A-312345, use of a temperature of 375° C. and a pressure of 4000 psi (27.58 Mpa) being suggested.

[0019] GB-A-470773 teaches a process for conversion of ethanol to ethyl acetate by dehydrogenating ethanol over a catalyst consisting of a reduced metal, for example, copper on infusorial earth with 10% uranium oxide as promoter, maintained at a temperature of 220° C. to 260° C., removing by condensation some of the gas-vapor product rich in hydrogen resulting from the reaction, and returning the gaseous remainder rich in hydrogen to the catalyzing zone.

[0020] EP-A-0151886 describes a process for the preparation of C2+ esters of alkyl carboxylic acids from C2+ primary alcohols which comprises contacting a vaporous mixture containing a primary C2+ alkanol and hydrogen in an alkanol:hydrogen molar ratio of from 1:10 to about 1000:1 at a combined partial pressure of alkanol and hydrogen of from about 0.1 bar (103 Pa) up to about 40 bar (4×10⁶ Pa) and at a temperature in the range of from about 180° C. to about 300° C. in a catalytic reaction zone with a catalyst consisting essentially of a reduced mixture of copper oxide and zinc oxide, and recovering a reaction product mixture containing a primary C2+ alkyl ester of an alkyl carboxylic acid which ester contains twice as many carbon atoms as the primary C2+ alkanol.

[0021] In EP-A-0201105 there is described a method for converting primary alcohols, such as ethanol, to their corresponding alkanoate esters which involves the regulation of the mole feed ratio of hydrogen gas to alkanol in the reaction zone of a copper-chromite containing catalyst.

[0022] One method of separating ethyl acetate from ethanol and water involves extractive distillation with an extractive agent comprising polyethylene glycol and dipropylene glycol, diethylene glycol, or triethylene glycol as described in U.S. Pat. No. 4,569,726 or with an extractive agent containing dimethyl sulphoxide as described in U.S. Pat. No. 4,379,028.

[0023] Separation of ethyl acetate from a composition comprising ethyl acetate, ethanol and water is described in JP-A-05/186392 by feeding the composition to a distillation column to obtain a quasi-azeotropic mixture comprising ethyl acetate, ethanol and water, condensing it, separating the condensate into an organic layer and an aqueous layer, returning

the organic layer to the column, and recovering ethyl acetate as a bottom product from the column.

[0024] EP-A-0331021 describes how carbonylation of olefins to produce monocarboxylate esters causes formation of aldehydes and acetals as byproducts. Monocarboxylate esters produced in this way are subjected to a three step purification process involving treatment with a strongly acidic agent, followed by hydrogenation and distillation. The initial treatment with a strongly acidic agent is intended to convert acetals to vinyl ethers and aldehydes and acetals to aldols. The subsequent hydrogenation step then converts these compounds to byproducts which are more easily separated from the desired monocarboxylate ester.

[0025] EP-A-0101910 contains a similar disclosure regarding carbonylation of olefins to give monocarboxylate esters. It proposes treatment of the monocarboxylate ester with hydrogen at elevated temperature in the presence of an acidic ion exchanger or zeolite doped with one or more metals of Group VIII of the Periodic Table, followed by hydrogenation. It is stated that acetals present as byproducts are converted to vinyl ethers which are converted by hydrogenation to low boiling esters or the aldehydes and acetals are converted to high boilers by an aldol reaction. Unsaturated ketones are converted to saturated ketones.

[0026] U.S. Pat. No. 4,435,595 describes the use of reactive distillation to produce high-purity methyl acetate, by esterifying methanol and acetic acid. The process provides for the use of acetic acid and methanol which flow in counter-current through a single reactive distillation column in the presence of an acid catalyst. The acetic acid, in addition to being a reagent, also acts as an extracting agent for the non-reacted methanol and for the water which has been produced. Therefore, the methyl acetate is separated continuously from the acetic acid and removed from the top of the column.

SUMMARY OF THE INVENTION

[0027] Current commercial methods for producing ethyl acetate present limitations in such areas as system complexity, the need for expensive prior syntheses, difficult product separations, and/or overall cost. The present invention addresses these limitations by providing a reactive distillation system in which ethanol is the sole or primary feed. In some embodiments, the ethanol feed is used in conjunction with a separate second feed of hydrogen.

[0028] Thus, the present invention provides a process (and corresponding system) for the production of ethyl acetate from ethanol which includes reacting ethanol over a suitable dehydrogenation catalyst in a reactive distillation column, thereby producing ethyl acetate and hydrogen. Preferably a single reactive distillation column is used. Hydrogen gas is removed (preferably continuously) from the top of the reactive distillation column as a top product. Ethyl acetate is removed (preferably continuously) from the bottom of the column as a liquid bottoms product.

[0029] Optionally but advantageously, contaminating byproducts present following reaction of the ethanol over the dehydrogenation catalyst can be reacted over a suitable hydrogenation catalyst in the lower part of the column or in a separate hydrogenation reactor. The hydrogenation can convert difficult to separate byproducts into species which are easier to separate from the ethyl acetate. Consequently, the process can also include purifying the ethyl acetate by distilling out resulting hydrogenated byproducts.

[0030] Thus, as indicated above, a first aspect of the invention concerns a reactive distillation process producing high purity ethyl acetate from ethanol, where the process involves dehydrogenating ethanol over a dehydrogenation catalyst in a reactive distillation column. Ethyl acetate is removed during the distillation process as a liquid bottoms product and hydrogen is removed during the distillation process as a gaseous top product.

[0031] In certain embodiments, the process also include hydrogenating contaminants or reaction byproducts in the liquid bottoms product or in the reacted fluid after is has passed over the dehydrogenation catalyst and separating the hydrogenated contaminants or byproducts from the ethyl acetate.

[0032] Some implementations of the process utilize a single feed of ethanol; the reactive distillation column contains a generally central dehydrogenation catalyst zone and the single feed of ethanol is delivered into the column above or near the top of the catalyst zone; the reactive distillation column contains a generally central dehydrogenation catalyst zone and the single feed of ethanol is delivered into the column below or near the bottom of the catalyst zone.

[0033] In particular embodiments, the process also includes passing reaction fluid, after it has passed over the dehydrogenation catalyst, through a hydrogenation reactor which includes a hydrogenation catalyst, e.g., such that n-butyraldehyde and/or butan-2-one, if present, are hydrogenated; the hydrogenation catalyst may, for example, include metals and/or oxides of nickel, palladium, platinum, ruthenium, iron, molybdenum and/or mixtures thereof as catalyst material, e.g., on a support material such as carbon, alumina, silica, chromia, and/or titania; bottoms product is separated in a separation column which receives product from the hydrogenation reactor, separating, for example, n-butanol and 2-butanol from ethyl acetate.

[0034] Some implementations of the process utilize dual feeds of ethanol and hydrogen fed to the reactive distillation column, where the ethanol feed is above the hydrogen feed. In many cases the reactive distillation column includes a dehydrogenation catalyst zone and the ethanol feed is above or near the top of that dehydrogenation catalyst zone (or alternatively within the dehydrogenation catalyst zone, e.g., within the upper $\frac{3}{4}$, $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$ of the dehydrogenation catalyst zone) and the hydrogen feed is below or near the bottom of the dehydrogenation catalyst zone. The reactive distillation column can advantageously also include a hydrogenation catalyst zone below the dehydrogenation catalyst zone; usually the hydrogen feed is below or near the bottom of that hydrogenation catalyst zone.

[0035] For many embodiments in which dual feeds of ethanol and hydrogen are used, the molar ratio of Ethanol:Hydrogen for the dual feeds is from 1:10 to 1000:1, e.g., from 1:10 to 1:1, 1:1 to 5:1, 1:1 to 10:1, 5:1 to 25:1, 5:1 to 50:1, 10:1 to 50:1, 10:1 to 100:1, 50:1 to 200:1, 50:1 to 400:1, 100:1 to 500:1, 100:1 to 1000:1, 200:1 to 1000:1, or 500:1 to 1000:1.

[0036] For any of the column configurations used in the present invention, in certain embodiments, the reactive distillation is performed at a pressure from 1 bar to 50 bar, e.g., 1 to 5, 5 to 10, 7 to 12, 13 to 15, 13 to 20, 15 to 20, 15 to 30, 20 to 30, 20 to 50, 30 to 40, 30 to 50, or 40 to 50 bar; the reactive distillation is performed at a pressure where ethanol-ethyl acetate azeotrope is not present; the number of stages or the number of height equivalents of a theoretical plate (HETP) is from 2 to 100, e.g., from 2 to 10, 10 to 20, 10 to 50,

20 to 30, 20 to 70, 30 to 40, 30 to 50, 30 to 100, 50 to 70, 50 to 100, or 70 to 100; the high purity ethyl acetate contains at least 95, 96, 97, 98, 99, or 99.5% ethyl acetate by weight.

[0037] In the present process, a number of different catalysts can be used for the dehydrogenation, e.g., where the dehydrogenation catalyst includes a catalyst material such as metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum and/or mixtures thereof, in most cases on a support such as carbon, alumina, silica, chromia, and/or titania. Such catalysts are useful for either the single feed or dual feed processes specified in embodiments above.

[0038] A related aspect of the invention concerns a reactive distillation system, e.g., as indicated in the preceding aspect. Thus, the invention also provides a reactive distillation system for producing high purity ethyl acetate from ethanol. The system includes a reactive distillation column which includes a dehydrogenation catalyst (usually located generally centrally or at intermediate level in the column), an ethanol feed which feeds ethanol into the column such that it passes over the dehydrogenation catalyst, a top product gaseous hydrogen removal passage, and a bottoms product liquid ethyl acetate removal passage.

[0039] In certain advantageous embodiments, the system also includes a hydrogenation catalyst positioned to contact liquid product following passage over the dehydrogenation catalyst, generally with a hydrogen feed located prior to or at the hydrogenation catalyst.

[0040] In some embodiments, the chemical feed to the reactive distillation column is a single ethanol feed; the reactive distillation column contains a generally central dehydrogenation catalyst zone and the single ethanol feed is delivered into the column above or near the top of that catalyst zone; the reactive distillation column contains a generally central dehydrogenation catalyst zone and the single ethanol feed is delivered into the column below or near the bottom of that catalyst zone.

[0041] In certain embodiments, the system also include a hydrogenation catalyst which hydrogenates contaminants or reaction byproducts in the liquid bottoms product or in the reacted fluid after is has passed over the dehydrogenation catalyst and separating the hydrogenated contaminants or byproducts from the ethyl acetate. The hydrogenation catalyst may be in the same column as the dehydrogenation catalyst or in a separate hydrogenation reactor.

[0042] Some embodiments of the system incorporate a single feed of ethanol into the reactive distillation column; the reactive distillation column contains a dehydrogenation catalyst zone (often generally central) and the single feed of ethanol is delivered into the column above or near the top of the catalyst zone; the reactive distillation column contains a generally central dehydrogenation catalyst zone and the single feed of ethanol is delivered into the column below or near the bottom of the catalyst zone.

[0043] In further embodiments, the system also includes a hydrogenation catalyst, e.g., in a hydrogenation reactor, over which reaction fluid (together with hydrogen) is passed after it has passed over the dehydrogenation catalyst; the reaction fluid, hydrogen, and hydrogenation catalyst are configured such that n-butyraldehyde and/or butan-2-one, if present, are hydrogenated, highly preferably without significantly hydrogenating ethyl acetate in the reaction fluid; the hydrogenation catalyst includes metals and/or oxides of nickel, palladium,

platinum, ruthenium, iron, molybdenum and/or mixtures thereof as catalyst material, e.g., on a support material such as carbon, alumina, silica, chromia, and/or titania; bottoms product is separated in a separation column which receives product from the hydrogenation reactor, separating, for example, n-butanol and 2-butanol from ethyl acetate.

[0044] Some of the present systems incorporate dual feeds of ethanol and hydrogen fed to the reactive distillation column, where the ethanol feed is above the hydrogen feed. Thus, in many cases the reactive distillation column includes a dehydrogenation catalyst zone and the ethanol feed is above or near the top of that dehydrogenation catalyst zone (or alternatively within the dehydrogenation catalyst zone, e.g., within the upper ¾, ⅔, ½, ⅓, or ¼ of the dehydrogenation catalyst zone) and the hydrogen feed is below or within the dehydrogenation catalyst zone but below the ethanol feed, e.g., near the bottom of the dehydrogenation catalyst zone. The reactive distillation column can advantageously also include a hydrogenation catalyst zone below the dehydrogenation catalyst zone; usually the hydrogen feed is below or within that hydrogenation catalyst zone, e.g., near the bottom of the hydrogenation catalyst zone.

[0045] For many embodiments in which dual feeds of ethanol and hydrogen are used, the molar ratio of Ethanol:Hydrogen for the dual feeds is from 1:10 to 1000:1, e.g., from 1:10 to 1:1, 1:1 to 5:1, 1:1 to 10:1, 5:1 to 25:1, 5:1 to 50:1, 10:1 to 50:1, 10:1 to 100:1, 50:1 to 200:1, 50:1 to 400:1, 100:1 to 500:1, 100:1 to 1000:1, 200:1 to 1000:1, or 500:1 to 1000:1.

[0046] For any of the column configurations used in the present invention, in certain embodiments, the reactive distillation is performed at a pressure from 1 bar to 50 bar, e.g., 1 to 5, 5 to 10, 7 to 12, 13 to 15, 13 to 20, 15 to 20, 15 to 30, 20 to 30, 20 to 50, 30 to 40, 30 to 50, or 40 to 50 bar; the reactive distillation is performed at a pressure where ethanol-ethyl acetate is not present; the number of stages or the number of height equivalents of a theoretical plate (HETP) is from 2 to 100, e.g., from 2 to 10, 10 to 20, 10 to 50, 20 to 30, 20 to 70, 30 to 40, 30 to 50, 30 to 100, 50 to 70, 50 to 100, or 70 to 100; the high purity ethyl acetate contains at least 95, 96, 97, 98, 99, or 99.5% ethyl acetate by weight.

[0047] In the present system, a number of different catalysts can be used for the dehydrogenation, e.g., where the dehydrogenation catalyst includes a catalyst material such as metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum and/or mixtures thereof, in most cases on a support such as carbon, alumina, silica, chromia, and/or titania. Such catalysts are useful for either the single feed or dual feed processes specified in embodiments above.

[0048] In some embodiments of the process, side reactors, usually external side reactors, can be used with the reactive distillation column, e.g., to increase the residence time for reaction. The feed to the side reactors is liquid for top-down flow and vapor for bottom-up flow. One or more side reactors can be used.

[0049] The term "reactive distillation column" is used conventionally to refer to a distillation column in which both reaction and separation is performed. In this case, the primary and desired reaction is the conversion of two ethanol molecules to one ethyl acetate molecule with release of two hydrogen molecules.

[0050] Reference to a "single feed" to a reactive distillation column means that the column has only one chemical feed

stream supplying intended reactant(s) to the column. Nonetheless, such a single feed distillation column may have recycling feed streams where a part of the reactant liquid is drawn from the column and fed back into the column at a different point or a partial distillate is fed back into the column at a different point, e.g., to achieve improved separation and/or more complete reaction. A "single ethanol feed" thus refers to a single feed stream, in which ethanol is the sole or at least the primary constituent.

[0051] In contrast, the term "dual feed" in the context of a distillation column refers to two separate chemical feed streams. For example, in some of the present embodiments, dual feeds are an ethanol feed and a separate hydrogen feed.

[0052] Additional embodiments will be apparent from the Detailed Description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0053] FIG. 1 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 1 and 5 atmospheres (atm).

[0054] FIG. 2 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 10 and 20 atm.

[0055] FIG. 3 shows a simplified schematic of a reactive distillation system for catalytic conversion of ethanol to ethyl acetate using a single ethanol feed and a single catalyst.

[0056] FIG. 4 shows a simplified schematic of a reactive distillation system for catalytic conversion of ethanol to ethyl acetate using a single ethanol feed and a single catalyst, but with a hydrogenation reactor for the bottoms product from the reactive distillation column.

[0057] FIG. 5 shows a simplified schematic of a reactive distillation system for catalytic conversion of ethanol to ethyl acetate using dual feeds of ethanol (top) and hydrogen (bottom) with a single catalyst.

[0058] FIG. 6 shows a simplified schematic of a reactive distillation system for catalytic conversion of ethanol to ethyl acetate using dual feeds of ethanol (top) and hydrogen (bottom) with an upper dehydrogenation catalyst and a lower hydrogenation catalyst.

[0059] FIG. 7 shows a simplified schematics of side reactor reactive distillation columns using dual feeds of ethanol (top) and hydrogen (bottom) with a single catalyst (a) upward flow feed to side reactor (b) downward flow feed to side reactor.

[0060] FIG. 8 shows a simplified schematics of side reactor reactive distillation columns using dual feeds of ethanol (top) and hydrogen (bottom)) with an upper dehydrogenation catalyst and a lower hydrogenation catalyst (a) upward flow feed to side reactor (b) downward flow feed to side reactor.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0061] The present invention concerns a reactive distillation process for producing high purity ethyl acetate from ethanol. This process is highly beneficial as it provides an improved commercial method of upgrading ethanol to ethyl acetate, a more valuable product. This improved commercial process is particularly desirable and advantageous where there is an over-capacity for ethanol. Further, this process obviates the need for a separate acetaldehyde or acetic acid plant to provide precursors for the ethyl acetate production process. These advantages are provided in a process which

can also be less expensive than those in the art for ethyl acetate production from ethanol.

[0062] Additionally the invention can provide a route to ethyl acetate by dehydrogenation of ethanol which is capable to yielding high purity ethyl acetate from ethanol feed streams containing significant amounts of impurities. One particular problem in production of ethyl acetate by dehydrogenation of ethanol is that the reaction product mixture is commonly a complex mixture including esters, alcohols, aldehydes and ketones. From a distillative separation point of view, the mixture is further complicated due to the presence of azeotropes. The reaction product mixtures commonly contain components with boiling points close to ethyl acetate (such as n-butyraldehyde and butan-2-one), including components which can form azeotropes with ethyl acetate, and/or other components of the mixture. This is a particular problem when high purity ethyl acetate is desired.

[0063] In conventional chemical processing, chemical reaction and the purification of the desired products by distillation are usually carried out sequentially. In many cases, the performance of this classic chemical process structure can be significantly improved by integration of reaction and distillation in a single multifunctional process unit. This integration concept is called 'reactive distillation'. As advantages of this integration, chemical equilibrium limitations can be overcome, higher selectivities can be achieved, the heat of reaction can be used in situ for distillation, auxiliary solvents can be avoided, and azeotropic or closely boiling mixtures can be more easily separated. Increased process efficiency and reduction in overall capital costs are the direct results of this approach.

[0064] Thus, as indicated above, the present invention provides a novel process for production of ethyl acetate from ethanol at a relatively low cost, along with a plant or distillation system with significantly reduced complexity using reactive distillation. The invention further provides an improved process for the production of high purity ethyl acetate from ethanol, or from a feedstock comprising a major proportion of ethanol and a minor proportion of impurities such as isopropanol and iso-butanol. While not commonly present in ethanol feed streams, impurities which could poison the particular catalyst used should be avoided or removed. For example, sulfur or nitrogen heterocyclic compounds can frequently act as catalyst poisons and, if present, should be removed before introducing the ethanol feed stream to the reactive distillation column.

[0065] Ethyl acetate can be produced from ethanol according to the following reactions:

$$C_2H_5OH \leftarrow \rightarrow CH_3CHO + H_2$$

$$2CH_3CHO \leftarrow \rightarrow CH_3COOC_2H_5$$
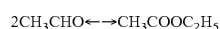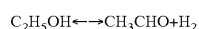
[0066] In the present process, ethanol reacts in a single continuous reactive distillation column which provides sufficient residence time to achieve high conversion of ethanol. Table 1 shows the effect of pressure on the boiling point of the pure components and azeotrope in the mixture. The azeotrope between ethanol and ethyl acetate disappears above a pressure of 13 atm.

TABLE 1

Boiling point of reaction components.

	Boiling Point, C.					
	P = 1 atm	P = 5 atm	P = 10 atm	P = 20 atm	P = 30 atm	P = 40 atm
Hydrogen	−161	−137.6	−123.7	−106.5	−94.3	−84.5
Acetaldehyde	20.4	71.9	101.1	136.4	160.7	180
Ethanol	78.3	125.2	150.2	179	198	212.7
Ethyl acetate	77	136	169.6	210.3	238.4	260.7
Ethanol/Ethyl acetate azeotrope	71.7	123.5	150.1	No Azeo	No Azeo	No Azeo

[0067] Residue curve maps can be used to indicate feasible product compositions for distillation columns. In the presence of reaction along with separation, reactive residue curve maps can be used to determine feasible products from a reactive distillation column. Reactive residue curve maps at a pressure of 1 atm and 5 atm respectively are shown in FIG. **1**. The stable nodes in the diagram are ethanol and ethyl acetate, and, therefore, it is possible to design a reactive distillation column where either ethanol or ethyl acetate can be obtained as the bottoms product. Hydrogen is an unstable node in the diagram and can be obtained as the distillate. Acetaldehyde and the ethanol/ethyl acetate azeotrope are saddle points in the diagram.

[0068] Reactive residue curve maps at pressures of 10 atm and 20 atm respectively are shown in FIG. **2**. The reactive residue curve map for any pressure above 20 atm is essentially identical to the reactive residue curve map at 20 atm.

[0069] In view of the reactive residue maps discussed above, a set of reactive distillation systems effective to produce high purity ethyl acetate from ethanol have been designed. The reactive distillation column can have single or multiple feed locations.

Reactive Distillation Column Configurations

[0070] As indicated above, the reactive distillation column is configured for the dehydrogenation of ethanol with the formation of ethyl acetate. The reaction is accomplished by passing the ethanol feed stream over a dehydrogenation catalyst under conditions where ethyl acetate is formed and hydrogen and ethyl acetate are withdrawn as top and bottoms products respectively. Such product draws drive the thermodynamics of the process toward the desired products. As one example of a useful reactive distillation column, a reactive distillation column with a single feed of ethanol as shown schematically in FIG. **3** can produce hydrogen as a distillate and ethyl acetate as a bottoms product. Column **10** contains a generally central catalyst zone **12**, and usually will include a top stage or non-reactive rectifying section **13** and a bottom state or non-reactive stripping section **15**. Ethanol feed **14** is commonly fed to the middle part of the reactive distillation column. Distillate removed at the top of the column is passed through a partial condenser **16**, and hydrogen is separated from lower boiling constituents in reflux tank **18**. The condensed lower boiling constituents (i.e., reflux) can be cycled back to the column for further reaction and/or separation. Bottoms product can be passed through reboiler **20**, where a portion of the bottoms product is evaporated and added back to the bottom of the column. The column reflux and reboil ratios are maintained such that essentially pure ethyl acetate is

obtained as the bottoms product. Ethyl acetate and hydrogen are produced due to the reaction over the dehydrogenation catalyst. Acetaldehyde may also be produced during the reaction if the conversion of acetaldehyde to ethyl acetate is incomplete.

[0071] Examples of useful catalysts for the reaction can include metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof. In many cases, the catalyst material will be supported, e.g., on carbon, alumina, silica, chromia or titania.

[0072] During operation, the reactants and products flow through the reactor/column reacting and flashing along the length of the reactor/column. The removal of hydrogen product, by flashing, preferentially to the other components along the reactive distillation column increases the extent of reaction. Also, hydrogen concentration increases from the middle part of the column towards the top of the column. At pressures of about 13 bar or lower, as ethyl acetate is formed from the reactants, azeotrope between ethyl acetate and ethanol occurs. The vapor product leaving the top of the reactive distillation column may contain ethanol and acetaldehyde in addition to hydrogen.

[0073] A partial condenser **16** allows hydrogen to be removed as a distillate, while acetaldehyde and ethanol is recycled back to the top of the reactive distillation column. As noted, the ethyl acetate and ethanol azeotrope disappears above a pressure of 13 atm, which improves the operation of the reactive distillation column. The column can be operated between a pressure of about 1 atm and about 50 atm. The temperature profile in the column is dictated by the mixture boiling point along the height of the column. High conversion of ethanol to products can be achieved by the counter-current flow of reactants and products in addition to overcoming the reaction equilibrium by removal of products.

[0074] Aldehydes and ketones such as n-butyraldehyde and butan-2-one may be produced in the reaction. These byproducts boil at temperatures close to the boiling point of ethyl acetate and may be difficult to separate from ethyl acetate. FIG. **4** shows a process schematic where the bottoms product from the reactive distillation column illustrated in FIG. **3** is sent to a hydrogenation reactor **24** containing a hydrogenation catalyst **26** with a hydrogen co-feed **28**. A suitable catalyst may comprise metals and/or oxides of nickel, palladium, platinum, ruthenium, iron, molybdenum, supported on carbon, alumina, silica, chromia or titania. The n-butyraldehyde and butan-2-one impurities are hydrogenated and can then be separated using a distillation column. The outlet of the hydrogenation reactor may be cooled in condenser **30** before entering the distillation column **32**. Ethyl acetate **36** with a purity of greater than 99% by weight can be obtained as the bottoms product of the distillation column. Unconverted hydrogen and the hydrogenated byproducts are removed as a distillate **34**, e.g., to be used as fuel. This distillation column is operated between a pressure of 1 atm and 50 atm.

[0075] In another embodiment of the invention, the reactive distillation column has two feeds. Ethanol is fed to the upper part of the column (upper feed). Hydrogen is fed to the lower part of the column (lower feed). A schematic for the double feed reactive distillation column is shown in FIG. **5**. This system includes column **40** containing catalyst **42** in catalyst zone **44**, and commonly will include a top stage or non-reactive rectifying section **50** and a bottom state or non-

reactive stripping section **52**. In the illustrated system, ethanol feed **46** is delivered at or near the top of the catalyst zone **44**, and the hydrogen feed **48** is delivered at or near the bottom of catalyst zone **44**. It should be recognized columns can be designed with the ethanol feed location in other locations, e.g., within the catalyst zone but above the hydrogen feed, such as from the approximate middle of the catalyst zone to the top of the column. Similarly, columns with the hydrogen feed in other locations can also be designed, e.g., with the hydrogen feed from the approximate middle of the catalyst zone to the bottom of the column or even higher within the catalyst zone but below the ethanol feed. Highly preferably the ethanol and hydrogen feeds are separated sufficiently to allow byproduct hydrogenation to be substantially completed before hydrogen from the feed reaches substantial concentrations of ethanol being dehydrogenated. Ethanol reacts over the catalyst producing ethyl acetate and hydrogen. Examples of catalysts may include metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof, supported, e.g., on carbon, alumina, silica, chromia or titania. Due to boiling point difference, hydrogen moves towards the top of the column and ethyl acetate moves towards the bottom of the column. Acetaldehyde may be produced during the reaction and moves up in the column, and can be condensed in partial condenser **54**, passed through reflux tank **56** and recycled back to the reaction zone. A part of the bottom draw is taken out as the ethyl acetate product stream **58**, while the remaining part is passed through reboiler **60** to be recycled to the column. Hydrogen product **59** is taken out as distillate from the reflux tank **56**. The stream passing through the reboiler provides the evaporation effect needed to operate the column.

[0076] Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction boil close to ethyl acetate. The lower hydrogen feed is useful in hydrogenating the by-products to produce components that can be separated easily from ethyl acetate. The ratio of the hydrogen feed to the ethanol feed can beneficially be adjusted to minimize the amount of close boiling byproducts, while not excessively reducing ethyl acetate to ethanol. Hydrogen product from the reaction leaves at the top of the column. The column is operated between a pressure of about 1 atm and about 50 atm.

[0077] As schematically illustrated in FIG. **6**, the reactive distillation column **70** has two feeds and uses two distinct catalyst zones, identified as an upper zone **72** containing Catalyst A **74** and a lower catalyst zone **76** containing Catalyst B **78**. Ethanol feed **80** is fed to the upper part of the column (upper feed). Hydrogen feed **82** is fed to the lower part of the column (lower feed). Ethanol reacts over the upper catalyst (Catalyst A) producing ethyl acetate and hydrogen. Examples of catalysts may include metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof, supported, e.g., on carbon, alumina, silica, chromia or titania. As with previous schematic designs shown, the column will usually include a top stage or non-reactive rectifying section **71** and a bottom state or non-reactive stripping section **79**.

[0078] Due to boiling point differences, hydrogen moves towards the top of the column and ethyl acetate moves towards the bottom of the column. Acetaldehyde may be produced during the reaction and moves up in the column, and

can be condensed in condenser **84** and recycled back to the reaction zone through reflux tank **86**. Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction boil close to ethyl acetate. The lower hydrogen feed is useful in hydrogenating the by-products over the lower catalyst (Catalyst B) to produce components that can be separated easily from ethyl acetate. Examples of hydrogenation catalysts (Catalyst B) may comprise metals and/or oxides of nickel, palladium, platinum, ruthenium, iron, molybdenum, and/or mixtures thereof supported, e.g., on carbon, alumina, silica, chromia or titania. Hydrogen product from the reaction leaves at the top of the column. Subsequent purification of ethyl acetate may be needed to remove the hydrogenated byproducts from ethyl acetate, e.g., using a distillation column such as that as shown in FIG. **4** as distillation column **32**. The column is operated between a pressure of about 1 atm and about 50 atm.

[0079] In the dual feed systems described above, the hydrogen feed should be at a sufficiently low level that it does not significantly adversely affect the dehydrogenation of ethanol in the zone above, while being effective to hydrogenate the undesirable close boiling point byproducts. Feed rates of hydrogen can be adjusted empirically to optimize this balance. Commonly, the ratio of product mixture:hydrogen will be in a range of about 500:1 to 1:1 molar ratio, more commonly about 500:1 to 10:1 or 500:1 to 100:1.

[0080] Side reactors connected to a reactive distillation column increases the catalyst holdup for improved reactant conversion. In the side reactor concept the reactor feed is withdrawn from the distillation column and the reactor effluent is returned back to the same column. The adequate catalyst amount is more easily arranged in a side reactor system where traditional reactor types and catalyst structures can be used. Also, the reaction conditions within the side reactor such as temperature can be adjusted independently of those prevailing in the distillation column by appropriate heat exchange.

[0081] Schematics for a side reactor reactive distillation column with a single catalyst are shown in FIG. **7**. A single side reactor is shown, however, multiple side reactors along the length of the reactive distillation column can be used. FIG. **7** (*a*) shows a configuration where the feed **93** to the side reactor is bottom up and vapor phase. The outlet from side reactor **94** is stream **95** which is sent back to the distillation column at any location in the column above the location of feed **93**. FIG. **7** (*b*) shows a configuration where the feed **96** to the side reactor is top down and liquid phase. The outlet from side reactor **97** is stream **98** which is sent back to the distillation column at any location in the column below the location of feed **96**. The side reactors **94** and **97** each contain catalyst for converting ethanol into ethyl acetate. Examples of catalysts may include metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof, supported, e.g., on carbon, alumina, silica, chromia or titania.

[0082] Schematics for a side reactor reactive distillation with two feeds and using two distinct catalyst zones are shown in FIG. **8**. A single side reactor is shown for each catalyst zone in the reactive distcillation column, however, multiple side reactors along the length of the reactive distillation column can be used for each catalyst zone. FIG. **8** (*a*) shows a configuration where the top zone feed **99** to the side reactor **100** is bottom up and vapor phase. The bottom zone feed **102** to another side reactor **103** is also bottom up and

vapor phase. The outlet from side reactor **100** is stream **101** which is sent back to the distillation column at any location in the column above the location of feed **99**. The outlet from side reactor **103** is stream **104** which is sent back to the distillation column at any location in the column above the location of feed **102**. FIG. **8** (*b*) shows a configuration where the top zone feed **105** to the side reactor **106** is top down and liquid phase. The bottom zone feed **108** to another side reactor **109** is also top down and liquid phase. The outlet from side reactor **106** is stream **107** which is sent back to the distillation column at any location in the column below the location of feed **105**. The outlet from side reactor **109** is stream **110** which is sent back to the distillation column at any location in the column below the location of feed **108**. Examples of catalysts for side reactors **100** and **106** may include metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof, supported, e.g., on carbon, alumina, silica, chromia or titania. Examples of hydrogenation catalysts for side reactors **103** and **109** may comprise metals and/or oxides of nickel, palladium, platinum, ruthenium, iron, molybdenum, and mixtures thereof supported, e.g., on carbon, alumina, silica, chromia or titania.

Production of Methyl Formate from Methanol

[0083] In addition to use of the systems and methods described herein for converting ethanol to ethyl acetate, those systems can also be used in processes with methanol as a feed instead of ethanol, with the production of methyl formate and H2 as products according to the following formula:

2CH3OH←→HCOOCH3+2H2
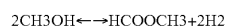
[0084] Such a system and method can utilize selections from the catalysts indicated for use with the ethanol feed. Products can be withdrawn in similar manner as described for the ethanol to ethyl acetate process.

EXAMPLES

Example 1

Production of Ethyl Acetate from Ethanol

[0085] A 10 cm diameter distillation column is used, which has been rendered adiabatic by heating casings with temperatures controlled in such a way that the temperature gradient in the column is reproduced. Over a height of 3.5 m, the column is comprised of rectification zone with 8 stages each with a catalytic cell consisting of a cylindrical container with a flat bottom. The bottom of the container is equipped with a grid for retaining the catalyst and also can act as a gas and liquid distributor. The stripping zone is comprised of 12 stages, also with catalyst-containing cells. The rectification section is considered to be above the feed stage and the stripping section is considered to be below the feed stage. Each catalyst cell contains 5 wt % copper oxide on silica. 200 proof ethanol is fed to the 13th stage of the column, starting from the bottom.

[0086] The column is regulated by establishing a reflux ratio which is equal to 2.5 and controlling the base temperature to 211° C. and the absolute pressure to 20 bar. The reflux stream is mostly ethanol with small amounts of acetaldehyde. Under stabilized conditions, a bottoms stream and a distillate stream are collected with respective throughputs of about 170

g/h and 4 g/h. The bottoms product gives ethyl acetate purity of 98.5% with small amounts of n-butyraldehyde and butan-2-one.

Example 2

Selective Hydrogenation of n-butyraldehyde and butan-2-one

[0087] Selective hydrogenation of n-butyraldehyde and butan-2-one in the presence of ethyl acetate was conducted over a hydrogenation catalyst. The reactor was filled with 20 g of 0.1 wt % Pd on silica catalyst. Before the selective hydrogenation reaction, the catalyst was reduced at a temperature of 250° C. for 30 minutes. The catalyst reduction was conducted at atmospheric pressure by delivering hydrogen using a mass flow controller. At the end of this procedure the catalyst was fully reduced.

[0088] The bottoms product from the reactive distillation column whose composition is given in Table 2 was introduced to a heater at a rate of 30 g/h and mixed with hydrogen prior to admission to the selective hydrogenation reactor. The reaction product was cooled using a jacketed condenser and the liquid condensate was analyzed by gas chromatography. The results are summarized in Table 2, showing n-butyraldehyde and butan-2-one reduced to trace levels.

TABLE 2

Hydrogenation Feed and Products
Temperature 250° C.
Pressure 20 atm

Component	Weight %	
	Feed	Products
Ethyl acetate	93	92.9
Ethanol	2	2.1
Iso-propanol	3	3
n-butyraldehyde	1.5	trace
butan-2-one	0.5	trace
2-butanol	0	0.48
n-butanol	0	1.52

[0089] All patents and other references cited in the specification are indicative of the level of skill of those skilled in the art to which the invention pertains, and are incorporated by reference in their entireties, including any tables and figures, to the same extent as if each reference had been incorporated by reference in its entirety individually.

[0090] One skilled in the art would readily appreciate that the present invention is well adapted to obtain the ends and advantages mentioned, as well as those inherent therein. The methods, variances, and compositions described herein as presently representative of preferred embodiments are exemplary and are not intended as limitations on the scope of the invention. Changes therein and other uses will occur to those skilled in the art, which are encompassed within the spirit of the invention, are defined by the scope of the claims.

[0091] It will be readily apparent to one skilled in the art that varying substitutions and modifications may be made to the invention disclosed herein without departing from the scope and spirit of the invention. Thus, such additional embodiments are within the scope of the present invention and the following claims.

[0092] The invention illustratively described herein suitably may be practiced in the absence of any element or ele-

ments, limitation or limitations which is not specifically disclosed herein. Thus, for example, in each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

[0093] In addition, where features or aspects of the invention are described in terms of Markush groups or other grouping of alternatives, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group or other group.

[0094] Also, unless indicated to the contrary, where various numerical values or value range endpoints are provided for embodiments, additional embodiments are described by taking any 2 different values as the endpoints of a range or by taking two different range endpoints from specified ranges as the endpoints of an additional range. Such ranges are also within the scope of the described invention. Further, specification of a numerical range including values greater than one includes specific description of each integer value within that range.

[0095] Thus, additional embodiments are within the scope of the invention and within the following claims.

1. A reactive distillation process producing high purity ethyl acetate from ethanol, comprising
    dehydrogenating ethanol over a catalyst in a reactive distillation column, wherein ethyl acetate is removed during said distillation process as a liquid bottoms product and hydrogen is removed during said distillation process as a gaseous top product.

2. The reactive distillation process of claim 1, further comprising hydrogenating contaminants in said liquid bottoms product and separating the hydrogenated contaminants from said ethyl acetate.

3. (canceled)

4. The reactive distillation process of claim 1, wherein said high purity ethyl acetate comprises at least 98% ethyl acetate.

5. The reactive distillation process of claim 1, wherein a single feed of ethanol is used.

6. The reactive distillation process of claim 5, wherein said reactive distillation column contains a generally central dehydrogenation catalyst zone and said single feed of ethanol is delivered into said column above or near the top of said catalyst zone.

7. The reactive distillation process of claim 5, wherein said reactive distillation column contains a generally central dehydrogenation catalyst zone and said single feed of ethanol is delivered into said column below or within said catalyst zone.

8. The reactive distillation process of claim 5, wherein said reactive distillation column contains a generally central dehy-

drogenation catalyst zone and said single feed of ethanol is delivered into said column at about the middle ⅓ of said catalyst zone.

9. The reactive distillation process of claim 6, wherein said dehydrogenation catalyst comprises a catalyst material selected from the group consisting of metals and/or oxides of copper, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, gold, thallium, manganese, aluminum, chromium, nickel, iron, molybdenum, and mixtures thereof.

10. The reactive distillation process of claim 9, wherein said catalyst material is on a support selected from the group consisting of carbon, alumina, silica, chromia, and titania.

11. The reactive distillation process of claim 5, further comprising a hydrogenation reactor comprising a hydrogenation catalyst, wherein n-butyraldehyde and butan-2-one, if present, are hydrogenated.

12. The reactive distillation process of claim 11, wherein said hydrogenation catalyst comprises a catalyst material selected from the group consisting of metals and/or oxides of nickel, palladium, platinum, ruthenium, iron, molybdenum, and mixtures thereof.

13. The reactive distillation process of claim 12, wherein said catalyst material is supported on a support material selected from the group consisting of carbon, alumina, silica, chromia and titania.

14. The reactive distillation process of claim 11, further comprising a separation column which receives product from said hydrogenation reactor, wherein n-butanol and 2-butanol are separated from ethyl acetate.

15. The reactive distillation process of claim 1, wherein dual feeds of ethanol and hydrogen are fed to said reactive distillation column, and wherein said ethanol feed is above said hydrogen feed.

16. The reactive distillation process of claim 15, wherein said reactive distillation column comprises a dehydrogenation catalyst zone and said ethanol feed is above or near the top of said dehydrogenation catalyst zone and said hydrogen feed is below or near the bottom of said dehydrogenation catalyst zone.

17. The reactive distillation process of claim 16, wherein said reactive distillation column further comprises a hydrogenation catalyst zone below said dehydrogenation catalyst zone, and said hydrogen feed is below, near the bottom of, or within said hydrogenation catalyst zone.

18. The reactive distillation process of claim 15, wherein the molar ratio of Ethanol:Hydrogen for the dual feed is from 1:10 to 1000:1.

19. The reactive distillation process of claim 1, wherein said reactive distillation is performed at a pressure from 1 bar to 50 bar.

20. The reactive distillation process of claim 1, wherein the number of stages or the number of height equivalents of a theoretical plate (HETP) is from 2 to 100.

21. A reactive distillation system for producing high purity ethyl acetate from ethanol, comprising
    a reactive distillation column comprising
        a dehydrogenation catalyst located generally centrally in said column;
        an ethanol feed which feeds ethanol into said column such that it passes over said dehydrogenation catalyst;
        a top product gaseous hydrogen removal passage;
        a bottoms product liquid ethyl acetate removal passage.

22. (canceled)

23. (canceled)

24. (canceled)
25. (canceled)
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28. (canceled)
29. (canceled)
30. (canceled)
31. (canceled)
32. (canceled)
33. (canceled)
34. (canceled)
35. (canceled)
36. (canceled)
37. (canceled)

38. (canceled)
39. (canceled)
40. (canceled)
41. (canceled)
42. (canceled)
43. A reactive distillation process producing high purity methyl formate from methanol, comprising
dehydrogenating methanol over a catalyst in a reactive distillation column, wherein methyl formate is removed during said distillation process as a liquid bottoms product and hydrogen is removed during said distillation process as a gaseous top product.

* * * * *

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(54) **ETHYL ACETATE PRODUCTION**

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(57)   **ABSTRACT**

A reactive distillation method comprises introducing an feed
stream comprising ethanol to a reactive distillation column,
contacting the feed stream with a catalyst in the reactive
distillation column during a distillation, where the feed
stream reacts in the presence of the catalyst to produce a
reaction product comprising ethyl acetate and hydrogen,
removing ethyl acetate during the distillation from the reac-
tive distillation column as a bottoms stream, and removing
hydrogen during the distillation from the reactive distillation
column as an overhead stream.

Side reactor configuration (a) upward flow feed to side reactor (b)
downward flow feed to side reactor.

Figure 1: Reactive residue curve maps at pressures of 1 atm and 5 atm.

Figure 2: Reactive residue curve maps at pressures of 10 atm and 20 atm.

Figure 3: Single feed reactive distillation column schematic.

Figure 4: Schematic for a reactive distillation system with subsequent product hydrogenation.

Figure 5: Double feed reactive distillation column schematic with an upper feed of ethanol and lower feed of hydrogen.

Figure 6: Double feed reactive distillation column schematic using dual catalyst beds with an upper feed of ethanol and lower feed of hydrogen.

167

Figure 7: Side reactor configuration (a) upward flow feed to side reactor (b) downward flow feed to side reactor.

Figure 8: Double Side reactor configuration (a) upward flow feed to multiple side reactors (b) downward flow feed to multiple side reactors.

FIG. 9

Figure 10: Process configuration for product purification and ethanol recycle.
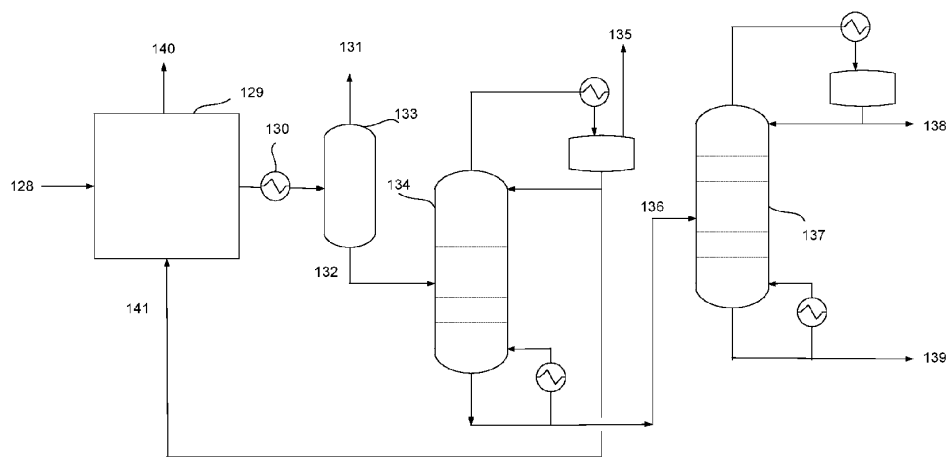
Figure 11: Indirect separation sequence for product purification and ethanol recycle.

ETHYL ACETATE PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] None.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

REFERENCE TO A MICROFICHE APPENDIX

[0003] Not applicable.

BACKGROUND

[0004] Ethyl acetate can be produced from several different reactions. The most common method for making ethyl acetate is the esterification of acetic acid and ethanol. This reaction requires two raw material supplies with the associated storage or production facilities. In locations without a sufficient supply of reliable, inexpensive acetic acid, this process may not be economically viable.

[0005] Ethyl acetate can also be produced from the oxidation of ethanol over supported precious metal catalysts. The high costs of precious metal catalyst can also make this option uneconomical. In addition, the oxidation of ethanol results in the presence of water in the product stream, which can result in a relatively expensive separation system to purify the product.

[0006] The Tishchenko reaction (dimerization of aldehydes into esters) is another alternative process for production of ethyl acetate. Dimerization of acetaldehyde results in ethyl acetate, however, aldol condensation also occurs, resulting in by-products such as 2-butnaone and 2-propanol, both of which form azeotropes with ethyl acetate. In addition, the Tishchenko reaction requires a supply of acetaldehyde, which may not be readily available and can be difficult to store and handle due to its high toxicity.

SUMMARY

[0007] In an embodiment, a reactive distillation method comprises introducing an feed stream to a reactive distillation column, wherein the feed stream comprises ethanol, contacting the feed stream with a catalyst in the reactive distillation column during a distillation, wherein the feed stream reacts in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen, removing ethyl acetate during the distillation from the reactive distillation column as a bottoms stream, and removing hydrogen during the distillation from the reactive distillation column as an overhead stream. The method may also include contacting the bottoms stream with a hydrogenation catalyst and hydrogen to hydrogenate at least a portion of a contaminant in the bottoms stream, and separating the hydrogenated portion of the contaminant from the bottoms stream. The hydrogenation catalyst may comprise a Group VIII metal, a Group VI metal, or any combination thereof. The catalyst may comprise at least one catalytic component selected from the group consisting of: copper, copper oxide, barium, barium oxide, ruthenium, ruthenium oxide, rhodium, rhodium oxide, platinum, platinum oxide, palladium, palladium oxide, rhenium, rhenium oxide, silver, silver oxide, cadmium, cadmium oxide, zinc, zinc oxide, zirconium, zirconium oxide, gold, gold

oxide, thallium, thallium oxide, magnesium, magnesium oxide, manganese, manganese oxide, aluminum, aluminum oxide, chromium, chromium oxide, nickel, nickel oxide, iron, iron oxide, molybdenum, molybdenum oxide, sodium, sodium oxide, sodium carbonate, strontium, strontium oxide, tin, tin oxide, and any mixture thereof. The catalyst may comprise a support, wherein the support comprises at least one support material selected from the group consisting of: carbon, silica, silica-alumina, alumina, zirconia, titania, ceria, vanadia, nitride, boron nitride, heteropolyacids, hydroxyapatite, zinc oxide, chromia, a zeolite, a carbon nanotube, carbon fullerene, and any combination thereof. The catalyst may comprise copper, and the catalyst may have a copper weight loading of between about 0.5% and about 80% of the catalyst.

[0008] The catalyst may comprise copper oxide and zinc oxide disposed on a support; copper oxide, zinc oxide, zirconium oxide, and alumina; and/or copper oxide, zinc oxide, zirconium oxide, and chromium oxide. The catalyst may comprise an alkaline earth metal or alkaline earth metal oxide, copper or copper oxide, and a support. The catalyst may comprise sodium carbonate, and/or the catalyst may be at least partially reduced in the presence of hydrogen. A conversion of ethanol in the feed stream may be at least about 10%, and/or a selectivity of the conversion of ethanol to ethyl acetate may be at least about 60%. The method may also include removing a side stream from the reactive distillation column, and contacting the side stream with a second catalyst, wherein the side stream reacts in the presence of the second catalyst to produce ethyl acetate. A liquid portion of the feed stream may react in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen.

[0009] In an embodiment, a reactive distillation system comprises a reactive distillation column comprising: a dehydrogenation catalyst located generally centrally in the column, an ethanol feed in fluid communication with the reactive distillation column and configured to pass ethanol over the dehydrogenation catalyst, an overhead product hydrogen removal passage, and a bottoms product ethyl acetate removal passage. The reactive distillation system also comprises a product separation system comprising an inlet configured to receive the bottoms product from the reactive distillation column, an ethyl acetate product removal passage, and an ethanol removal passage; and a recycle line coupling the ethanol removal passage from the product separation system and an inlet to the reactive distillation column. The system may also include a hydrogenation catalyst positioned to contact a liquid product following passage over the dehydrogenation catalyst. The product separation system may also include at least one of a lights product removal passage or a heavies product removal passage. 20. The reactive distillation column may comprise a batch reactor configured to contact a liquid ethanol feed with the dehydrogenation catalyst and remove hydrogen during the contacting of the liquid ethanol feed with the dehydrogenation catalyst.

[0010] In an embodiment, a reactive distillation method comprises introducing an feed stream to a reactive distillation column, wherein the feed stream comprises ethanol; contacting the feed stream with a catalyst in the reactive distillation column during a distillation, wherein the feed stream reacts in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen; separating bottoms stream during the distillation from the reactive distillation

column, wherein the bottoms stream comprises ethyl acetate and ethanol; separating a recycle stream from the bottoms stream, wherein the recycle stream comprises at least a portion of the ethanol from the bottoms stream; and recycling the recycle stream to the reactive distillation column. The method may also include separating the bottoms stream into an overhead stream and the recycle stream at a first pressure, where the overhead stream comprises ethanol and ethyl acetate; and separating the overhead stream into an ethanol stream and an ethyl acetate product stream at a second pressure, where the second pressure is greater than the first pressure. The method may also include combining the ethanol stream with the bottoms stream in the separation of the bottoms stream into the overhead stream and the recycle stream. The method may also include separating at least one byproduct from the recycle stream after separation of the recycle stream from the bottoms stream and prior to recycling the recycle stream to the reactive distillation column. The method may also include separating the bottoms stream into a product stream and the recycle stream; and separating the product stream into a byproduct stream and an ethyl acetate product stream

[0011] These and other features will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description.

[0013] FIG. 1 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 1 and 5 atmospheres (atm) for an embodiment.

[0014] FIG. 2 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 10 and 20 atm for an embodiment.

[0015] FIG. 3 shows a simplified schematic of a reactive distillation system according to an embodiment.

[0016] FIG. 4 shows a simplified schematic of a reactive distillation system according to another embodiment.

[0017] FIG. 5 shows a simplified schematic of a reactive distillation system according to still another embodiment.

[0018] FIG. 6 shows a simplified schematic of a reactive distillation system according to yet another embodiment.

[0019] FIGS. 7(a) and 7(b) shows a simplified schematic of a reactive distillation system according to an embodiment.

[0020] FIGS. 8(a) and 8(b) shows a simplified schematic of a reactive distillation system according to another embodiment.

[0021] FIG. 9 illustrates a schematic flow diagram of a reactive distillation system with a recycle according to an embodiment.

[0022] FIG. 10 illustrates a schematic flow diagram of a product separation system according to an embodiment.

[0023] FIG. 11 illustrates a schematic flow diagram of a product separation system according to another embodiment.

DETAILED DESCRIPTION

[0024] A reactive distillation system and process are disclosed herein for producing high purity ethyl acetate from ethanol. This process is beneficial as it provides an improved commercial method of upgrading ethanol to ethyl acetate, a more valuable product. This improved commercial process

may be used where there is a supply and/or a surplus supply of ethanol. Further, this process reduces and/or eliminates the need for a separate acetaldehyde or acetic acid plant to provide the precursors for the ethyl acetate production process. The raw material may comprise only ethanol, which may present an advantage relative to other processes requiring multiple feedstocks. In addition, bio-derived ethanol may be used to allow the process to be operated from renewable ethanol sources. Further, the present system and method may utilize base-metal catalysts, which may be less expensive than the precious metal based catalysts of other ethyl acetate production routes. Such catalysts can comprise copper, and may be composed of copper oxide mixed with one or more additional metals and/or metal oxides. The present systems and methods may allow for a one-step ethyl acetate production process, which may be advantageous relative to other processes that require further steps to purify the ethyl acetate product, including a selective removal of 2-butnaone, which forms a low boiling azeotrope with ethyl acetate. Each of these advantages may be provided in a process that can also be less expensive than alternative processes by ethyl acetate production from ethanol.

[0025] In an embodiment, the present systems and methods can provide a route to ethyl acetate by dehydrogenation and dimerization of ethanol which is capable of yielding high purity ethyl acetate from ethanol feed streams containing significant amounts of impurities. One issue in the production of ethyl acetate by dehydrogenation of ethanol is that the reaction product mixture is commonly a complex mixture including esters, alcohols, aldehydes and ketones. From a distillative separation point of view, the mixture is further complicated due to the presence of azeotropes. The reaction product mixtures commonly contain components with boiling points close to ethyl acetate (such as n-butyraldehyde and/or butan-2-one), including components which can form azeotropes with ethyl acetate, and/or other components of the mixture. This may present a challenge when high purity ethyl acetate is desired.

[0026] In chemical processing, chemical reaction and the purification of the desired products by distillation may be carried out sequentially. The performance of this chemical process structure may be improved by the integration of reaction and distillation in a single multifunctional process unit. This integration concept is called "reactive distillation." As advantages of this integration, chemical equilibrium limitations may be overcome, higher selectivities may be achieved, the heat of reaction may be used in situ for distillation, auxiliary solvents may be avoided, and/or azeotropic and/or closely boiling mixtures may be more easily separated. Increased process efficiency and reduction in overall capital costs may result from the use of this approach.

[0027] A reactive distillation system comprises at least one separator (e.g., a distillation tower) in which a reaction is occurring. In general, suitable separators may include any process equipment suitable for separating at least one inlet stream into a plurality of effluent streams having different compositions, states, temperatures, and/or pressures. For example, the separator may be a column having trays, packing, or some other type of complex internal structure. Examples of such columns include scrubbers, strippers, absorbers, adsorbers, packed columns, and distillation columns having valve, sieve, or other types of trays. Such columns may employ weirs, downspouts, internal baffles, temperature control elements, and/or pressure control elements.

Such columns may also employ some combination of reflux condensers and/or reboilers, including intermediate stage condensers and reboilers. In an embodiment, the reactive distillation system described herein may comprise a distillation tower having at least one catalyst disposed therein.

[0028] As indicated above, the present systems and methods provide for the production of ethyl acetate from ethanol at a relatively low cost, along with a plant or distillation system with significantly reduced complexity using reactive distillation. The present disclosure further provides an improved process for the production of high purity ethyl acetate from ethanol, or from a feedstock comprising a major proportion of ethanol and a minor proportion of impurities such as isopropanol and iso-butanol. While not commonly present in ethanol feed streams, impurities that can poison the particular catalyst used should be limited, avoided and/or removed. For example, sulfur or nitrogen heterocyclic compounds can frequently act as catalyst poisons and, if present, should be removed before introducing the ethanol feed stream to the reactive distillation column. In an embodiment, the ethanol feed may comprise water. The presence of water in the ethanol feed does not severely reduce the performance of the catalysts, which can tolerate up to 5% water by weight in the ethanol. Ethanol conversion is reduced when using an ethanol source with significant water content, but the reaction selectivity increases. The use of an ethanol feed comprising a small amount of water may be advantageous by allowing for the use a potentially less expensive ethanol source in the form of the ethanol/water azeotrope (about 4.4% water by weight). The effects of water are demonstrated in the Examples described herein.

[0029] Ethyl acetate can be produced from ethanol according to the following reactions:

$$C_2H_5OH \leftarrow \rightarrow CH_3CHO + H_2 \tag{Eq. 1}$$

$$CH_3CHO + C_2H_5OH \leftarrow \rightarrow CH_3COOC_2H_5 + H_2 \tag{Eq. 2}$$

[0030] In an embodiment, ethanol reacts in a single continuous reactive distillation column which provides sufficient residence time to achieve a relatively high conversion of ethanol. In an embodiment, the reactive distillation column may be configured to provide a conversion of ethanol of at least about 10% and a selectivity of at least about 60%, as described in more detail herein. Table 1 shows the effect of pressure on the boiling point of the pure components and azeotrope in the mixture. The azeotrope between ethanol and ethyl acetate is substantially avoided above a pressure of 13 atm.

[0031] Residue curve maps can be used to indicate feasible product compositions for distillation columns. In the presence of reaction along with separation, reactive residue curve maps can be used to determine feasible products from a reactive distillation column. Reactive residue curve maps at a pressure of 1 atm and 5 atm respectively are shown in FIG. 1. The stable nodes in the diagram are ethanol and ethyl acetate, and, therefore, it is possible to design a reactive distillation column where either ethanol or ethyl acetate can be obtained as the bottoms product. Hydrogen is an unstable node in the diagram and can be obtained as the distillate. Acetaldehyde and the ethanol/ethyl acetate azeotrope are saddle points in the diagram.

[0032] Reactive residue curve maps at pressures of 10 atm and 20 atm respectively are shown in FIG. 2. The reactive residue curve maps for any pressure above 20 atm substantially similar to the reactive residue curve map at 20 atm.

[0033] In view of the reactive residue maps discussed above, a set of reactive distillation systems effective to produce high purity ethyl acetate from ethanol have been designed. The reactive distillation column can have single or multiple feed locations.

Reactive Distillation Column Configurations

[0034] The present systems and methods provide a reactive distillation system in which ethanol may be the sole or primary component of the feed. In some embodiments, the ethanol feed is used in conjunction with a separate, second feed of hydrogen. Reference to a "single feed" to a reactive distillation column means that the column has only one chemical feed stream supplying intended reactant(s) to the column. Nonetheless, such a single feed distillation column may have multiple entry points for the reactant, or recycling feed streams where a part of the reactant liquid or a partial distillate is drawn from the column and fed back into the column at a different point, e.g., to achieve improved separation and/or more complete reaction. A "single ethanol feed" thus refers to a single feed stream, in which ethanol is the sole or at least the primary constituent. In contrast, the term "dual feed" in the context of a distillation column refers to two separate chemical feed streams. For example, in some of the present embodiments, dual feeds are an ethanol feed and a separate hydrogen feed. The term "reactive distillation column" is used conventionally to refer to a distillation column in which both reaction and separation is performed. In this case, the primary and desired reaction is the conversion of two ethanol molecules to one ethyl acetate molecule with release of two hydrogen

TABLE 1

Boiling point of reaction components.

	Boiling Point, C.					
	P = 1 atm	P = 5 atm	P = 10 atm	P = 20 atm	P = 30 atm	P = 40 atm
Hydrogen	−161	−137.6	−123.7	−106.5	−94.3	−84.5
Acetaldehyde	20.4	71.9	101.1	136.4	160.7	180
Ethanol	78.3	125.2	150.2	179	198	212.7
Ethyl acetate	77	136	169.6	210.3	238.4	260.7
Ethanol/Ethyl acetate azeotrope	71.7	123.5	150.1	No Azeo	No Azeo	No Azeo

molecules. Thus, the present invention provides systems and methods for the production of ethyl acetate from ethanol which includes reacting ethanol over a suitable dehydrogenation and/or dimerization catalyst in a reactive distillation column, thereby producing ethyl acetate and hydrogen.

[0035] In an embodiment, a single reactive distillation column is used. Hydrogen gas is removed (e.g., continuously) from the top of the reactive distillation column as an overhead stream. Ethyl acetate is removed (e.g., continuously) from the bottom of the column as a bottoms stream. Optionally, contaminating byproducts present following reaction of the ethanol over the dehydrogenation catalyst can be reacted over a suitable hydrogenation catalyst in the lower part of the column or in a separate hydrogenation reactor. The hydrogenation can convert difficult to separate byproducts into species which are easier to separate from the ethyl acetate. Consequently, the process can also include purifying the ethyl acetate by distilling out resulting hydrogenated byproducts.

[0036] In an embodiment, the reactive distillation column is configured for the dehydrogenation of ethanol with the formation of ethyl acetate. The reaction is accomplished by passing the ethanol feed stream over a dehydrogenation catalyst under conditions where ethyl acetate is formed and hydrogen and ethyl acetate are withdrawn as top and bottoms products respectively. Such product draws drive the thermodynamics of the process toward the desired products. In its simplest form, a reactive distillation system may comprise a reactor vessel operating with a liquid phase reaction in which hydrogen and/or other light gases are removed as the overhead product and a reaction product is removed as the bottoms product. Such a system may comprise a batch reactor in which hydrogen is removed during the reaction and the liquid product is removed after completion of the reaction to a desired degree of conversion.

[0037] In an embodiment of a reactive distillation column, a reactive distillation column with a single feed of ethanol as shown schematically in FIG. 3 can produce hydrogen as a distillate and ethyl acetate as a bottoms product. Column 10 contains a generally central catalyst zone 12, and usually will include a top stage or non-reactive rectifying section 13 and a bottom state or non-reactive stripping section 15. Ethanol feed 14 is commonly fed to the middle part of the reactive distillation column. Distillate removed at the top of the column is passed through a partial condenser 16, and hydrogen is separated from lower boiling constituents in reflux tank 18. The hydrogen may leave the system as an overhead product stream 19, which in an embodiment may comprise trace amounts of additional components including ethanol, ethyl acetate, and/or one or more reaction byproducts. The condensed lower boiling constituents (i.e., reflux), or at least some portion thereof, can be cycled back to the column for further reaction and/or separation. The bottoms product can be passed through reboiler 20, where a portion of the bottoms product is evaporated and added back to the bottom of the column. The remaining bottoms product may pass out of the system as product stream 22. Alternatively, only a portion of the bottoms product may be passed through reboiler 20, with the vapor portion passing back to the bottom of the column and the remainder of the bottoms product being combined with any bottoms product bypassing the reboiler 20 and passing out of the system as product stream 22 for further processes and/or use as a final product. The product stream 22 may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products pro-

duced by the reaction. The column reflux and reboil ratios are maintained such that essentially pure ethyl acetate is obtained as the bottoms product. In an embodiment, the bottoms product stream 22 may comprise greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0038] During operation, the reactants and products flow through the reactor/column reacting and flashing along the length of the reactor/column. In an embodiment, the reaction of the reactants and/or products may occur in the catalyst zone 12, and the reactions may occur in the vapor and/or liquid phase. Specific catalysts useful in the reactive distillation systems and methods disclosed herein are discussed in more detail below. Ethyl acetate and hydrogen are produced due to the reaction over the dehydrogenation and dimerization catalyst. Acetaldehyde may also be produced during the reaction if the conversion of acetaldehyde to ethyl acetate is incomplete. The removal of the overhead stream 19 comprising hydrogen, which may occur by flashing, increases the extent of reaction. In general, the hydrogen concentration increases from the middle part of the column towards the top of the column. At pressures of about 13 bar or lower, as ethyl acetate is formed from the reactants, an azeotrope between ethyl acetate and ethanol occurs. This azeotrope may result in the overhead product 19 that leaves the top of the reactive distillation column 10 containing ethanol/ethyl acetate and/or acetaldehyde in addition to hydrogen. A partial condenser 16 allows hydrogen to be removed as a distillate, while acetaldehyde and ethanol are recycled back to the top of the reactive distillation column. At a pressure above about 13 atm, the ethyl acetate and ethanol azeotrope disappears, which improves the operation of the reactive distillation column.

[0039] The column 10 can be operated at any suitable pressure between about 1 atm and about 80 atm. In an embodiment, the column 10 may be operated at a pressure ranging from about 1 atm to about 5 atm, about 5 atm to about 10 atm, about 7 atm to about 12 atm, about 13 atm to about 15 atm, about 13 atm to about 20 atm, about 15 atm to about 20 atm, about 15 atm to about 30 atm, about 20 atm to about 30 atm, about 20 atm to about 50 atm, about 30 atm to about 40 atm, about 40 atm to about 50 atm, or about 50 atm to about 60 atm, about 60 atm to about 70 atm, about 60 atm to about 80 atm, or about 70 atm to about 80 atm. In an embodiment, the reactive distillation is performed at a pressure where ethanol-ethyl acetate azeotrope is not present. The temperature profile in the column is dictated by the mixture boiling point along the height of the column. In an embodiment the temperature within the column may range from about 100° C. to about 350° C., alternatively about 150° C. to about 250° C. The column 10 may comprise any number of stages equivalent to a number of theoretical stages sufficient to effect the reaction and separation of ethyl acetate to a desired purity. In an embodiment, the number of stages or the number of height equivalents of a theoretical plate (HETP) may range from about 1 to about 100, including for example from about 1 to about 10, about 10 to about 20, about 10 to about 50, about 20 to about 30, about 20 to about 70, about 30 to about 40, about 30 to about 50, about 30 to about 100, about 50 to about 70, about 50 to about 100, or about 70 to about 100. As described in more detail below, a relatively high conversion of ethanol to products can be achieved by the counter-current flow of reactants and products in addition to overcoming the reaction

equilibrium by removal of products through the concurrent distillation within the column **10**.

[0040] In an embodiment, the systems and methods may also include hydrogenating contaminants or reaction byproducts in the bottoms stream or in the reacted fluid after it has passed over the dehydrogenation catalyst and separating the hydrogenated contaminants or byproducts from the ethyl acetate. Aldehydes and/or ketones such as n-butyraldehyde and butan-2-one may be produced as byproducts in the reaction. These byproducts boil at temperatures close to the boiling point of ethyl acetate and may be difficult to separate from ethyl acetate. FIG. **4** shows a process schematic where the bottoms product **22** from the reactive distillation column **10** illustrated in FIG. **3** is sent to a hydrogenation reactor **24** comprising a hydrogenation catalyst **26** with a hydrogen co-feed **28**. Suitable hydrogenation catalyst(s) may comprise various components and are described in more detail herein. At least a portion of the n-butyraldehyde and/or butan-2-one impurities can be hydrogenated and can then be separated using a separator **32**. The separator **32** may comprise any of the types of separators described herein with respect to the reactive distillation system. Alternatively or in addition to the separators already described, the separator **32** may be a phase separator, which is a vessel that separates an inlet stream into a substantially vapor stream and a substantially liquid stream, such as a knock-out drum, flash drum, reboiler, condenser, or other heat exchanger. Such vessels also may have some internal baffles, temperature control elements, and/or pressure control elements, but generally lack any trays or other type of complex internal structure commonly found in columns. The separator also may be any other type of separator, such as a membrane separator. In a specific embodiment, the separator is a knockout drum. Finally, the separator may be any combination of the aforementioned separators arranged in series, in parallel, or combinations thereof. In an embodiment, separator **32** comprises a distillation column. The outlet of the hydrogenation reactor **24** may be passed through a heat exchanger **30** (e.g., a condenser) and cooled before entering the separator **32**. The heat exchanger **30** may be any equipment suitable for heating or cooling one stream using another stream. Generally, the heat exchanger **30** is a relatively simple device that allows heat to be exchanged between two fluids without the fluids directly contacting each other. Examples of suitable heat exchangers **30** include, but are not limited to, shell and tube heat exchangers, double pipe heat exchangers, plate fin heat exchangers, bayonet heat exchangers, reboilers, condensers, evaporators, and air coolers. In the case of air coolers, one of the fluids comprises atmospheric air, which may be forced over tubes or coils using one or more fans.

[0041] The bottoms product stream **36** from the separator **32** may comprise ethyl acetate and may have a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight. Unconverted hydrogen and the hydrogenated byproducts may be removed as an overhead product **34**, and may be used, for example, as fuel or a feed to one or more processes. In an embodiment, the separator **32** may be operated between a pressure of 1 atm and 80 atm.

[0042] In an embodiment, the bottoms product stream **36** may pass to another separator. The separator may then separate the bottoms product stream into an ethyl acetate stream and a byproduct stream comprising one or more heavier hydrogenation products produced in the hydrogenation reac-

tor **26**. This separation scheme may allow the resulting ethyl acetate stream to have a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0043] In another embodiment of the invention, the reactive distillation column has two feeds. Ethanol may be fed to the upper part of the column (upper feed), and hydrogen may be fed to the lower part of the column (lower feed). A schematic for the double feed reactive distillation column is schematically illustrated in FIG. **5**. This system includes column **40** containing catalyst **42** in catalyst zone **44**, and commonly may include a top stage or non-reactive rectifying section **50** and a bottom stage or non-reactive stripping section **52**. In the illustrated system, ethanol feed **46** is delivered at or near the top of the catalyst zone **44**, and the hydrogen feed **48** is delivered at or near the bottom of catalyst zone **44**. It should be recognized columns can be designed with the ethanol feed **46** location in other locations, e.g., within the catalyst zone **44** but above the hydrogen feed **48**, such as from the approximate middle of the catalyst zone **44** to the top of the column **40**. Similarly, columns with the hydrogen feed **48** in other locations can also be designed, e.g., with the hydrogen feed **48** from the approximate middle of the catalyst zone **44** to the bottom of the column **40** or even higher within the catalyst zone **44** but below the ethanol feed **46**. In an embodiment, the ethanol feed **46** and the hydrogen feed **48** are separated sufficiently to allow byproduct hydrogenation to be substantially completed before hydrogen from the feed reaches substantial concentrations of ethanol being dehydrogenated. Ethanol reacts over the catalyst producing ethyl acetate and hydrogen. Examples of suitable dehydrogenation and dimerization catalysts are described in more detail herein.

[0044] Due to boiling point differences, hydrogen moves towards the top of the column **40** and ethyl acetate moves towards the bottom of the column **40**. Acetaldehyde may be produced during the reaction and may move up in the column **40**. At least a portion of the acetaldehyde, if present, can be condensed in condenser **54** (e.g., a partial condenser, or a total condenser), passed through reflux tank **56**, and recycled back to column **40** as reflux. A product stream **59** comprising hydrogen is taken out as distillate from the reflux tank **56**. A part of the bottom draw is taken out as the ethyl acetate product stream **58**, while the remaining part is passed through reboiler **60** to be recycled to the column **40**. In an embodiment, the bottom draw may be passed through a reboiler (e.g., similar to reboiler **60**) and optionally passed to a separator where the vapor portion may pass to the column **40** while at least a portion of the remainder is taken out as the ethyl acetate product stream **58**. The stream passing through the reboiler **60** provides the evaporation effect and vapor flow for operating the column **40**. The product stream **58** may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products produced by the reaction.

[0045] Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction may have boiling points close to the boiling point of ethyl acetate. The lower hydrogen feed **48** is useful in hydrogenating the by-products to produce components that can be separated easily from ethyl acetate. The ratio of the hydrogen feed to the ethanol feed can beneficially be adjusted to minimize the amount of close boiling byproducts, while not excessively reducing ethyl acetate to ethanol. In an embodiment, the molar ratio of ethanol to hydrogen ranges from about 1:10 to about 1000:1, e.g., from about 1:10

to about 1:1, from about 1:1 to about 5:1, from about 1:1 to about 10:1, from about 5:1 to about 25:1, from about 5:1 to about 50:1, from about 10:1 to about 50:1, from about 10:1 to about 100:1, from about 50:1 to about 200:1, from about 50:1 to about 400:1, from about 100:1 to about 500:1, from about 100:1 to about 1000:1, from about 200:1 to about 1000:1, or from about 500:1 to about 1000:1. Hydrogen product from the reaction leaves at the top of the column. In an embodiment, the column **40** may operate at any of the conditions (e.g., operating pressure, operating temperature, etc.) discussed herein with respect to column **10** in FIG. **3**. In addition, the column **40** may have any number of stages, and in an embodiment have any number of stages as described with respect to column **10** in FIG. **3**.

[0046] As schematically illustrated in FIG. **6**, the reactive distillation column **70** has two feeds **80**, **82** and uses two catalyst zones, identified as an upper zone **72** containing Catalyst A **74** and a lower catalyst zone **76** containing Catalyst B **78**. Ethanol feed **80** is fed to the upper part of the column **70** (upper feed). Hydrogen feed **82** is fed to the lower part of the column **70** (lower feed). The molar ratio of ethanol to hydrogen may fall within any of the ranges described above with respect to FIG. **5** (e.g., from about 1:10 to about 1000:1, and all sub-ranges). Ethanol may react over the upper catalyst (Catalyst A **74**) producing ethyl acetate and hydrogen. Examples of suitable upper catalysts are described in more detail herein with respect to the dehydrogenation and dimerization catalysts. As with previous schematic designs shown, the column **70** will usually include a top stage or non-reactive rectifying section **71** and a bottom state or non-reactive stripping section **79**.

[0047] Due to boiling point differences, hydrogen moves towards the top of the column **70** and ethyl acetate moves towards the bottom of the column **70**. Acetaldehyde may be produced during the reaction and may move up in the column **70**. At least a portion of the acetaldehyde, if present, can be condensed in condenser **84** and recycled back to the reaction zone through reflux tank **86**. Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction can have boiling points close to the boiling point of ethyl acetate. The lower hydrogen feed is useful in hydrogenating the by-products over the lower catalyst (Catalyst B) to produce components that can be separated easily from ethyl acetate. Examples of hydrogenation catalysts (Catalyst B) are described in more detail herein. A product stream **88** comprising hydrogen from the reaction leaves at the top of the column **70**. A portion of the bottom draw is taken out as the ethyl acetate product stream **92**, while the remaining portion is passed through reboiler **90** to be recycled to the column **70**. In an embodiment, the bottom draw may be passed through a reboiler (e.g., similar to reboiler **90**) and optionally passed to a separator where the vapor portion may pass to the column **70** while at least a portion of the remainder is taken out as the ethyl acetate product stream **92**. The stream passing through the reboiler **90** provides the evaporation effect and vapor flow for operating the column **70**. The product stream **92** may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products produced by the reaction. Subsequent purification of product stream **92** comprising ethyl acetate may be needed to remove the hydrogenated byproducts from the ethyl acetate, e.g., using a separator such as that as shown in FIG. **4** as separator **32**, which in an embodiment may comprise a distillation column.

[0048] In an embodiment, the column **70** may operate at any of the conditions (e.g., operating pressure, operating temperature, etc.) discussed herein with respect to column **10** in FIG. **3**. In addition, the column **70** may have any number of stages, and in an embodiment have any number of stages as described with respect to column **10** in FIG. **3**.

[0049] In the dual feed systems described above with respect to FIGS. **5** and **6**, the hydrogen feed should be at a sufficiently low level that it does not significantly adversely affect the dehydrogenation of ethanol in the zone above, while being effective to hydrogenate the undesirable close boiling point byproducts. Feed rates of hydrogen can be adjusted empirically to optimize this balance. Commonly, the ratio of ethanol:hydrogen will be in a range of about 500:1 to 1:1 molar ratio, more commonly about 500:1 to 10:1 or 500:1 to 100:1.

[0050] In an embodiment, side reactors can be connected to a reactive distillation column to increase the catalyst holdup for improved reactant conversion. In the side reactor embodiment, the side reactor feed is withdrawn from the distillation column and the reactor effluent is returned back to the same column. An adequate amount of catalyst may be arranged in a side reactor system where traditional reactor types and catalyst structures can be used. Also, the reaction conditions within the side reactor such as temperature can be adjusted independently of those prevailing in the distillation column by appropriate heat exchange.

[0051] Schematics for a side reactor reactive distillation column with a single catalyst are shown in FIG. **7**. A single side reactor is shown, however, multiple side reactors along the length of the reactive distillation column can be used. FIG. **7**(*a*) shows a configuration where the feed **93** to the side reactor **94** is bottom up and vapor phase. The outlet from side reactor **94** is stream **95** which is sent back to the distillation column **40** at any location in the column **40** above the location of feed **93**. FIG. **7**(*b*) shows a configuration where the feed **96** to the side reactor **97** is top down and liquid phase. The outlet from side reactor **97** is stream **98** which is sent back to the distillation column **40** at any location in the column **40** below the location of feed **96**. The side reactors **94** and **97** each contain catalyst for converting ethanol into ethyl acetate. Examples of suitable catalysts are described in more detail herein.

[0052] The use of a side reactor using a liquid feed may allow for the reaction to occur in the liquid phase. While not intending to be limited by theory, it is believed that the dehydrogenative dimerization of ethanol to ethyl acetate may occur over the dehydrogenation and dimerization catalysts described herein in the liquid phase. It has not been previously recognized that the dehydrogenation and dimerization conversion of ethanol to ethyl acetate would occur in the liquid phase. The use of a liquid phase reaction may allow for reactive distillation to be effectively used for converting ethanol into ethyl acetate and hydrogen.

[0053] While illustrated as a bottom up vapor phase design and a top down liquid phase design in FIGS. **7**(*a*) and **7**(*b*), the side reactors **94**, **97** may also operate bottom up using a liquid phase draw from the column **40** and top down using a vapor phase draw from the column with the appropriate equipment such as pumps, compressors, valves, piping, etc. In an embodiment, the side reactors **94**, **97** may be implemented as a single reactor vessel, or as a plurality of reactor vessels arranged in series and/or parallel. In an embodiment, a plurality of side reactors may be implemented as shown in FIGS.

7(*a*) and 7(*b*) along the length of the column as needed. In addition, the catalyst in both the column **40** and the side reactor **94** may convert ethanol into ethyl acetate, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **40** and the side reactor **94**, **97** may be the same or different. Suitable catalysts for converting ethanol into ethyl acetate may be selected based on the expected operating conditions, which may vary between the column **40** and the side reactor **94**, **97**.

[0054] Schematics for a side reactor reactive distillation with two feeds and using two distinct catalyst zones are shown in FIG. **8**. A single side reactor is shown for each catalyst zone in the reactive distillation column **70**, however, multiple side reactors along the length of the reactive distillation column **70** can be used for each catalyst zone. FIG. **8** (*a*) shows a configuration where the top zone feed **99** to the side reactor **100** is bottom up and vapor phase. The bottom zone feed **102** to another side reactor **103** is also bottom up and vapor phase. The outlet from side reactor **100** is stream **101** which is sent back to the distillation column at any location in the column above the location of feed **99**. The outlet from side reactor **103** is stream **104** which is sent back to the distillation column at any location in the column above the location of feed **102**. FIG. **8** (*b*) shows a configuration where the top zone feed **105** to the side reactor **106** is top down and liquid phase. The bottom zone feed **108** to another side reactor **109** is also top down and liquid phase. The outlet from side reactor **106** is stream **107** which is sent back to the distillation column at any location in the column below the location of feed **105**. The outlet from side reactor **109** is stream **110** which is sent back to the distillation column at any location in the column below the location of feed **108**. Examples of suitable catalysts for side reactors **100** and **106** may include may include any of the dehydrogenation and dimerization catalysts described in more detail herein. Examples of hydrogenation catalysts for side reactors **103** and **109** include any of the hydrogenation catalysts described in more detail herein.

[0055] While illustrated as a bottom up vapor phase design and a top down liquid phase design in FIGS. **8**(*a*) and **8**(*b*), the side reactors **100**, **103**, **106**, **109** may also operate bottom up using a liquid phase draw from the column **70** and top down using a vapor phase draw from the column **70** with the appropriate equipment such as pumps, compressors, valves, piping, etc. In an embodiment, the side reactors **100**, **103**, **106**, **109** may be implemented as a single reactor vessel, or as a plurality of reactor vessels arranged in series and/or parallel. In an embodiment, a plurality of side reactors may be implemented as shown in FIGS. **8**(*a*) and **8**(*b*) along the length of the column as needed. In addition, the respective catalysts in both the column **70** and the side reactors **100**, **106** may convert ethanol into ethyl acetate, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **40** and the side reactors **100**, **106** may be the same or different. Suitable catalysts for converting ethanol into ethyl acetate may be selected based on the expected operating conditions, which may vary between the column **40** and the side reactors **100**, **106**. Similarly, the respective catalysts in both the column **70** and the side reactors **103**, **109** may comprise hydrogenation catalysts, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **70** and the side reactors **103**, **109** may be the same or different. Suitable hydrogenation catalysts

may be selected based on the expected operating conditions, which may vary between the column **70** and the side reactors **100**, **106**.

[0056] As schematically illustrated in FIG. **9**, an ethyl acetate production process may comprise a products separation section for use in separating the product stream and allowing at a least a portion of any unreacted ethanol to be recycled to the inlet of the process. The products separation section may be configured to provide at least one product stream comprising ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight. At least one additional stream may be produced comprising the remaining components of the product stream from the reactive distillation column. In an embodiment, a plurality of streams are produced in the separation section comprising a stream predominantly comprising ethyl acetate, a stream comprising hydrogen, a stream comprising ethanol, and/or a heavies stream comprising one or more reaction products with boiling points above the boiling point of ethyl acetate. In an embodiment, the stream comprising ethanol may be recycled to the reactive distillation column. In an embodiment, at least a portion of the stream comprising hydrogen may be recycled to the reactive distillation column to provide at least a portion of the hydrogen feed.

[0057] As schematically illustrated in FIG. **9**, a system **200** for producing ethyl acetate may comprise a feed stream **202** comprising ethanol that may be combined with a recycle stream **220** comprising ethanol to form the inlet stream **204** to the reactive distillation system **206**. The system **200** may be useful for embodiments in which there is an incomplete conversion of ethanol in the reactive distillation system **208**. While illustrated as being combined prior to introduction to the reactive distillation system **206**, the feed stream **202** and the recycle stream **220** may be fed individually to the reactive distillation system **206**. In an embodiment, the reactive distillation system **206** may comprise any of the reactive distillation systems described with respect to FIG. **3-8** herein. The reactive distillation system may produce an overhead product stream **208** and a bottoms product stream **210**. The overhead product stream **208** may comprise hydrogen and may generally correspond to any of the streams **19**, **59**, and/or **88** as illustrated in FIGS. **3-8**. Similarly, the bottoms product stream **210** may comprise ethyl acetate and at least a portion of any unreacted ethanol and/or additional reaction products, and the bottoms product stream **210** may generally correspond to any of the streams **22**, **36**, **58**, and/or **92** as illustrated in FIGS. **3-8**.

[0058] A products separation section **212** may receive the bottoms product stream **210** from the reactive distillation system **206**, and, in some embodiments, the overhead product stream **208**. The products separation section **212** may comprise any number or type of separation units, which may employ pressure- or temperature-swing distillation, pressure- or temperature-swing adsorption, membrane-based separation, cryogenic distillation, and/or any other suitable separation technology, all of which may be used to generate a desired product distribution. The products separation section **212** may generally produce an ethyl acetate product stream **216**. The ethyl acetate product stream **216** may comprise ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%,

or greater than about 99.5% ethyl acetate by weight. In addition to the ethyl acetate product stream 216, one or more additional streams may be produced by the products separation section 212. In an embodiment, a lights product stream 214 may be produced. The lights product stream 214 may comprise hydrogen and minor amounts of ethanol and/or other light components. In an embodiment, a heavies product stream 218 may comprise one or more reaction products (e.g., butanol, one or more aldehydes and/or ketones, etc.). In an embodiment, a recycle stream 220 may be produced. The recycle stream may comprise ethanol for use as a feed for the reactive distillation system 206. In some embodiments, the ethanol stream may not be recycled to the reactive distillation system, but rather may exit the system 200 as a separate product stream. Each of the potential product streams 214, 216, 218, and/or 220 may exit the system as separate product stream and/or exit the system 200 for use as fuel and/or as a feed to additional downstream processes. While illustrated as separate streams 214, 216, 218, and/or 220, one or more of these streams may exit the system 220 as a combined product stream.

[0059] In an embodiment illustrated in FIG. 10, a product separation system may comprise a plurality of separation units coupled to the reactive distillation system 113. In this embodiment, the reactive distillation system 113 may be the same or similar to the reactive distillation system 206 described above with respect to FIG. 9. A feed stream 111 comprising ethanol enters the reaction distillation system 113 along with a recycle stream 127. A product stream may be produced from the reactive distillation system 113 and cooled in heat exchanger 114. Stream 112 contains light boiling components such as H$_2$ and may pass out of the reactive distillation system 113. Heat exchanger 114 may comprise any of the heat exchanger types described herein. The product stream passing out of the heat exchanger 114 may pass to separator 117. The separator 117 may comprise any of the types of separators described herein, and in an embodiment, may comprise a phase separator of any of the types described herein. The separator 117 may produce a vapor stream 115 and a liquid stream 116. Vapor stream 115 predominantly comprises hydrogen, and the liquid stream 116 comprises higher boiling components. The separator 117 may operate at a pressure ranging from about 1 atm to about 80 atm.

[0060] The liquid stream 116 passes to separator 120. Separator 120 may comprise any of the types of separators described herein, and, in an embodiment, comprises a distillation column. The separator 120 may generally operate at a pressure of between about 1 atm to about 30 atm, and in an embodiment, may operate at a pressure of less or equal to about 5 atm. In an embodiment, separator 120 operates at a pressure below the pressure of separator 122 as described below. The temperature profile in the column may be dictated by the mixture boiling point along the height of the column. The separator 120 may separate the liquid stream 116 into an overhead stream and a bottoms stream 119. The overhead stream may pass through a heat exchanger and separator to produce a vapor overhead stream 121 and a liquid overhead stream 118. The vapor overhead stream 121 may comprise hydrogen and ethanol. The vapor overhead stream 121 can be used as fuel within the system, and/or the overhead stream 121 can be recycled within the system for use as a feed to the reactive distillation system 113. The liquid overhead stream 118 may predominantly comprise ethanol and ethyl acetate. The bottoms stream 119 may predominantly comprise etha-

nol in addition to minor amounts of ethyl acetate, butanol, and/or additional reaction products.

[0061] Bottoms stream 119 may pass to a separator 125. Separator 125 may comprise any of the separators described herein, and, in an embodiment, separator 125 comprises a distillation column. Separator 125 may separate the bottoms stream 119 into an overhead stream 127 comprising ethanol and a bottoms stream 126 comprising the higher boiling components including butanol. Overhead stream 127 may be recycled to the reactive distillation system 113 for use a feed to the ethyl acetate production system. The bottoms stream 126 may exit the system for use as fuel, as a final product, and/or as a feed to one or more suitable downstream processes.

[0062] The liquid overhead stream 118 from separator 120 may pass to separator 122. Separator 122 may comprise any of the separators described herein, and, in an embodiment, comprises a distillation column. Separator 122 may operate at a higher pressure than separator 120. In an embodiment, separator 122 may operate a pressure of greater than about 160%, greater than about 200%, greater than about 250%, greater than about 300%, greater than about 400%, greater than about 500%, greater than about 600%, or greater than about 700% of the pressure of separator 120. In an embodiment, separator 122 may operate between about 8 atm and 80 atm, including between about 8 atm and about 20 atm, between about 15 atm and about 40 atm, between about 35 atm and about 60 atm, or between about 50 atm and about 80 atm. The increased operating pressure of separator 122 relative to separator 120 may provide for an improved separation of the components in the liquid overhead stream 118. Separator 122 may separate the liquid overhead stream 118 into an overhead stream 123 and a bottoms stream 124. Overhead stream 123 may comprise ethanol, ethyl acetate, and/or acetaldehyde in addition to other reaction products. Overhead stream 123 may pass back to separator 120 for further separation of the components. The bottoms stream 124 may comprise ethyl acetate as a product stream. In an embodiment, the bottoms stream 124 may comprise greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0063] The product separation system illustrated in FIG. 10 produces an ethyl acetate product stream 124, a first lights product stream 112, a second lights product stream 115, a third lights product stream 121, a heavies product stream 126, and a recycle stream 127 comprising ethanol. Some portion of the lights streams 112, 115, 121 may be recycled back to the reactive distillation system 113 for use as a hydrogen and/or ethanol feed. While illustrated as a separate feed to the reactive distillation system, the recycle stream 127 may be combined with the feed stream 111 comprising ethanol prior to the combined stream entering the reactive distillation system 113.

[0064] In an embodiment illustrated in FIG. 11, another product separation system may comprise a plurality of separation units coupled to a reactive distillation system 129. In this embodiment, the reactive distillation system 129 may be the same or similar to the reactive distillation system 206 described above with respect to FIG. 9. A feed stream 128 comprising ethanol enters the reaction distillation system 129 along with a recycle stream 141. Stream 140 contains light boiling components such as H$_2$ and may pass out of the reactive distillation system 129. A product stream may be

separated from the reactive distillation system **129** and cooled in heat exchanger **130**. Heat exchanger **114** may comprise any of the heat exchanger types described herein. The product stream passing out of the heat exchanger **130** may pass to separator **133**. The separator **133** may comprise any of the types of separators described herein, and in an embodiment, may comprise a phase separator of any of the types described herein. The separator **133** may separate the product stream into a vapor stream **131** and a liquid stream **132**. Vapor stream **131** may predominantly comprise hydrogen, and the liquid stream **132** may comprise higher boiling components. The separator **133** may operate at a pressure ranging from about 1 atm to about 80 atm.

[0065]   The liquid stream **132** passes to separator **134**. Separator **134** may comprise any of the types of separators described herein, and, in an embodiment, comprises a distillation column. The separator **134** may generally operate at a pressure of between about 1 atm to about 80 atm, and the temperature profile in the column may be dictated by the mixture boiling point along the height of the column. The separator **134** may separate the liquid stream **132** into an overhead stream and a bottoms stream **119**. The overhead stream may pass through a heat exchanger and separator to produce a vapor overhead stream **135** and a liquid overhead stream **141**. The vapor overhead stream **135** may comprise hydrogen and ethanol. The vapor overhead stream **135** can be used as fuel within the system, and/or the overhead stream **135** can be recycled within the system for use as a feed to the reactive distillation system **129**. The liquid overhead stream **141** may predominantly comprise ethanol, and may be recycled to the reactive distillation system **129** for use a feed to the ethyl acetate production system. The bottoms stream **136** may comprises ethyl acetate, butanol, and/or additional reaction products.

[0066]   The bottoms stream **136** from separator **134** may pass to separator **137**. Separator **137** may comprise any of the separators described herein, and, in an embodiment, comprises a distillation column. In an embodiment, separator **134** may operate between about 1 atm and 80 atm, and may have a similar or different pressure than separator **134**. Separator **137** may separate the bottoms stream **136** into an overhead stream **138** and a bottoms stream **139**. Bottoms stream **139** may comprise butanol and higher boiling components in addition to other reaction products. The bottoms stream **139** may exit the system for use as fuel, as a final product, and/or as a feed to one or more suitable downstream processes. The overhead stream **138** may comprise ethyl acetate as a product stream. In an embodiment, the overhead stream **138** may comprise greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0067]   The product separation system illustrated in FIG. **11** produces an ethyl acetate product stream **138**, a first lights product stream **140**, a second lights product stream **131**, a third lights product stream **135**, a heavies product stream **139**, and a recycle stream **141** comprising ethanol. Some portion of the lights streams **131**, **135** may be recycled back to the reactive distillation system **129** for use as a hydrogen and/or ethanol feed. While illustrated as a separate feed to the reactive distillation system, the recycle stream **141** may be combined with the feed stream **128** comprising ethanol prior to the combined stream entering the reactive distillation system **129**. The embodiment illustrated in FIG. **11** may allow both

separator **134** and **137** to operate at similar pressures, which can range from about 1 atm to about 80 atm, from about 5 atm to about 75 atm, from about 10 atm to about 70 atm, or from about 15 atm to about 60 atm.

Dehydrogenation and Dimerization Catalysts

[0068]   Suitable dehydrogenation and dimerization catalysts are capable of converting at least a portion of the alcohol (e.g., ethanol) in a feed stream to a higher valued product such as ethyl acetate. Any catalyst capable of carrying out a dehydrogenation and dimerization reaction may be used alone or in combination with additional catalytic materials in the reactors. In an embodiment, suitable dehydrogenation and dimerization catalysts can generally comprise metals and/or oxides of copper, barium, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, zirconium, gold, thallium, magnesium, manganese, aluminum, chromium, nickel, iron, molybdenum, sodium, strontium, tin, and mixtures thereof. In many cases, the catalyst material will be provided on a support material. The catalyst can be treated with a carbonate (e.g., sodium carbonate), reduced with hydrogen, and/or other suitable treatments prior to use.

[0069]   In certain embodiments, the dehydrogenation and dimerization catalyst may include a catalyst support. The catalyst support stabilizes and supports the catalyst. The type of catalyst support used depends on the chosen catalyst and the reaction conditions. Suitable supports may include, but are not limited to, carbon, silica, silica-alumina, alumina, zirconia, titania, ceria, vanadia, nitride, boron nitride, heteropolyacids, hydroxyapatite, zinc oxide, chromia, zeolites, carbon nanotubes, carbon fullerenes, and any combination thereof.

[0070]   The dehydrogenation and dimerization catalyst can be employed in any of the conventional types or structures known to the art. It may be employed in the form of extrudates, pills, pellets, granules, broken fragments, or various special shapes. In an embodiment, consideration of the use of the catalyst in the reactive distillation system and/or as a mass transfer surface within the distillation column may be taken into account when determining a suitable shape. For example, the catalyst may have a shape similar to structured packing material or suitable for insertion in a structured packing. When the hydrogenation catalyst is used with one or more side reactors, the catalyst may be disposed within a reaction zone, and the feed may be passed therethrough in the liquid, vapor, or mixed phase, and in either upward or downward, or inward or outward flow.

[0071]   The dehydrogenation and dimerization catalyst may typically have a range of metal loadings. In an embodiment, the catalyst may have a copper oxide weight loading (i.e., weight percentage) of between about 0.5% and about 80%, between about 10% and about 70%, between about 20% and about 65%, between about 30% and about 60%, or about 40% and about 50%. In an embodiment, the catalyst may have a zinc oxide weight loading of between about 20% and about 60%, between about 30% and about 50%, or between about 40% and about 50%. In an embodiment, the catalyst may have a chromium oxide weight loading of between about 20% and about 60%, or between about 30% and about 50%.

[0072]   In an embodiment, the catalyst may comprise CuO/ZnO/Al$_2$O$_3$. In this embodiment, the catalyst may have a copper oxide weight loading of between about 0.5% and about 80%, between about 10% and about 70%, between about 20% and about 65%, between about 30% and about

60%, or about 40% and about 50%, and the zinc oxide and alumina may comprise the balance of the weight. In an embodiment, the catalyst may comprise $CuO/ZnO/ZrO_2/Al_2O_3$, and the catalyst may have a copper oxide weight loading of between about 40% to about 80%, with the remainder of the components forming the balance of the catalyst weight. In an embodiment, the catalyst may comprise $CuO/ZnO/ZrO_2/Cr_2O_3$, and the catalyst may have a copper oxide weight loading of between about 20% to about 70% and a chromium oxide weight loading between about 30% and about 50%, with the remainder of the components forming the balance of the catalyst weight. In an embodiment, the catalyst comprises an alkaline earth metal and/or alkaline earth metal oxide and copper and/or copper oxide on a support. In this embodiment, the support may comprise silica.

[0073] Any of the materials useful as hydrogenation and dimerization catalysts, may be synthesized using a variety of methods. In an embodiment, the dehydrogenation and dimerization catalyst may be prepared via wet impregnation of a catalyst support. Using the wet-impregnation technique, a metal nitrate dissolved in a suitable solvent may be used to prepare the catalyst, however any soluble compound would be suitable. A sufficient amount of solvent should be used to fully dissolve the metal nitrate and appropriately wet the support. In one embodiment, copper nitrate and ethanol and/or water may be mixed in an amount sufficient such that the copper nitrate dissolves. Additional metal nitrates may also be added to provide a catalyst with additional components. The solute may then be combined with a suitable support material of appropriate particle size. The mixture may then be refluxed at a temperature of approximately 100° C. for approximately several hours (e.g., three to five hours) and then allowed to dry at a temperature of about 110° C. The dried material may then be heated to 200° C. to remove the NO_x component, and then the materials may be calcined at about 450° C. to about 550° C. at a heating rate of about one to ten ° C./min. The amount of metal nitrate used in the wet-impregnation technique can be adjusted to achieve a desired final metal weight loading of the catalyst support.

[0074] When multiple components are used to provide a catalyst disposed on a support, each component can be added via the wet-impregnation technique. The appropriate salts can be dissolved and impregnated on a support in a co-impregnation process or a sequential process. In a co-impregnation process, measured amount of the appropriate plurality of metal salts may be dissolved in a suitable solvent and used to wet the desired catalyst support. The impregnated support can then be dried and calcined to provide a final catalyst with a desired weight loading. In the sequential impregnation process, one or more measured amounts of salts may be dissolved in a suitable solvent and used to wet the desired catalyst support. The impregnated support can then be dried and calcined. The resulting material can then be wetted with one or more additional salts that are dissolved in a suitable solvent. The resulting material can then be dried and calcined again. This process may be repeated to provide a final catalyst material with a desired loading of each component. In an embodiment, a single metal may be added with each cycle. The order in which the metals are added in the sequential process can be varied. Various metal weight loadings may be achieved through the wet-impregnation technique. In an embodiment, the wet-impregnation technique may be used to provide a catalyst having a copper weight loading ranging

from about 0.5% and about 50%, with one or more additional components having a weight loading between about 0.1% and about 10%.

[0075] The dehydrogenation and dimerization catalysts may also be prepared via a co-precipitation technique. In this technique, a measured amount of one or more appropriate metal nitrates are dissolved in de-ionized water. The total metal concentration can vary and may generally be between about 1 M and about 3 M. The metal-nitrate solution may then be precipitated through the drop-wise addition of the solution to a stirred, equal volume of a sodium hydroxide solution at room temperature. The sodium hydroxide solution may generally have a concentration of about 4M, though other concentrations may also be used as would be known to one of skill in the art with the benefit of this disclosure. After addition of the metal nitrate solution, the resulting suspension can be filtered and washed with de-ionized water. The filtered solids can be dried overnight, for example, at a temperature of about 110° C. The resulting mixed metal oxide can then be processed to a desired particle size. For example, the resulting mixed metal oxide can be pressed to a desired form, ground, and then sieved to recover a catalyst material with a particle size in a desired range. Catalysts prepared using the co-precipitation technique may have higher metal loadings than the catalysts prepared using the wet-impregnation technique.

[0076] The catalyst prepare via the co-precipitation technique may be used in the prepared form and/or a catalyst binder can be added to impart additional mechanical strength. In an embodiment, the prepared catalyst may be ground to a fine powder and then stirred into a colloidal suspension (e.g., a colloidal suspension of silica and/or alumina) in an aqueous solution. The resulting suspension may be stirred while being heated and allowed to evaporate to dryness. The heating may take place at about 80° C. to about 130° C. The resulting solid can then be processed to a desired particle size. For example, the resulting solid can be pressed to a desired form, ground, and then sieved to recover a catalyst material with a particle size in a desired range. Alternatively, the colloidal suspension may be added to the 4M sodium hydroxide precipitation solution prior to addition of the metal nitrate solution in the co-precipitation technique. Various metal weight loadings may be achieved through the co-precipitation technique. In an embodiment, the co-precipitation technique may be used to provide a catalyst having a copper weight loading ranging from about 2% and about 80%, with one or more additional components having a weight loading between about 2% and about 40%.

[0077] The resulting catalyst from either the wet-impregnation technique and/or the co-precipitation technique may be further treated prior to use in the reactive distillation system disclosed herein. In an embodiment, the catalyst may be treated with a sodium carbonate solution for a period of time to improve the selectivity of the catalyst. In this process, the catalyst may be soaked in an aqueous solution of sodium carbonate for a period of time ranging from about 1 hour to about 48 hours, or alternatively about 2 hours to about 24 hours. In an embodiment, the sodium carbonate solution may have a concentration of about 0.2 M. The catalyst may then be filtered and allowed to dry at about room temperature. In an embodiment, the sodium carbonate may comprise from about 0.2 to about 3.0 weight percent of the catalyst after being contacted with the sodium carbonate solution.

[0078] In another treatment process, the catalyst may be reduced with hydrogen prior to use. In this embodiment, the

catalyst may be heated and contacted with hydrogen, which may be flowing over the catalyst, for a period of time sufficient to reduce the catalyst to a desired degree. In an embodiment, the catalyst may be contacted with hydrogen at a temperature of about 190° C. to about 240° C. The hydrogen treatment may be conducted in combination with the sodium carbonate treatment, and may be performed prior to and/or after the sodium carbonate treatment.

[0079] Without intending to be limited by theory, it is believed that the production of hydrogen during the dehydrogenation and dimerization reaction within the process may result in contact between the dehydrogenation and dimerization catalyst and a hydrogen stream sufficient to at least partially reduce the catalyst. Thus, the process described herein may have the potential for the in-situ reduction of the catalyst during use. This may result in an initial break-in period in which the catalyst conversion and selectivity may change before reaching a steady state conversion and selectivity. This in-situ reduction may be taken into account when considering the degree to which a catalyst should be pre-reduced with hydrogen.

[0080] In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a relatively high conversion and/or selectivity of ethanol to ethyl acetate. As used herein, the "conversion" of ethanol to ethyl acetate refers to the amount of ethanol consumed in the conversion reaction as represented by the formula:

$$X_{ethanol} = 100 \left(\frac{F_{EtOH,0} - F_{EtOH}}{F_{EtOH,0}} \right)$$

[0081] where F_{EtOH} represents the molar flow rates of ethanol in the reactor effluent (e.g., the product stream comprising the ethyl acetate), and $F_{EtOH,0}$ represents the molar flow rate of ethanol into the reactor inlet. As used herein, the "selectivity" of the conversion refers to the amount of ethanol that is consumed in the conversion reaction that is converted to ethyl acetate as represented by the formula:

$$S = 100 \left(\frac{2F_{EtOAC} + F_{AcH}}{F_{EtOH,0} - F_{EtOH}} \right)$$

where F_{EtOAc} and F_{AcH} represent the molar flow rate of ethyl acetate and acetaldehyde in the reactor effluent (e.g., the product stream comprising the ethyl acetate), respectively, and the remaining terms are the same as described above with respect to the conversion of ethanol. In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a conversion of ethanol in the reactive distillation process described herein of at least about 10%, at least about 20%, at least about 30%, at least about 40%, or at least about 50%. In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a selectivity of ethyl acetate in the reactive distillation process described herein of at least about 60%, at least about 70%, at least about 80%, at least about 85%, at least about 90%, or at least about 95%.

Hydrogenation Catalysts

[0082] The hydrogenation catalyst generally can include a Group VIII metal and/or a Group VI metal. Examples of such

a catalyst can include, but is not limited to, Cu, Re, Ni, Fe, Co, Ru, Pd, Rh, Pt, Os, Ir, and alloys or any combination thereof, either alone or with promoters such as W, Mo, Au, Ag, Cr, Zn, Mn, Sn, B, P, Bi, and alloys or any combination thereof. Other effective hydrogenation catalyst materials include either supported nickel or ruthenium modified with rhenium. In an embodiment, the hydrogenation catalyst also includes any one of the supports described below, depending on the desired functionality of the catalyst. The hydrogenation catalysts may be prepared by methods known to those of ordinary skill in the art.

[0083] In an embodiment, the hydrogenation catalyst includes a supported Group VIII metal catalyst and a metal sponge material (e.g., a sponge nickel catalyst). Raney nickel provides an example of an activated sponge nickel catalyst suitable for use in this invention. In an embodiment, the hydrogenation reaction in the invention is performed using a catalyst comprising a nickel-rhenium catalyst or a tungsten-modified nickel catalyst. One example of a suitable catalyst for the hydrogenation reaction of the invention is a carbon-supported nickel-rhenium catalyst.

[0084] In an embodiment, a suitable Raney nickel catalyst may be prepared by treating an alloy of approximately equal amounts by weight of nickel and aluminum with an aqueous alkali solution, e.g., containing about 25 weight % of sodium hydroxide. The aluminum is selectively dissolved by the aqueous alkali solution resulting in a sponge shaped material comprising mostly nickel with minor amounts of aluminum. The initial alloy includes promoter metals (e.g., molybdenum or chromium) in the amount such that 1 to 2 weight % remains in the formed sponge nickel catalyst. In another embodiment, the hydrogenation catalyst is prepared using a solution of ruthenium(III) nitrosylnitrate, ruthenium (III) chloride in water to impregnate a suitable support material. The solution is then dried to form a solid having a water content of less than 1% by weight. The solid is then reduced at atmospheric pressure in a hydrogen stream at 300° C. (uncalcined) or 400° C. (calcined) in a rotary ball furnace for 4 hours. After cooling and rendering the catalyst inert with nitrogen, 5% by volume of oxygen in nitrogen is passed over the catalyst for 2 hours.

[0085] In certain embodiments, the hydrogenation catalyst may include a catalyst support, which may be the same or different than a catalyst support used with the dehydrogenation and dimerization catalyst. In an embodiment, any of the catalyst supports discussed herein may be used to support a hydrogenation catalyst. The hydrogenation catalyst can be employed in any of the conventional types or structures known to the art. In an embodiment, any of the catalyst shapes and/or types discussed herein with respect to the dehydrogenation and dimerization catalyst may be used with the hydrogenation catalyst.

Production of Methyl Formate from Methanol

[0086] In addition to use of the systems and methods described herein for converting ethanol to ethyl acetate, those systems can also be used in processes with methanol as a feed instead of ethanol, with the production of methyl formate and H_2 as products according to the following formula:

$$2CH_3OH \leftarrow \rightarrow HCOOCH_3 + 2H_2$$
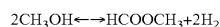
[0087] Such a system and method can utilize selections from the catalysts indicated for use with the ethanol feed. Products can be withdrawn in similar manner as described for the ethanol to ethyl acetate process.

EXAMPLES

[0088] The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

Example 1

Production of Ethyl Acetate from Ethanol

[0089] A 10 cm diameter distillation column is used, which has been rendered adiabatic by heating casings with temperatures controlled in such a way that the temperature gradient in the column is reproduced. Over a height of 3.5 m, the column is comprised of rectification zone with 8 stages each with a catalytic cell consisting of a cylindrical container with a flat bottom. The bottom of the container is equipped with a grid for retaining the catalyst and also can act as a gas and liquid distributor. The stripping zone is comprised of 12 stages, also with catalyst-containing cells. The rectification section is considered to be above the feed stage and the stripping section is considered to be below the feed stage. Each catalyst cell contains $CuO/ZnO/Al_2O_3$. 200 proof ethanol is fed to the 13th stage of the column, starting from the bottom.

[0090] The column is regulated by establishing a reflux ratio which is equal to 0.8, reboil ratio which is equal to 4 and controlling the base temperature to 211° C. and the absolute pressure to 20 bar. The reflux stream is mostly ethanol with small amounts of acetaldehyde. Under stabilized conditions, a bottoms stream and a distillate stream are collected with respective throughputs of about 170 g/h and 4 g/h. The bottoms product gives ethyl acetate purity of 98.5% with small amounts of n-butyraldehyde and butan-2-one.

Example 2

Selective Hydrogenation of n-Butyraldehyde and Butan-2-One

[0091] Selective hydrogenation of n-butyraldehyde and butan-2-one in the presence of ethyl acetate was conducted over a hydrogenation catalyst. The reactor was filled with 20 g of 0.1 wt % Pd on silica catalyst. Before the selective hydrogenation reaction, the catalyst was reduced at a temperature of 250° C. for 30 minutes. The catalyst reduction was conducted at atmospheric pressure by delivering hydrogen using a mass flow controller. At the end of this procedure, the catalyst was fully reduced.

[0092] The bottoms product from the reactive distillation column, whose composition is given in Table 2, was introduced to a heater at a rate of 30 g/h and mixed with hydrogen prior to admission to the selective hydrogenation reactor. The reaction product was cooled using a jacketed condenser and the liquid condensate was analyzed by gas chromatography. The results are summarized in Table 2, showing n-butyraldehyde and butan-2-one reduced to trace levels.

TABLE 2

Hydrogenation Feed and Products		
Temperature	250° C.	
Pressure	20 atm	
	Weight %	
Component	Feed	Products
Ethyl acetate	93	92.9
Ethanol	2	2.1

TABLE 2-continued

Hydrogenation Feed and Products		
Iso-propanol	3	3
n-butyraldehyde	1.5	trace
butan-2-one	0.5	trace
2-butanol	0	0.48
n-butanol	0	1.52

Example 3

Wet-Impregnation Catalyst Preparation

[0093] Various catalysts including CuO/SiO_2, CuO/SiO_2—Al_2O_3, CuO/ZnO, CuO/ZrO_2, CuO/SiO_2—ZrO_2, $CuO/ZnO/Al_2O_3$, $CuO/Cr_2O_3/BaO$, CuO/Cr_2O_3 and CuO/Al_2O_3 were prepared via impregnation of the corresponding oxide catalyst support. The preparation involved dissolving 4 grams (g) of $Cu(NO_3)_2.2.5H_2O$ in 30 mL of de-ionized water, which was then added to 30 g of the appropriate oxide support and stirred until well mixed. The impregnated support was then dried in air at 110° C., followed by calcination in air at 450° C. The amount of $Cu(NO_3)_2.2.5H_2O$ was adjusted to achieve a desired final Cu weight loading. Enough water was used to wet the entire oxide support. Copper loadings between 0.5% and 20% by weight were achieved.

Example 4

Co-Impregnation and Sequential Impregnation Catalyst Preparation

[0094] Various catalysts including $CuO/ZnO/SiO_2$, $CuO/ZrO_2/SiO_2$, $CuO/MgO/SiO_2$, $CuO/CaO/SiO_2$, $CuO/SrO/SiO_2$, $CuO/BaO/SiO_2$, and $CuO/Na_2O/SiO_2$ were prepared via co-impregnation and sequential impregnation of a silica catalyst support. For the co-impregnation, measured amounts of $Cu(NO_3)_2.2.5H_2O$ and $M(NO_3)_8.YH_2O$ (M=Zn, Zr, Mg, Ca, Sr, Ca, or Na; X=1, 2, 4; Y=2-6) were dissolved in de-ionized water. The solution was added to the silica support and stirred until well mixed. The impregnated silica was dried in air at 110° C., followed by calcination in air at 450° C.

[0095] For the sequential impregnation, a measured amount of $M(NO_3)_x.YH_2O$ (M=Mg, Ca, Sr, Ca, or Na; X=1 or 2; Y=2-6) was dissolved in de-ionized water. The solution was then added to the silica support and mixed well. The silica was dried at 110° C. and then calcined at 450° C. in air. This procedure was then repeated using $Cu(NO_3)_2.2.5H_2O$ in place of the first metal nitrate. Copper loadings between 0.5% and 20% by weight and an addition metal loading between 0.1% and 10% by weight were achieved.

Example 5

Co-Precipitation Catalyst Preparation

[0096] Mixed-metal oxide catalysts were prepared via co-precipitation from nitrate solutions. In the co-precipitation synthesis, a measured amount of the appropriate metal nitrate (Cu, Zn, Zr, Al, Cr, Fe, Ni, and/or Ba) were dissolved in de-ionized water (total metal concentration ranges from 1-3 M). The metal-nitrate solution was then precipitated by drop-wise addition to a stirred, equal volume of 4 M aqueous NaOH at room temperature. After addition of all the metal nitrate solution, the suspension was stirred for an additional

hour to ensure complete precipitation of the metals. The precipitated solid was then filtered and washed with excess deionized water. The solids were then dried overnight at 110° C. The resulting mixed metal oxide was then pressed, ground, and sieved to recover a catalyst with particle sizes between 450 and 850 μm. Catalysts prepared in this manner had copper oxide loadings between 40% and 80% by weight. The loadings of other metal oxides ranged from 2% to 40% by weight. In particular, $CuO/ZnO/ZrO_2/Al_2O_3$, and $CuO/ZnO/ZrO_2/Cr_2O_3$ catalysts were found to be especially active and selective for the dehydrogenative dimerization of ethanol, as illustrated below in Example 6.

[0097] In addition to the catalysts prepare above, various catalysts were prepared via co-precipitation and then a binder was incorporated. The catalyst binder was added to the mixed-metal oxide prepared as described above by first grinding the mixed-metal oxide to a fine powder and then stirring it into a colloidal suspension of silica or alumina in water. The resulting suspension was stirred while heating at 80-130° C. to dryness. The resulting solid was then be pressed, ground, and sieved to appropriate particle sizes.

Example 6

Dehydrogenative Dimerization of Ethanol

[0098] A portion of the catalysts prepared as described in Examples 3 to 5 were treated with a Na_2CO_3 solution by soaking the catalyst in a 0.2 M aqueous solution of Na_2CO_3 for 2-24 hrs. The catalyst was then filtered and allowed to dry in air at room temperature. Another portion of the catalysts prepared as described in Examples 3 to 5 were reduced in a hydrogen environment at 175-240° C. for a period of 4-12 hours. These catalysts were then tested in ethanol dehydrogenation reactions. Conversion and selectivity for gas phase reactions were determined from use in a fixed bed reactor operating at 190-240° C. and 1-24 atm. Pure ethanol was fed to the reactor with a weight hourly space velocity (WHSV) between 0.1-1.5 hr^{-1}. Conversion and selectivity for liquid phase and mixed liquid/vapor phase reactions were determined in both a fixed bed reactor, operating at 190° C. and at pressures above 25 atm. Liquid phase reactions were also conducted in a batch reactor at 180-200° C. and 20-31 atm (the reactor pressure was maintained above the vapor pressure of ethanol at the operating temperature).

[0099] Table 3 shows the conversion and selectivity of the catalysts in a dehydrogenative dimerization reaction conducted in a fixed bed reactor. Conversion (X) and selectivity (S) were calculated from the composition of the reactor effluent as

$$X_{ethanol} = 100\left(\frac{F_{EtOH,0} - F_{EtOH}}{F_{EtOH,0}}\right)$$

$$S = 100\left(\frac{2F_{EtOAC} + F_{AcH}}{F_{EtOH,0} - F_{EtOH}}\right)$$

[0100] Where F_{EtOH}, F_{EtOAc}, and F_{AcH} represent the molar flow rates of ethanol, ethyl acetate, and acetaldehyde in the reactor effluent, respectively, and $F_{EtOH,0}$ represents the molar flow rate of ethanol into the reactor inlet. Acetaldehyde is a reaction intermediate and so was included in the selectivity calculation.

TABLE 3

Conversion and Selectivity for selected catalysts in a fixed bed reactor at 220° C. and 1 atm

Catalyst sample	As prepared/ received		Reduced in H_2	
	X	S	X	S
Pellet catalysts				
$CuO/ZnO/Al_2O_3$	18.9	92.4	35.0	89.7
$CuO/Cr_2O_3/BaO$	43.5	89.4	36.0	74.6
Impregnated catalysts				
CuO/SiO_2	19.6	96.2	22.5	80.9
CuO/SiO_2—Al_2O_3	43.0	17.0		
CuO/Al_2O_3	50.2	47.3		
CuO/ZnO	19.7	65.5		
CuO/ZrO_2	41.5	63.4		
CuO/SiO_2—ZrO_2	40.0	59.7		
$CuO/MgO/SiO_2$	37.9	70.0	32.1	65.7
$CuO/CaO/SiO_2$	33.3	73.4	29.0	42.7
$CuO/SrO/SiO_2$	25.1	77.2	31.5	69.6
$CuO/BaO/SiO_2$	31.0	73.2	33.6	73.6
$CuO/Na_2O/SiO_2$	19.4	95.9		
$CuO/ZrO_2/SiO_2$	39.1	58.7	54.0	61.6
Co-precipitation catalysts				
$CuO/ZnO/ZrO_2/Al_2O_3$	8.7	83.6	21.4	72.6
$CuO/ZnO/ZrO_2/Al_2O_3/Na_2CO_3$	26.1	40.1	39.0	86.1
$CuO/ZnO/ZrO_2/Cr_2O_3$	28.8	92.0	20.9	80.9
$CuO/ZnO/ZrO_2/Cr_2O_3/Na_2CO_3$	37.0	90.2	35.9	87.5
$CuO/ZnO/ZrO_2/Fe_2O_3$	34.1	92.1	17.0	94.2
$CuO/ZnO/ZrO_2/Fe_2O_3/Na_2CO_3$	30.7	72.6		
$CuO/ZnO/ZrO_2/Al_2O_3/Cr_2O_3$	24.5	88.4	18.5	79.4
$CuO/ZnO/ZrO_2/Al_2O_3/Cr_2O_3/Na_2CO_3$	33.2	86.3		

Example 7

Pressure Effects on the Conversion

[0101] A fixed bed reactor operated under similar conditions to those described with respect to Example 6 was used to test the reaction conversion and selectivity of a catalyst under varying reaction pressures. Table 4 shows a typical trend in the conversion and selectivity of these catalysts when operated at elevated pressures. Similar trends were seen for all catalysts tested at elevated pressures.

TABLE 4

Conversion and Selectivity for $CuO/ZnO/ZrO_2/Al_2O_3/Na_2CO_3$ (reduced at 240° C. in H_2) in a fixed bed reactor at 220° C.

Pressure (atm)	X	S
1	39.0	86.1
9.4	43.6	96.1
14.5	43.3	96.4
21.4	39.3	97.4

[0102] As seen by the results in Table 4, operation of catalysts at higher pressures increases the selectivity of the catalyst significantly. Increasing the pressure had little effect on the conversion achieved by the catalysts.

Example 8

Liquid Phase Reaction

[0103] The dehydrogenative dimerization of ethanol was also conducted in the liquid phase. Reaction temperatures

ranged from 180 to 200° C. and pressures were kept above the vapor pressure of ethanol at the reaction temperature (25-36 atm). Liquid phase reactions were conducted in both a fixed bed reactor and batch reactor. Table 5 shows the results for a CuO/ZnO/Al$_2$O$_3$ catalyst in a batch reactor operating in the liquid phase. During a typical batch reaction, the pressure initially reached the vapor pressure of ethanol and then slowly increased beyond that pressure as the reaction generated H$_2$ gas. The batch reactor results demonstrated that the dehdrogenative dimerization reaction occurs in the liquid phase.

TABLE 5

Conversion and Selectivity for CuO/ZnO/Al$_2$O$_3$ (reduced at 240° C. in H$_2$) after 2 hrs in a batch reactor.

Temperature (° C.)	X	S
180	4.4	84.1
190	6.1	81.5
200	13.0	96.1

[0104] Based on the results of Examples 3 through 8, it can be seen that a high selectivity to ethyl acetate using the dehydrogenation and dimerization catalysts described herein (e.g., CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Na$_2$CO$_3$ and/or CuO/ZnO/Al$_2$O$_3$) should enable the use of the system embodiments as illustrated in FIGS. **3**, **5** and **7** of the present disclosure. For catalysts where 2 butanone is produced above acceptable levels, the use of the system embodiments as illustrated in FIGS. **4**, **6** and **8** of the present disclosure may be used.

Example 9

Effect of Water in the Ethanol Feed

[0105] In this example, the effect of water in the ethanol feed was investigated. A 4 wt % water in ethanol solution was fed to a CuO/ZnO/Al$_2$O$_3$ catalyst in a fixed bed reactor to demonstrate the water tolerance of the catalyst. The reactor was maintained at 21.4 atm and the catalyst was heated to 200-240° C. Table 6 compares the conversion and selectivity achieved for both the 4 wt % water in ethanol and a pure ethanol feed.

TABLE 6

Conversion and selectivity for CuO/ZnO/Al$_2$O$_3$ in a fixed bed reactor operating at 21.4 atm for ethanol feeds with and without water.

Temperature (° C.)	Pure Ethanol Feed		4% Water in Ethanol Feed	
	Conversion	Selectivity	Conversion	Selectivity
200	23.2	98.1	14.2	99.2
220	37.9	97.1	29.2	98.6
240	47.9	94.4	42.6	98.0

Example 10

Process Simulation of FIG. **10**

[0106] In an example, a process simulation was performed using the reactive distillation system and product separation system shown in FIG. **10**. The simulation was performed using the Aspen Plus V7.1 (Build 23.0.2.4563) software package. The physical properties are provided in degrees

Celsius (° C.), psig, pounds per hour (lb/hr), U.S. gallons per minute (USGPM), and British thermal units per hour (Btu/hr). The material streams, their compositions, and the associated unit properties produced by the simulation are provided in Tables 7, 8, and 9 below, respectively.

TABLE 7A

Material Streams

	Feed Stream	Recycle Stream
Name	111	127
Vapor Fraction	0	0
Temperature (° C.)	50	169
Pressure (psig)	294	382
Molar Flow (lbmol/h)	502.4	877.9
Mass Flow (lb/hr)	23142	43511.5
Liquid Volume Flow (USGPM)	60.1	143.6
Heat Flow (Btu/hr)	−5.92E7	−1.01E8

TABLE 7B

Material Streams

Name	Liquid Stream 116	Bottoms Stream 119	Vapor Overhead Stream 121
Vapor Fraction	0	0	1
Temperature (° C.)	−10	88.3	74.4
Pressure (psig)	274.8	352.7	10
Molar Flow (lbmol/h)	1141	892	12.6
Mass Flow (lb/hr)	65659	44260	630.8
Liquid Volume Flow (USGPM)	148.9	120.2	—
Heat Flow (Btu/hr)	−1.65E8	−1.09E8	−1.3E6

TABLE 7C

Material Streams

Name	Overhead Stream 123	Bottoms Stream 124	Heavies Product Stream 126
Vapor Fraction	0	0	0
Temperature (° C.)	175	208	224
Pressure (psig)	279	285	338
Molar Flow (lbmol/h)	1016	236	7.4
Mass Flow (lb/hr)	54267	20756	581
Liquid Volume Flow (USGPM)	180.2	69.6	0.3
Heat Flow (Btu/hr)	−1.2E8	−4.4E7	−1.05E6

TABLE 8A

Stream Compositions

Name	Feed Stream 111	Recycle Stream 127
Comp Mole Frac (Ethanol)	1	0.87
Comp Mole Frac (Ethyl Acetate)	0	0.13
Comp Mole Frac (Hydrogen)	0	0
Comp Mole Frac (Butanol)	0	0
Comp Mole Frac (n-butyraldehyde)	0	0
Comp Mole Frac (butan-2-one)	0	0

TABLE 8B

Stream Compositions

Name	Liquid Stream 116	Bottoms Stream 119	Vapor Overhead Stream 121
Comp Mole Frac (Ethanol)	0.69	0.85	0.39
Comp Mole Frac (Ethyl Acetate)	0.29	0.13	0.32
Comp Mole Frac (Hydrogen)	0	0	0.13
Comp Mole Frac (Butanol)	0	0	0
Comp Mole Frac (n-butyraldehyde)	0	0	0
Comp Mole Frac (butan-2-one)	0	0	0

TABLE 8C

Stream Compositions

Name	Overhead Stream 123	Bottoms Stream 124	Heavies Product Stream 126
Comp Mole Frac (Ethanol)	0.61	0	0.01
Comp Mole Frac (Ethyl Acetate)	0.29	99.8	0.57
Comp Mole Frac (Hydrogen)	0	0	0
Comp Mole Frac (Butanol)	0	0.1	0.40
Comp Mole Frac (n-butyraldehyde)	0	0	0
Comp Mole Frac (butan-2-one)	0	0.1	0

TABLE 9

Unit Properties

Name	Separator 120	Separator 122	Separator 125
Pressure (psig)	10	279	338
Theoretical Stages	30	20	32
Condenser Duty (Btu/hr)	−3.3E7	−2.5E7	−2.3E7
Reboiler Duty (Btu/hr)	2.2E7	3.6E7	2.9E7

Example 11

Process Simulation of FIG. 11

[0107] As another example, a similar process simulation was performed using the reactive distillation system and product separation system shown in FIG. 11. The material streams, their compositions, and the associated unit properties produced by the simulation are provided in Tables 10, 11, and 12 below, respectively.

TABLE 10A

Material Streams

Name	Feed Stream 128	Recycle Stream 141
Vapor Fraction	0	0
Temperature (° C.)	50	168
Pressure (psig)	294	382
Molar Flow (lbmol/h)	502.4	893
Mass Flow (lb/hr)	23148	44429

TABLE 10A-continued

Material Streams

Name	Feed Stream 128	Recycle Stream 141
Liquid Volume Flow (USGPM)	60	146
Heat Flow (Btu/hr)	−5.9E7	−1E8

TABLE 10B

Material Streams

Name	Liquid Stream 132	Vapor Overhead Stream 135	Bottoms Stream 136
Vapor Fraction	0	1	0
Temperature (° C.)	−10	125	205
Pressure (psig)	275	265	270
Molar Flow (lbmol/h)	1155	1.76	250
Mass Flow (lb/hr)	66568	26.2	21894
Liquid Volume Flow (USGPM)	150.8	6	72.6
Heat Flow (Btu/hr)	−1.6E8	−48670	−4.6E7

TABLE 10C

Material Streams

Name	Overhead Stream 138	Bottoms Stream 139
Vapor Fraction	0	0
Temperature (° C.)	202	210
Pressure (psig)	250	260
Molar Flow (lbmol/h)	240	9.7
Mass Flow (lb/hr)	21101	792
Liquid Volume Flow (USGPM)	68	2.6
Heat Flow (Btu/hr)	−4.5E7	−1.5E6

TABLE 11A

Stream Compositions

Name	Feed Stream 128	Recycle Stream 141
Comp Mole Frac (Ethanol)	1.0	0.91
Comp Mole Frac (Ethyl Acetate)	0	0.09
Comp Mole Frac (Hydrogen)	0	0
Comp Mole Frac (Butanol)	0	0
Comp Mole Frac (n-butyraldehyde)	0	0
Comp Mole Frac (butan-2-one)	0	0

TABLE 11B

Stream Compositions

Name	Liquid Stream 132	Vapor Overhead Stream 135	Bottoms Stream 136
Comp Mole Frac (Ethanol)	0.70	0.23	0
Comp Mole Frac (Ethyl Acetate)	0.27	0.03	0.97
Comp Mole Frac (Hydrogen)	0	0.73	0

TABLE 11B-continued

Stream Compositions

Name	Liquid Stream 132	Vapor Overhead Stream 135	Bottoms Stream 136
Comp Mole Frac (Butanol)	0.01	0	0
Comp Mole Frac (n-butyraldehyde)	0	0	0.02
Comp Mole Frac (butan-2-one)	0	0	0

TABLE 11C

Stream Compositions

Name	Overhead Stream 138	Bottoms Stream 139
Comp Mole Frac (Ethanol)	0	0
Comp Mole Frac (Ethyl Acetate)	0.99	0.57
Comp Mole Frac (Hydrogen)	0	0
Comp Mole Frac (Butanol)	0	0.40
Comp Mole Frac (n-butyraldehyde)	0	0
Comp Mole Frac (butan-2-one)	0.01	0

TABLE 12

Unit Properties

Name	Separator 133	Separator 134	Separator 137
Pressure (psig)	274.8	264.5	250
Theoretical Stages	1	40	32
Condenser Duty (Btu/hr)	−5.6E6	−4E7	−2.2E7
Reboiler Duty (Btu/hr)	—	4.6E7	2.2E7

[0108] In the preceding discussion and in the claims, the terms "including" and "comprising" are used in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to.". At least one embodiment is disclosed and variations, combinations, and/or modifications of the embodiment(s) and/or features of the embodiment(s) made by a person having ordinary skill in the art are within the scope of the disclosure. Alternative embodiments that result from combining, integrating, and/or omitting features of the embodiment(s) are also within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, Rl, and an upper limit, Ru, is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R=Rl+k*(Ru-Rl)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, . . . , 50 percent, 51 percent, 52 percent, . . . , 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with

respect to any element of a claim means that the element is required, or alternatively, the element is not required, both alternatives being within the scope of the claim. Use of broader terms such as comprises, includes, and having should be understood to provide support for narrower terms such as consisting of, consisting essentially of, and comprised substantially of. Accordingly, the scope of protection is not limited by the description set out above but is defined by the claims that follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated as further disclosure into the specification and the claims are embodiment(s) of the present invention.

1. A reactive distillation method comprising:
introducing an feed stream to a reactive distillation column, wherein the feed stream comprises ethanol;
contacting the feed stream with a catalyst in the reactive distillation column during a distillation, wherein the feed stream reacts in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen;
removing ethyl acetate during the distillation from the reactive distillation column as a bottoms stream; and
removing hydrogen during the distillation from the reactive distillation column as an overhead stream.

2. The reactive distillation method of claim 1, further comprising:
contacting the bottoms stream with a hydrogenation catalyst and hydrogen to hydrogenate at least a portion of a contaminant in the bottoms stream; and
separating the hydrogenated portion of the contaminant from the bottoms stream.

3. The reactive distillation method of claim 2, wherein the hydrogenation catalyst comprises a Group VIII metal, a Group VI metal, or any combination thereof.

4. The reactive distillation method of claim 1, wherein the catalyst comprises at least one catalytic component selected from the group consisting of: copper, copper oxide, barium, barium oxide, ruthenium, ruthenium oxide, rhodium, rhodium oxide, platinum, platinum oxide, palladium, palladium oxide, rhenium, rhenium oxide, silver, silver oxide, cadmium, cadmium oxide, zinc, zinc oxide, zirconium, zirconium oxide, gold, gold oxide, thallium, thallium oxide, magnesium, magnesium oxide, manganese, manganese oxide, aluminum, aluminum oxide, chromium, chromium oxide, nickel, nickel oxide, iron, iron oxide, molybdenum, molybdenum oxide, sodium, sodium oxide, sodium carbonate, strontium, strontium oxide, tin, tin oxide, and any mixture thereof.

5. The reactive distillation method of claim 1, wherein the catalyst comprises a support, wherein the support comprises at least one support material selected from the group consisting of: carbon, silica, silica-alumina, alumina, zirconia, titania, ceria, vanadia, nitride, boron nitride, heteropolyacids, hydroxyapatite, zinc oxide, chromia, a zeolite, a carbon nanotube, carbon fullerene, and any combination thereof.

6. The reactive distillation method of claim 1, wherein the catalyst comprises copper, and wherein the catalyst has a copper weight loading of between about 0.5% and about 80% of the catalyst.

7. The reactive distillation method of claim 1, wherein the catalyst comprises copper oxide and zinc oxide disposed on a support.

8. The reactive distillation method of claim **1**, wherein the catalyst comprises copper oxide, zinc oxide, zirconium oxide, and alumina.

9. The reactive distillation method of claim **1**, wherein the catalyst comprises copper oxide, zinc oxide, zirconium oxide, and chromium oxide.

10. The reactive distillation method of claim **1**, wherein the catalyst comprises:

an alkaline earth metal or alkaline earth metal oxide,

copper or copper oxide, and

a support.

11. The reactive distillation method of claim **1**, wherein the catalyst comprises sodium carbonate.

12. The reactive distillation method of claim **1**, wherein the catalyst is at least partially reduced in the presence of hydrogen.

13. The reactive distillation method of claim **1**, wherein a conversion of ethanol in the feed stream is at least about 10%.

14. The reactive distillation method of claim **13**, wherein a selectivity of the conversion of ethanol to ethyl acetate is at least about 60%.

15. The reactive distillation method of claim **1**, further comprising:

removing a side stream from the reactive distillation column, and

contacting the side stream with a second catalyst, wherein the side stream reacts in the presence of the second catalyst to produce ethyl acetate.

16. The reactive distillation method of claim **1**, wherein a liquid portion of the feed stream reacts in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen.

17. A reactive distillation system comprising:

a reactive distillation column comprising:

a dehydrogenation catalyst located generally centrally in the column,

an ethanol feed in fluid communication with the reactive distillation column and configured to pass ethanol over the dehydrogenation catalyst,

an overhead product hydrogen removal passage, and

a bottoms product ethyl acetate removal passage;

a product separation system comprising an inlet configured to receive the bottoms product from the reactive distillation column, an ethyl acetate product removal passage, and an ethanol removal passage; and

a recycle line coupling the ethanol removal passage from the product separation system and an inlet to the reactive distillation column.

18. The reactive distillation system of claim **17**, further comprising a hydrogenation catalyst positioned to contact a liquid product following passage over the dehydrogenation catalyst.

19. The reactive distillation system of claim **17**, wherein the product separation system further comprises at least one of a lights product removal passage or a heavies product removal passage.

20. The reactive distillation system of claim **17**, wherein the reactive distillation column comprises a batch reactor configured to contact a liquid ethanol feed with the dehydrogenation catalyst and remove hydrogen during the contacting of the liquid ethanol feed with the dehydrogenation catalyst.

21. A reactive distillation method comprising:

introducing an feed stream to a reactive distillation column, wherein the feed stream comprises ethanol;

contacting the feed stream with a catalyst in the reactive distillation column during a distillation, wherein the feed stream reacts in the presence of the catalyst to produce a reaction product comprising ethyl acetate and hydrogen;

separating bottoms stream during the distillation from the reactive distillation column, wherein the bottoms stream comprises ethyl acetate and ethanol;

separating a recycle stream from the bottoms stream, wherein the recycle stream comprises at least a portion of the ethanol from the bottoms stream; and

recycling the recycle stream to the reactive distillation column.

22. The reactive distillation method of claim **21**, further comprising;

separating the bottoms stream into an overhead stream and the recycle stream at a first pressure, wherein the overhead stream comprises ethanol and ethyl acetate; and

separating the overhead stream into an ethanol stream and an ethyl acetate product stream at a second pressure, wherein the second pressure is greater than the first pressure.

23. The reactive distillation method of claim **22**, further comprising;

combining the ethanol stream with the bottoms stream in the separation of the bottoms stream into the overhead stream and the recycle stream.

24. The reactive distillation method of claim **22**, further comprising,

separating at least one byproduct from the recycle stream after separation of the recycle stream from the bottoms stream and prior to recycling the recycle stream to the reactive distillation column.

25. The reactive distillation method of claim **21**, further comprising;

separating the bottoms stream into a product stream and the recycle stream; and

separating the product stream into a byproduct stream and an ethyl acetate product stream.

26. A reactive distillation system comprising:

a reactive distillation column configured to separate ethanol from ethyl acetate,

wherein the reactive distillation column comprises:

an ethanol feed configured to pass a feed stream comprising ethanol into the reactive distillation column,

an overhead product hydrogen removal passage, and

a bottoms product ethyl acetate removal passage;

a side reactor in fluid communication with the reactive distillation column, wherein the side reactor comprises a dehydrogenation catalyst;

an inlet in fluid communication with the side reactor and the reactive distillation column, wherein the inlet is configured to pass a fluid comprising ethanol from the reactive distillation column over the dehydrogenation catalyst to produce ethyl acetate, and

an outlet in fluid communication with the side reactor and the reactive distillation column, and configured to pass the fluid from an outlet of the side reactor to the reactive distillation column.

27. The reactive distillation system of claim **26**, wherein at least one of the reactive distillation column or the side reactor comprises a hydrogenation catalyst.

28. The reactive distillation system of claim **27**, wherein the reactive

distillation system further comprises:

a hydrogen feed in fluid communication configured to pass hydrogen over at least a portion of the hydrogenation catalyst.

29. The reactive distillation system of claim **26**, further comprising:

a second side reactor in fluid communication with the reactive distillation column, wherein the side reactor comprises a second catalyst,

a second inlet in fluid communication with the second side reactor and the reactive distillation column, and configured to pass a second fluid from the reactive distillation column over the second catalyst, and

a second outlet in fluid communication with the second side reactor and the reactive distillation column, and configured to pass the second fluid from an outlet of the second side reactor to the reactive distillation column.

30. The reactive distillation system of claim **29**, wherein the second catalyst comprises a hydrogenation catalyst.

31. The reactive distillation system of claim **29**, wherein the second catalyst comprises a hydrogenation catalyst that is the same as the dehydrogenation catalyst in the side reactor.

32. The reactive distillation system of claim **29**, wherein the second catalyst comprises a second dehydrogenation catalyst that is different than the dehydrogenation catalyst in the side reactor.

33. The reactive distillation system of claim **29**, wherein the side reactor and the second side reactor are configured to each provide a different catalyst holdup.

34. A reactive distillation process comprising:

introducing a feed stream to a reactive distillation column, wherein the feed stream comprises ethanol;

contacting a first fluid drawn from the reactive distillation column with a dehydrogenation catalyst in a side reactor,

producing a reaction product comprising ethyl acetate in response to contacting the first fluid with the dehydrogenation catalyst in the side reactor;

introducing ethyl acetate to the reactive distillation column from the side reactor during the distillation;

removing ethyl acetate during the distillation from the reactive distillation column as a bottoms stream; and

removing hydrogen during the distillation from the reactive distillation column as an overhead stream.

35. The reactive distillation process of claim **34**, wherein at least one of the reactive distillation column or the side reactor comprises a hydrogenation catalyst.

36. The reactive distillation process of claim **35**, further comprising:

introducing a second feed stream to a reactive distillation column, wherein the second feed stream comprises hydrogen; and

contacting the hydrogen with the hydrogenation catalyst during the reactive distillation process.

37. The reactive distillation process of claim **35**, wherein producing a reaction product comprising ethyl acetate further produces by-products, and wherein the reactive distillation process further comprises:

hydrogenating at least a portion of the by-products over the hydrogenation catalyst to produce hydrogenated by-products.

38. The reactive distillation process of claim **34**, further comprising:

contacting a second fluid drawn from the reactive distillation column with a second catalyst in a second side reactor.

39. The reactive distillation process of claim **38**, wherein the second catalyst comprises at least one of dehydrogenation catalyst or a hydrogenation catalyst.

* * * * *

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(54) **ETHYL ACETATE PRODUCTION**

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(22) Filed: **Sep. 10, 2013**

Related U.S. Application Data

(63) Continuation-in-part of application No. 12/925,460, filed on Oct. 20, 2010, now Pat. No. 8,558,025.

(60) Provisional application No. 61/253,349, filed on Oct. 20, 2009.

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$\quad$ USPC **560/239**; 560/248; 422/187

(57) **ABSTRACT**

A method of purifying an ethyl acetate stream comprises contacting an inlet stream with a solvent, transferring at least a portion of the impurity compound from the inlet stream into the solvent to form an extract and a purified product, separating the extract from the purified product, separating the portion of the impurity compound from the extract, forming an impurities stream and a regenerated solvent, and recycling at least a portion of the regenerated solvent to contact the inlet stream. The inlet stream comprises ethyl acetate and an impurity compound, and the extract comprises the solvent and the portion of the impurity compound transferred from the inlet stream.

191

Figure 1: Reactive residue curve maps at pressures of 1 atm and 5 atm.

Figure 2: Reactive residue curve maps at pressures of 10 atm and 20 atm.

Figure 3: Single feed reactive distillation column schematic.

Figure 4: Schematic for a reactive distillation system with subsequent product hydrogenation.

Figure 5: Double feed reactive distillation column schematic with an upper feed of ethanol and lower feed of hydrogen.

Figure 6: Double feed reactive distillation column schematic using dual catalyst beds with an upper feed of ethanol and lower feed of hydrogen.

197

Figure 7: Side reactor configuration (a) upward flow feed to side reactor (b) downward flow feed to side reactor.

Figure 8: Double Side reactor configuration (a) upward flow feed to multiple side reactors (b) downward flow feed to multiple side reactors.

FIG. 9

200

FIG. 10

Figure 11. Schematic for Extraction-Stripping Process
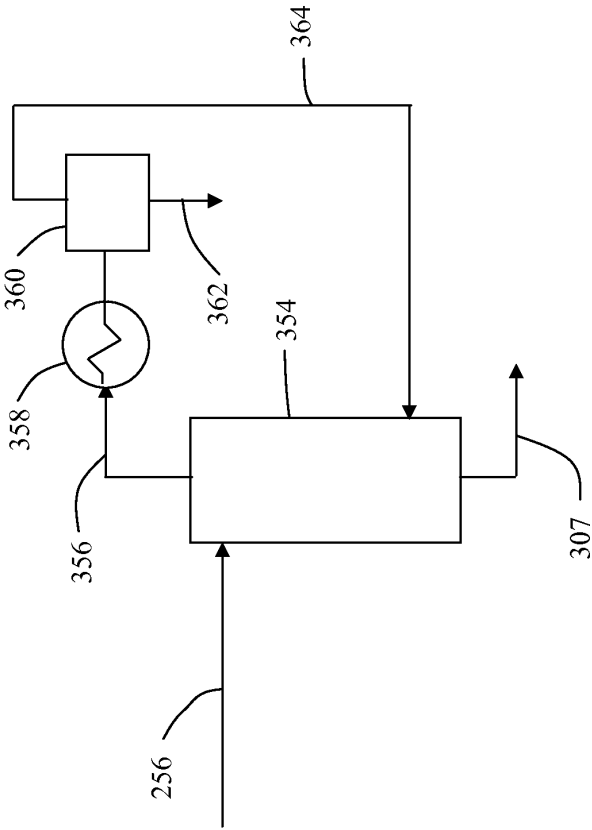
Figure 12. Schematic for Stripping Process
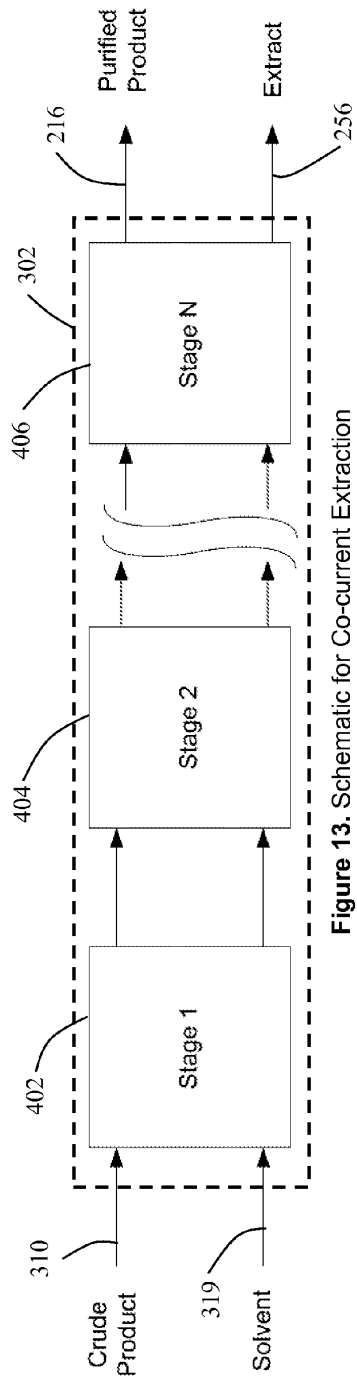
Figure 13. Schematic for Co-current Extraction
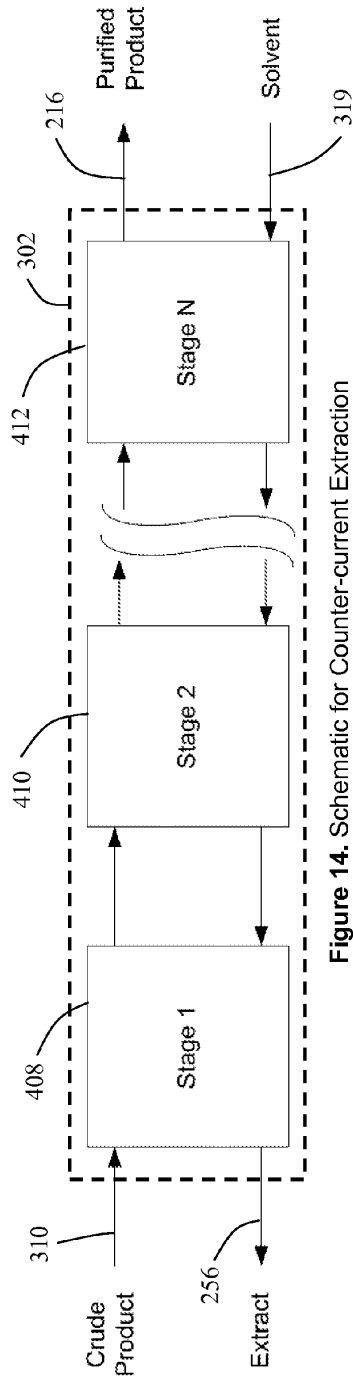
Figure 14. Schematic for Counter-current Extraction
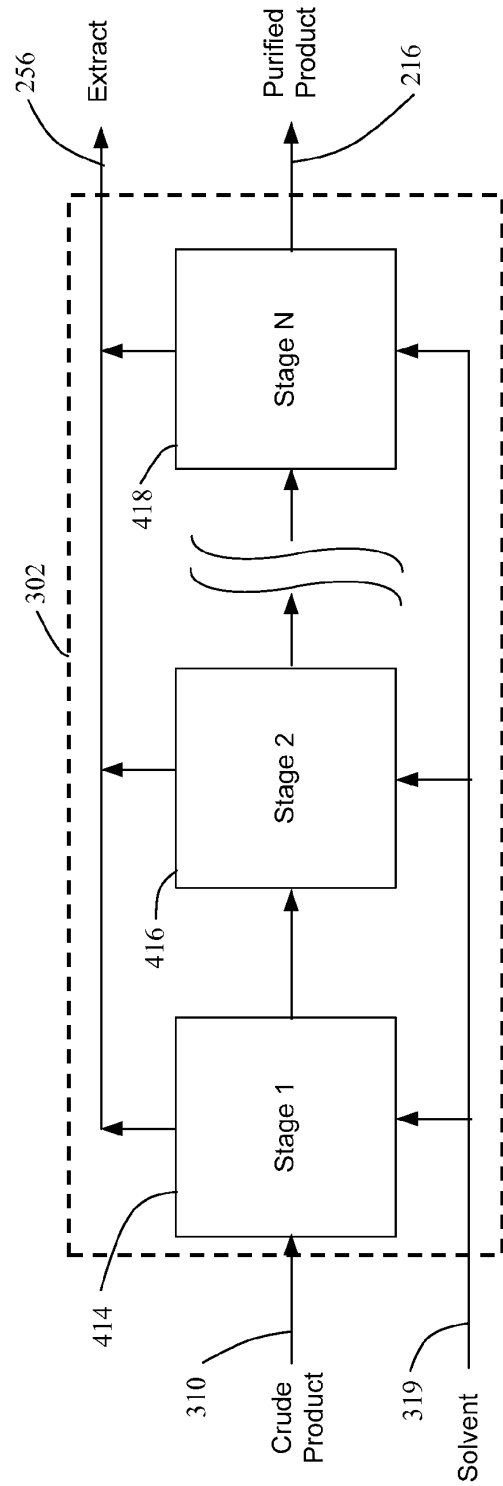
Figure 15. Schematic for Cross-flow Extraction
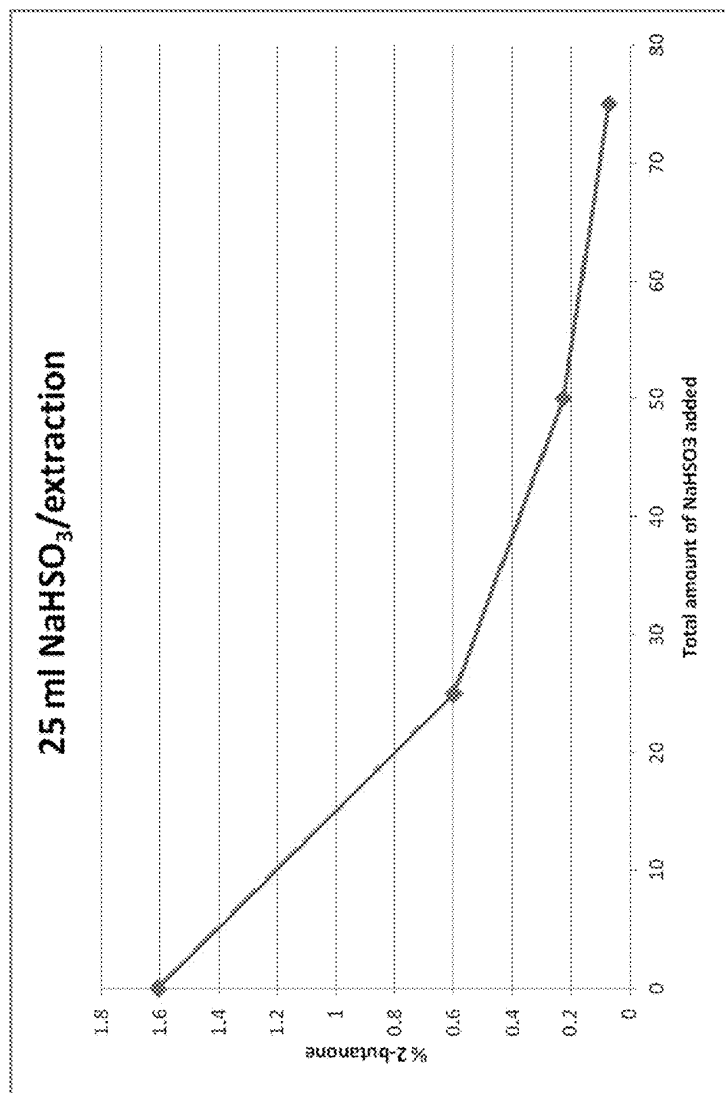
Figure 16
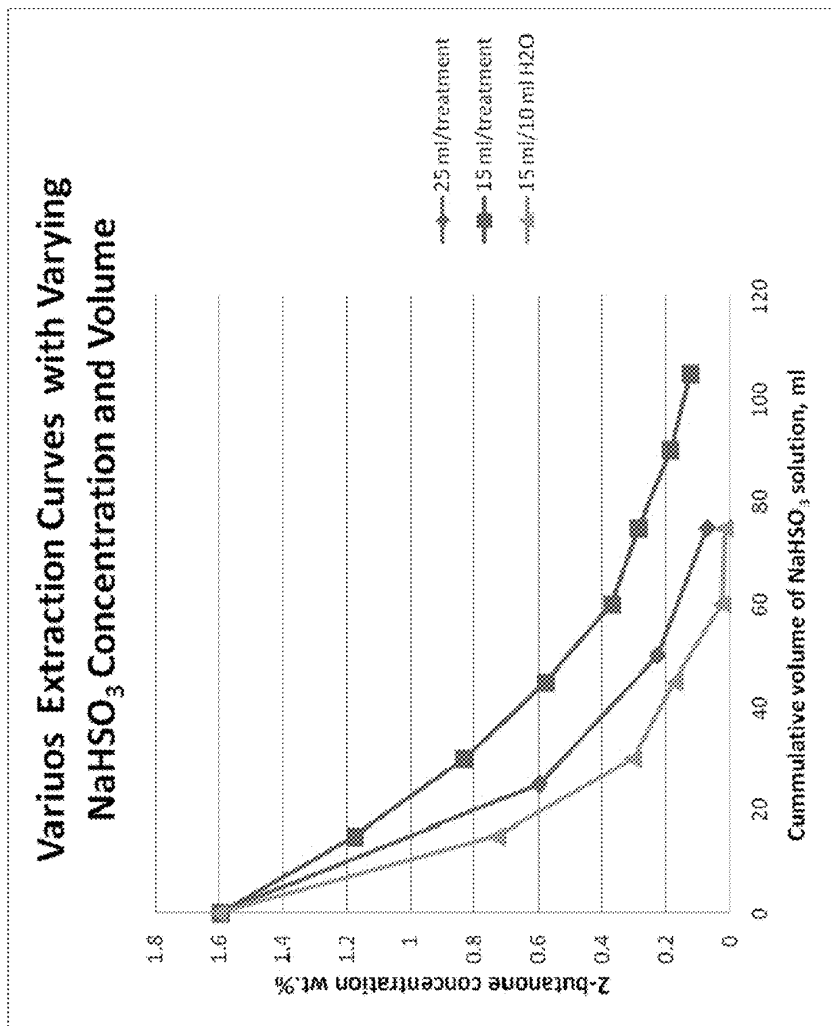
Figure 17
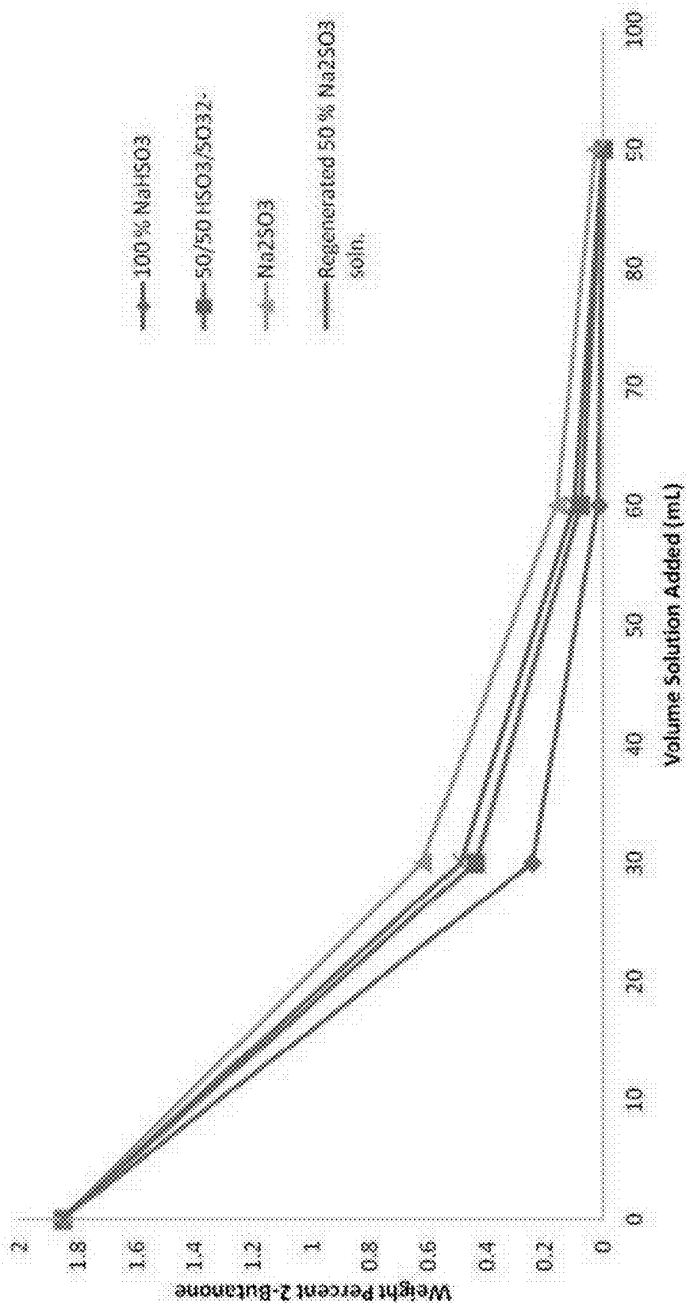
Figure 18

ETHYL ACETATE PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of and claims priority to U.S. patent application Ser. No. 12/925,460 filed on Oct. 20, 2010 to Sagar B. Gadewar and entitled "Ethyl Acetate Production," which is a Non-Provisional application of and claims priority to U.S. Provisional Application No. 61/253,349, filed Oct. 20, 2009 to Sagar B. Gadewar and entitled "Ethyl Acetate Production," both of which are incorporated herein by reference in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

REFERENCE TO A MICROFICHE APPENDIX

[0003] Not applicable.

BACKGROUND

[0004] The following discussion is provided solely to assist the understanding of the reader, and does not constitute an admission that any of the information discussed or references cited constitute prior art to the present invention.

[0005] Ethyl acetate can be produced from acetaldehyde according to the Tischenko reaction:

$$2CH_3CHO \longleftrightarrow CH_3COOC_2H_5$$
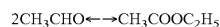
[0006] When acetaldehyde is produced from ethanol, ethyl acetate can be produced from ethanol according to the following reaction:

$$2C_2H_5OH \longleftrightarrow CH_3COOC_2H_5 + 2H_2$$

[0007] Alternately, ethanol can react with acetaldehyde according to the following reaction:

$$C_2H_5OH + CH_3CHO \longleftrightarrow CH_3COOC_2H_5 + H_2$$
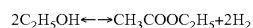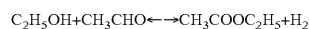
[0008] Conversion of primary alcohols into esters and ketones using copper catalyst is described by K. Takeshita in the Bulletin of the Chemical Society of Japan, (1978) vol. 51(9), pp 2622-2627.

[0009] U.S. Pat. No. 4,996,007 describes a process for the oxidation of primary alcohols to aldehydes, esters and acids. A primary alcohol is reacted with oxygen, with a catalyst selected from ruthenium, rhodium, platinum, palladium, rhenium and mixtures thereof, with the option of quaternary C1 to C20 alkyl ammonium co-catalyst, and dihydrodihydroxynaphthalene, dihydroxyanthracene or a mixture thereof as an oxygen activator.

[0010] In U.S. Pat. No. 4,220,803 catalytic dehydrogenation of ethanol for the production of acetaldehyde and acetic acid using a supported copper oxide essentially free of barium is proposed.

[0011] U.S. Pat. No. 4,052,424 suggested a silver-cadmium alloy catalyst for use in production of alkyl alkanoate esters, by contacting a primary alkanol in the vapor phase with the catalyst at a temperature of between about 250° C. and 600° C.

[0012] In U.S. Pat. No. 4,440,946 there is described a process for producing a carboxylate ester which comprises contacting a mixture of alcohol and aldehyde in the vapor phase with a co-precipitate composition comprising silver-cadmium-zinc-zirconium which is substantially in the free metal form.

[0013] Use of the Tischenko reaction for the production of mixed esters from aldehydes is described in U.S. Pat. No. 3,714,236.

[0014] U.S. Pat. No. 5,334,751 describes production of ethyl acetate by reaction of ethanol and oxygen in the presence of a solid catalyst that contains crystalline TiP_2O_7 and has the formula $Pd_aM_bTiP_cO_x$, where M is Cd, Au, Zn, Tl, or an alkali metal or alkaline earth metal, a is 0.0005-0.2, b is 0.3a, c is 0.5-2.5, x has a value to satisfy the valencies, and Ti and P of the crystalline TiP_2O_7 represent part of the crystalline TiP_2O_7.

[0015] BR-A-91/04652 describes pre-treatment of a palladium on a silica carrier catalyst for production of ethyl acetate by direct oxidation of ethanol with air.

[0016] Production of esters from primary alcohols by dehydrogenation using bromous acid or a salt thereof in acid medium is described in JP-A-59/025334.

[0017] In SU-A-362814 there is described a process for production of ethyl acetate by dehydrogenation of ethanol at 180° C. to 300° C. in the presence of a copper catalyst containing zinc as an activator with an ethanol feed rate of 250 to 700 liters per liter of catalyst per hour.

[0018] The dehydrogenation of ethanol to form ethyl acetate is described in GB-A-287846. This proposes use of a dehydrogenating agent, such as a copper catalyst, a temperature of from 250° C. to 500° C., and a pressure of more than 10 atmospheres (1.013×10^6 Pa).

[0019] Vapor phase contact of ethanol at a temperature above its critical temperature with a catalyst comprising copper and a difficultly reducible oxide, such as zinc oxide or manganese oxide, is proposed in GB-A-312345, use of a temperature of 375° C. and a pressure of 4000 psi (27.58 Mpa) being suggested.

[0020] GB-A-470773 teaches a process for conversion of ethanol to ethyl acetate by dehydrogenating ethanol over a catalyst consisting of a reduced metal, for example, copper on infusorial earth with 10% uranium oxide as promoter, maintained at a temperature of 220° C. to 260° C., removing by condensation some of the gas-vapor product rich in hydrogen resulting from the reaction, and returning the gaseous remainder rich in hydrogen to the catalyzing zone.

[0021] EP-A-0151886 describes a process for the preparation of C2+ esters of alkyl carboxylic acids from C2+ primary alcohols which comprises contacting a vaporous mixture containing a primary C2+ alkanol and hydrogen in an alkanol: hydrogen molar ratio of from 1:10 to about 1000:1 at a combined partial pressure of alkanol and hydrogen of from about 0.1 bar (103 Pa) up to about 40 bar (4×10^6 Pa) and at a temperature in the range of from about 180° C. to about 300° C. in a catalytic reaction zone with a catalyst consisting essentially of a reduced mixture of copper oxide and zinc oxide, and recovering a reaction product mixture containing a primary C2+ alkyl ester of an alkyl carboxylic acid which ester contains twice as many carbon atoms as the primary C2+ alkanol.

[0022] In EP-A-0201105 there is described a method for converting primary alcohols, such as ethanol, to their corresponding alkanoate esters which involves the regulation of the mole feed ratio of hydrogen gas to alkanol in the reaction zone of a copper-chromite containing catalyst.

[0023] One method of separating ethyl acetate from ethanol and water involves extractive distillation with an extractive agent comprising polyethylene glycol and dipropylene glycol, diethylene glycol, or triethylene glycol as described in U.S. Pat. No. 4,569,726 or with an extractive agent containing dimethyl sulphoxide as described in U.S. Pat. No. 4,379,028.

[0024] Separation of ethyl acetate from a composition comprising ethyl acetate, ethanol and water is described in JP-A-05/186392 by feeding the composition to a distillation column to obtain a quasi-azeotropic mixture comprising ethyl acetate, ethanol and water, condensing it, separating the condensate into an organic layer and an aqueous layer, returning the organic layer to the column, and recovering ethyl acetate as a bottom product from the column.

[0025] EP-A-0331021 describes how carbonylation of olefins to produce monocarboxylate esters causes formation of aldehydes and acetals as byproducts. Monocarboxylate esters produced in this way are subjected to a three step purification process involving treatment with a strongly acidic agent, followed by hydrogenation and distillation. The initial treatment with a strongly acidic agent is intended to convert acetals to vinyl ethers and aldehydes and acetals to aldols. The subsequent hydrogenation step then converts these compounds to byproducts which are more easily separated from the desired monocarboxylate ester.

[0026] EP-A-0101910 contains a similar disclosure regarding carbonylation of olefins to give monocarboxylate esters. It proposes treatment of the monocarboxylate ester with hydrogen at elevated temperature in the presence of an acidic ion exchanger or zeolite doped with one or more metals of Group VIII of the Periodic Table, followed by hydrogenation. It is stated that acetals present as byproducts are converted to vinyl ethers which are converted by hydrogenation to low boiling esters or the aldehydes and acetals are converted to high boilers by an aldol reaction. Unsaturated ketones are converted to saturated ketones.

[0027] U.S. Pat. No. 4,435,595 describes the use of reactive distillation to produce high-purity methyl acetate, by esterifying methanol and acetic acid. The process provides for the use of acetic acid and methanol which flow in counter-current through a single reactive distillation column in the presence of an acid catalyst. The acetic acid, in addition to being a reagent, also acts as an extracting agent for the non-reacted methanol and for the water which has been produced. Therefore, the methyl acetate is separated continuously from the acetic acid and removed from the top of the column.

SUMMARY

[0028] In an embodiment, a method of purifying an ethyl acetate stream comprises contacting an inlet stream with a solvent, transferring at least a portion of the impurity compound from the inlet stream into the solvent to form an extract and a purified product, separating the extract from the purified product, separating the portion of the impurity compound from the extract, forming an impurities stream and a regenerated solvent, and recycling at least a portion of the regenerated solvent to contact the inlet stream. The inlet stream comprises ethyl acetate and an impurity compound, and the extract comprises the solvent and the portion of the impurity compound transferred from the inlet stream.

[0029] In an embodiment, a reactive distillation system for producing high purity ethyl acetate from ethanol comprises a reactive distillation column, an extraction unit, and a stripping unit. The reactive distillation column comprises a dehy-

drogenation catalyst, an ethanol inlet configured to pass an ethanol feed over the dehydrogenation catalyst, a top product gaseous hydrogen removal passage, and a bottoms product liquid ethyl acetate removal passage. The extraction unit is configured to receive a liquid ethyl acetate product stream from the reactive distillation column through the bottoms product liquid ethyl acetate removal passage, contact a liquid solvent feed stream with the liquid ethyl acetate product stream, provide an extract stream comprising a portion of any impurities in the liquid ethyl acetate product stream, and provide a purified product stream. The stripping unit is configured to receive the extract stream from the extraction unit, separate the portion of the impurities from the extract stream, provide an outlet impurities stream, and provide a regenerated solvent stream back to the extraction unit as at least a portion of the liquid solvent feed stream.

[0030] In an embodiment, a reactive distillation process producing high purity ethyl acetate from ethanol comprises feeding a feed stream comprising ethanol to a reactive distillation column, contacting the ethanol with a catalyst, dehydrogenating ethanol over the catalyst in the liquid phase during the distillation process, removing ethyl acetate during the distillation process as a bottoms product, and removing hydrogen during the distillation process as a top product.

[0031] These and other features will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description.

[0033] FIG. 1 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 1 and 5 atmospheres (atm) for an embodiment.

[0034] FIG. 2 shows reactive residue maps for conversion of ethanol to ethyl acetate at pressures of 10 and 20 atm for an embodiment.

[0035] FIG. 3 shows a simplified schematic of a reactive distillation system according to an embodiment.

[0036] FIG. 4 shows a simplified schematic of a reactive distillation system according to another embodiment.

[0037] FIG. 5 shows a simplified schematic of a reactive distillation system according to still another embodiment.

[0038] FIG. 6 shows a simplified schematic of a reactive distillation system according to yet another embodiment.

[0039] FIGS. 7(a) and 7(b) shows a simplified schematic of a reactive distillation system according to an embodiment.

[0040] FIGS. 8(a) and 8(b) shows a simplified schematic of a reactive distillation system according to another embodiment.

[0041] FIG. 9 illustrates a schematic flow diagram of a reactive distillation system with a recycle according to an embodiment.

[0042] FIG. 10 illustrates a schematic flow diagram of a product separation system according to an embodiment.

[0043] FIG. 11 illustrates a schematic flow diagram of a product separation system according to another embodiment.

[0044] FIG. 12 illustrates a schematic flow diagram of a stripping section according to another embodiment.

[0045] FIG. 13 illustrates a schematic co-current extraction flow scheme according to an embodiment.

[0046] FIG. **14** illustrates a schematic counter-current extraction flow scheme according to an embodiment.

[0047] FIG. **15** illustrates a schematic cross-current extraction flow scheme according to an embodiment.

[0048] FIG. **16** illustrates a chart demonstrating the results of an extraction of 2-butanone from ethyl acetate.

[0049] FIG. **17** illustrates another chart demonstrating the results of an extraction of 2-butanone from ethyl acetate.

[0050] FIG. **18** illustrates another chart demonstrating the results of an extraction of 2-butanone from ethyl acetate using several extracting solution compositions.

DETAILED DESCRIPTION

[0051] A reactive distillation system and process are disclosed herein for producing high purity ethyl acetate from ethanol. This process is beneficial as it provides an improved commercial method of upgrading ethanol to ethyl acetate, a more valuable product. This improved commercial process may be used where there is a supply and/or a surplus supply of ethanol. Further, this process reduces and/or eliminates the need for a separate acetaldehyde or acetic acid plant to provide the precursors for the ethyl acetate production process. The raw material may comprise only ethanol, which may present an advantage relative to other processes requiring multiple feedstocks. In addition, bio-derived ethanol may be used to allow the process to be operated from renewable ethanol sources. Further, the present system and method may utilize base-metal catalysts, which may be less expensive than the precious metal based catalysts of other ethyl acetate production routes. Such catalysts can comprise copper, and may be composed of copper oxide mixed with one or more additional metals and/or metal oxides. The present systems and methods may allow for a one-step ethyl acetate production process, which may be advantageous relative to other processes that require further steps to purify the ethyl acetate product, including a selective removal of 2-butanone, which forms a low boiling azeotrope with ethyl acetate. Each of these advantages may be provided in a process that can also be less expensive than alternative processes by ethyl acetate production from ethanol.

[0052] In an embodiment, the present systems and methods can provide a route to ethyl acetate by dehydrogenation and dimerization of ethanol which is capable of yielding high purity ethyl acetate from ethanol feed streams containing significant amounts of byproducts or impurities. One issue in the production of ethyl acetate by dehydrogenation of ethanol is that the reaction product mixture is commonly a complex mixture including esters, alcohols, aldehydes and ketones. From a distillative separation point of view, the mixture is further complicated due to the presence of azeotropes. The reaction product mixtures commonly contain components with boiling points close to ethyl acetate (such as n-butyraldehyde and/or butan-2-one), including components which can form azeotropes with ethyl acetate, and/or other components of the mixture. This may present a challenge when high purity ethyl acetate is desired.

[0053] In chemical processing, chemical reaction and the purification of the desired products by distillation may be carried out sequentially. The performance of this chemical process structure may be improved by the integration of reaction and distillation in a single multifunctional process unit. This integration concept is called "reactive distillation." As advantages of this integration, chemical equilibrium limitations may be overcome, higher selectivities may be achieved,

the heat of reaction may be used in situ for distillation, auxiliary solvents may be avoided, and/or azeotropic and/or closely boiling mixtures may be more easily separated. Increased process efficiency and reduction in overall capital costs may result from the use of this approach.

[0054] A reactive distillation system comprises at least one separator and/or reactor (e.g., a distillation tower, side reactor, etc.) in which a reaction is occurring. In general, suitable separators may include any process equipment suitable for separating at least one inlet stream into a plurality of effluent streams having different compositions, states, temperatures, and/or pressures. For example, the separator may be a column having trays, packing, or some other type of complex internal structure. Examples of such columns include scrubbers, strippers, absorbers, adsorbers, packed columns, and distillation columns having valve, sieve, or other types of trays. Such columns may employ weirs, downspouts, internal baffles, temperature control elements, and/or pressure control elements. Such columns may also employ some combination of reflux condensers and/or reboilers, including intermediate stage condensers and reboilers. In an embodiment, the reactive distillation system described herein may comprise a distillation tower having at least one catalyst disposed therein. The catalyst may take a variety of forms, and the separator may comprise any combination of catalyst and separator structures. For example, the separator may comprise sequential layers of catalysts and distillation packing and/or the packing may comprise catalytic elements such as pellets that act as a structured packing. In some embodiments, the reactive distillation system described herein may comprise a distillation tower comprising one or more side reactors comprising at least one catalyst disposed therein, where the one or more side reactors are coupled to and are in fluid communication with the distillation tower

[0055] As indicated above, the present systems and methods provide for the production of ethyl acetate from ethanol at a relatively low cost, along with a plant or distillation system with significantly reduced complexity using reactive distillation. The present disclosure further provides an improved process for the production of high purity ethyl acetate from ethanol, or from a feedstock comprising a major proportion of ethanol and a minor proportion of impurities such as isopropanol and iso-butanol. While not commonly present in ethanol feed streams, impurities that can poison the particular catalyst used should be limited, avoided and/or removed. For example, sulfur or nitrogen heterocyclic compounds can frequently act as catalyst poisons and, if present, should be removed before introducing the ethanol feed stream to the reactive distillation column. In an embodiment, the ethanol feed may comprise water. The presence of water in the ethanol feed does not severely reduce the performance of the catalysts, which can tolerate up to 5% water by weight in the ethanol. Ethanol conversion is reduced when using an ethanol source with significant water content, but the reaction selectivity increases. The use of an ethanol feed comprising a small amount of water may be advantageous by allowing for the use a potentially less expensive ethanol source in the form of the ethanol/water azeotrope (about 4.4% water by weight). The effects of water are demonstrated in the Examples described herein.

[0056] Ethyl acetate can be produced from ethanol according to the following reactions:

$$C_2H_5OH \longleftrightarrow CH_3CHO + H_2$$

$$CH_3CHO + C_2H_5OH \longleftrightarrow CH_3COOC_2H_5 + H_2$$
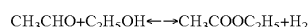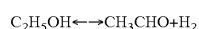
The Tishchenko reaction may also provide a potential reaction route for the production of ethyl acetate from ethanol:

$$C_2H_5OH \leftarrow \rightarrow CH_3CHO + H_2$$

$$2CH_3CHO \leftarrow \rightarrow CH_3COOC_2H_5$$

[0057] In an embodiment, ethanol reacts in a single continuous reactive distillation column which provides sufficient residence time to achieve a relatively high conversion of ethanol. In an embodiment, the reactive distillation column may be configured to provide a conversion of ethanol of at least about 10% and a selectivity of at least about 60%, as described in more detail herein. Table 1 shows the effect of pressure on the boiling point of the pure components and azeotrope in the mixture. The azeotrope between ethanol and ethyl acetate is substantially avoided above a pressure of 13 atm.

TABLE 1

Boiling point of reaction components.

	Boiling Point, C.					
	P = 1 atm	P = 5 atm	P = 10 atm	P = 20 atm	P = 30 atm	P = 40 atm
Hydrogen	−161	−137.6	−123.7	−106.5	−94.3	−84.5
Acetaldehyde	20.4	71.9	101.1	136.4	160.7	180
Ethanol	78.3	125.2	150.2	179	198	212.7
Ethyl acetate	77	136	169.6	210.3	238.4	260.7
Ethanol/Ethyl acetate azeotrope	71.7	123.5	150.1	No Azeo	No Azeo	No Azeo

[0058] Residue curve maps can be used to indicate feasible product compositions for distillation columns. In the presence of reaction along with separation, reactive residue curve maps can be used to determine feasible products from a reactive distillation column. Reactive residue curve maps at a pressure of 1 atm and 5 atm respectively are shown in FIG. **1**. The stable nodes in the diagram are ethanol and ethyl acetate, and, therefore, it is possible to design a reactive distillation column where either ethanol or ethyl acetate can be obtained as the bottoms product. Hydrogen is an unstable node in the diagram and can be obtained as the distillate. Acetaldehyde and the ethanol/ethyl acetate azeotrope are saddle points in the diagram.

[0059] Reactive residue curve maps at pressures of 10 atm and 20 atm respectively are shown in FIG. **2**. The reactive residue curve maps for any pressure above 20 atm are substantially similar to the reactive residue curve map at 20 atm.

[0060] In view of the reactive residue maps discussed above, a set of reactive distillation systems effective to produce high purity ethyl acetate from ethanol have been designed. The reactive distillation column can have single or multiple feed locations.

Reactive Distillation Column Configurations

[0061] The present systems and methods provide a reactive distillation system in which ethanol may be the sole or primary component of the feed. In some embodiments, the ethanol feed is used in conjunction with a separate, second feed of hydrogen. Reference to a "single feed" to a reactive distillation column means that the column has only one chemical feed stream supplying intended reactant(s) to the column. Nonetheless, such a single feed distillation column may have multiple entry points for the reactant, or recycling feed

streams where a part of the reactant liquid or a partial distillate is drawn from the column and fed back into the column at a different point, e.g., to achieve improved separation and/or more complete reaction. A "single ethanol feed" thus refers to a single feed stream, in which ethanol is the sole or at least the primary constituent. In contrast, the term "dual feed" in the context of a distillation column refers to two separate chemical feed streams. For example, in some of the present embodiments, dual feeds are an ethanol feed and a separate hydrogen feed. The term "reactive distillation column" is used conventionally to refer to a distillation column in which both reaction and separation is performed. In this case, the primary and desired reaction is the conversion of two ethanol molecules to one ethyl acetate molecule with release of two hydrogen molecules. Thus, the present invention provides systems and methods for the production of ethyl acetate from ethanol which includes reacting ethanol over a suitable dehydrogenation and/or dimerization catalyst, thereby producing ethyl acetate and hydrogen.

[0062] In an embodiment, a single reactive distillation column is used. Hydrogen gas is removed (e.g., continuously) from the top of the reactive distillation column as an overhead stream. Ethyl acetate is removed (e.g., continuously) from the bottom of the column as a bottoms stream. Optionally, contaminating byproducts present following reaction of the ethanol over the dehydrogenation catalyst can be separated from the ethyl acetate product stream. Various byproduct separation schemes are possible including, but not limited to, reacting the byproducts in the product stream over a suitable hydrogenation catalyst in the lower part of the column or in a separate hydrogenation reactor. The hydrogenation can convert difficult to separate byproducts into species which are easier to separate from the ethyl acetate. Consequently, the process can also include purifying the ethyl acetate by distilling out resulting hydrogenated byproducts. In some embodiments, an extraction process may be used selectively remove one or more byproducts from the ethyl acetate products stream. Consequently, the process may also include purifying the ethyl acetate by contacting the product stream with an extractant, which can be regenerated and recycled to the extraction system.

[0063] In an embodiment, the reactive distillation column is configured for the dehydrogenation of ethanol with the formation of ethyl acetate. The reaction is accomplished by passing the ethanol feed stream over a dehydrogenation catalyst under conditions where ethyl acetate is formed and hydrogen and ethyl acetate are withdrawn as top and bottoms products respectively. Such product draws drive the thermodynamics of the process toward the desired products. In its

simplest form, a reactive distillation system may comprise a reactor vessel operating with a liquid phase reaction in which hydrogen and/or other light gases are removed as the overhead product and a reaction product is removed as the bottoms product. Such a system may comprise a batch reactor in which hydrogen is removed during the reaction and the liquid product is removed after completion of the reaction to a desired degree of conversion.

[0064] An embodiment of a reactive distillation column with a single feed of ethanol is shown schematically in FIG. **3** can produce hydrogen as a distillate and ethyl acetate as a bottoms product. Column **10** contains a generally central catalyst zone **12**, and usually will include a top stage or non-reactive rectifying section **13** and a bottom stage or non-reactive stripping section **15**. Ethanol feed **14** is commonly fed to the middle part of the reactive distillation column. Distillate removed at the top of the column is passed through a partial condenser **16**, and hydrogen is separated from lower boiling constituents in reflux tank **18**. The hydrogen may leave the system as an overhead product stream **19**, which in an embodiment may comprise trace amounts of additional components including ethanol, ethyl acetate, and/or one or more reaction byproducts. The condensed lower boiling constituents (i.e., reflux), or at least some portion thereof, can be cycled back to the column for further reaction and/or separation. The bottoms product can be passed through reboiler **20**, where a portion of the bottoms product is evaporated and added back to the bottom of the column. The remaining bottoms product may pass out of the system as product stream **22**. Alternatively, only a portion of the bottoms product may be passed through reboiler **20**, with the vapor portion passing back to the bottom of the column and the remainder of the bottoms product being combined with any bottoms product bypassing the reboiler **20** and passing out of the system as product stream **22** for further processes and/or use as a final product. The product stream **22** may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products produced by the reaction. The column reflux and reboil ratios are maintained such that essentially pure ethyl acetate is obtained as the bottoms product. In an embodiment, the bottoms product stream **22** may comprise greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0065] During operation, the reactants and products flow through the reactor/column reacting and flashing along the length of the reactor/column. In an embodiment, the reaction of the reactants and/or products may occur in the catalyst zone **12**, and the reactions may occur in the vapor and/or liquid phase. While not intending to be limited by theory, it is believed that the dehydrogenative dimerization of ethanol to ethyl acetate may occur over the dehydrogenation and dimerization catalysts described herein in the liquid phase. It has not been previously recognized that the dehydrogenation and dimerization conversion of ethanol to ethyl acetate would occur in the liquid phase. The use of a liquid phase reaction may allow for reactive distillation to be effectively used for converting ethanol into ethyl acetate and hydrogen. Specific catalysts useful in the reactive distillation systems and methods disclosed herein are discussed in more detail below. Ethyl acetate and hydrogen are produced due to the reaction over the dehydrogenation and dimerization catalyst. Byproducts including, but not limited to, aldehydes, such as acetaldehyde,

n-butyraldehyde, and/or crotonaldehyde; ethers, such as ethyl ether and n-butyl ether; ethyl acetate; ketones such as 2-butanone, acetone; and other alcohols, such as isobutanol, 2-butanol, 2-ethylbutanol, n-hexanol, and/or 2-ethylhexanol may also be produced during the reaction. The removal of the overhead stream **19** comprising hydrogen, which may occur by flashing, increases the extent of reaction. In general, the hydrogen concentration increases from the middle part of the column towards the top of the column. At pressures of about 13 bar or lower, as ethyl acetate is formed from the reactants, an azeotrope between ethyl acetate and ethanol occurs. This azeotrope may result in the overhead product **19** that leaves the top of the reactive distillation column **10** containing ethanol/ethyl acetate and/or acetaldehyde in addition to hydrogen. A partial condenser **16** allows hydrogen to be removed as a distillate, while acetaldehyde and ethanol are recycled back to the top of the reactive distillation column. At a pressure above about 13 atm, the ethyl acetate and ethanol azeotrope disappears, which improves the operation of the reactive distillation column.

[0066] The column **10** can be operated at any suitable pressure between about 1 atm and about 80 atm. In an embodiment, the column **10** may be operated at a pressure ranging from about 1 atm to about 5 atm, about 5 atm to about 10 atm, about 7 atm to about 12 atm, about 13 atm to about 15 atm, about 13 atm to about 20 atm, about 15 atm to about 20 atm, about 15 atm to about 30 atm, about 20 atm to about 30 atm, about 20 atm to about 50 atm, about 30 atm to about 40 atm, about 40 atm to about 50 atm, or about 50 atm to about 60 atm, about 60 atm to about 70 atm, about 60 atm to about 80 atm, or about 70 atm to about 80 atm. In an embodiment, the reactive distillation is performed at a pressure where ethanol-ethyl acetate azeotrope is not present. The temperature profile in the column is dictated by the mixture boiling point along the height of the column. In an embodiment the temperature within the column may range from about 100° C. to about 350° C., alternatively about 150° C. to about 250° C. The column **10** may comprise any number of stages equivalent to a number of theoretical stages sufficient to effect the reaction and separation of ethyl acetate to a desired purity. In an embodiment, the number of stages or the number of height equivalents of a theoretical plate (HETP) may range from about 1 to about 100, including for example from about 1 to about 10, about 10 to about 20, about 10 to about 50, about 20 to about 30, about 20 to about 70, about 30 to about 40, about 30 to about 50, about 30 to about 100, about 50 to about 70, about 50 to about 100, or about 70 to about 100. As described in more detail below, a relatively high conversion of ethanol to products can be achieved by the counter-current flow of reactants and products in addition to overcoming the reaction equilibrium by removal of products through the concurrent distillation within the column **10**.

[0067] In an embodiment, the systems and methods may also include hydrogenating contaminants or reaction byproducts in the bottoms stream or in the reacted fluid after it has passed over the dehydrogenation catalyst and separating the hydrogenated contaminants or byproducts from the ethyl acetate. As noted above, aldehydes and/or ketones such as n-butyraldehyde and butan-2-one may be produced as byproducts in the reaction. These byproducts boil at temperatures close to the boiling point of ethyl acetate and may be difficult to separate from ethyl acetate. FIG. **4** shows a process schematic where the bottoms product **22** from the reactive distillation column **10** illustrated in FIG. **3** is sent to a hydro-

genation reactor **24** comprising a hydrogenation catalyst **26** with a hydrogen co-feed **28**. Suitable hydrogenation catalyst (s) may comprise various components and are described in more detail herein. At least a portion of the n-butyraldehyde and/or butan-2-one impurities and/or byproducts can be hydrogenated and can then be separated using a separator **32**. The separator **32** may comprise any of the types of separators described herein with respect to the reactive distillation system. Alternatively or in addition to the separators already described, the separator **32** may be a phase separator, which is a vessel that separates an inlet stream into a substantially vapor stream and a substantially liquid stream, such as a knock-out drum, flash drum, reboiler, condenser, or other heat exchanger. Such vessels also may have some internal baffles, temperature control elements, and/or pressure control elements, but generally lack any trays or other type of complex internal structure commonly found in columns. The separator also may be any other type of separator, such as a membrane separator. In a specific embodiment, the separator is a knock-out drum. Finally, the separator may be any combination of the aforementioned separators arranged in series, in parallel, or combinations thereof. In an embodiment, separator **32** comprises a distillation column. The outlet of the hydrogenation reactor **24** may be passed through a heat exchanger **30** (e.g., a condenser) and cooled before entering the separator **32**. The heat exchanger **30** may be any equipment suitable for heating or cooling one stream using another stream. Generally, the heat exchanger **30** is a relatively simple device that allows heat to be exchanged between two fluids without the fluids directly contacting each other. Examples of suitable heat exchangers **30** include, but are not limited to, shell and tube heat exchangers, double pipe heat exchangers, plate fin heat exchangers, bayonet heat exchangers, reboilers, condensers, evaporators, and air coolers. In the case of air coolers, one of the fluids comprises atmospheric air, which may be forced over tubes or coils using one or more fans.

[0068] The bottoms product stream **36** from the separator **32** may comprise ethyl acetate and may have a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight. Unconverted hydrogen and the hydrogenated byproducts may be removed as an overhead product **34**, and may be used, for example, as fuel or a feed to one or more processes. In an embodiment, the separator **32** may be operated between a pressure of 1 atm and 80 atm.

[0069] In an embodiment, the bottoms product stream **36** may pass to another separator. The separator may then separate the bottoms product stream into an ethyl acetate stream and a byproduct stream comprising one or more heavier hydrogenation products produced in the hydrogenation reactor **26**. This separation scheme may allow the resulting ethyl acetate stream to have a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0070] In another embodiment of the invention, the reactive distillation column has two feeds. Ethanol may be fed to the upper part of the column (upper feed), and hydrogen may be fed to the lower part of the column (lower feed). A schematic for the double feed reactive distillation column is schematically illustrated in FIG. **5**. This system includes column **40** containing catalyst **42** in catalyst zone **44**, and commonly may include a top stage or non-reactive rectifying section **50**

and a bottom stage or non-reactive stripping section **52**. In the illustrated system, ethanol feed **46** is delivered at or near the top of the catalyst zone **44**, and the hydrogen feed **48** is delivered at or near the bottom of catalyst zone **44**. It should be recognized columns can be designed with the ethanol feed **46** location in other locations, e.g., within the catalyst zone **44** but above the hydrogen feed **48**, such as from the approximate middle of the catalyst zone **44** to the top of the column **40**. Similarly, columns with the hydrogen feed **48** in other locations can also be designed, e.g., with the hydrogen feed **48** from the approximate middle of the catalyst zone **44** to the bottom of the column **40** or even higher within the catalyst zone **44** but below the ethanol feed **46**. In an embodiment, the ethanol feed **46** and the hydrogen feed **48** are separated sufficiently to allow byproduct hydrogenation to be substantially completed before hydrogen from the feed reaches substantial concentrations of ethanol being dehydrogenated. Ethanol reacts over the catalyst producing ethyl acetate and hydrogen. Examples of suitable dehydrogenation and dimerization catalysts are described in more detail herein.

[0071] Due to boiling point differences, hydrogen moves towards the top of the column **40** and ethyl acetate moves towards the bottom of the column **40**. Acetaldehyde may be produced during the reaction and may move up in the column **40**. At least a portion of the acetaldehyde, if present, can be condensed in condenser **54** (e.g., a partial condenser, or a total condenser), passed through reflux tank **56**, and recycled back to column **40** as reflux. A product stream **59** comprising hydrogen is taken out as distillate from the reflux tank **56**. A part of the bottom draw is taken out as the ethyl acetate product stream **58**, while the remaining part is passed through reboiler **60** to be recycled to the column **40**. In an embodiment, the bottom draw may be passed through a reboiler (e.g., similar to reboiler **60**) and optionally passed to a separator where the vapor portion may pass to the column **40** while at least a portion of the remainder is taken out as the ethyl acetate product stream **58**. The stream passing through the reboiler **60** provides the evaporation effect and vapor flow for operating the column **40**. The product stream **58** may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products produced by the reaction.

[0072] Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction may have boiling points close to the boiling point of ethyl acetate. The lower hydrogen feed **48** is useful in hydrogenating the by-products to produce components that can be separated easily from ethyl acetate. The ratio of the hydrogen feed to the ethanol feed can beneficially be adjusted to minimize the amount of close boiling byproducts, while not excessively reducing ethyl acetate to ethanol. In an embodiment, the molar ratio of ethanol to hydrogen ranges from about 1:10 to about 1000:1, e.g., from about 1:10 to about 1:1, from about 1:1 to about 5:1, from about 1:1 to about 10:1, from about 5:1 to about 25:1, from about 5:1 to about 50:1, from about 10:1 to about 50:1, from about 10:1 to about 100:1, from about 50:1 to about 200:1, from about 50:1 to about 400:1, from about 100:1 to about 500:1, from about 100:1 to about 1000:1, from about 200:1 to about 1000:1, or from about 500:1 to about 1000:1. Hydrogen product from the reaction leaves at the top of the column. In an embodiment, the column **40** may operate at any of the conditions (e.g., operating pressure, operating temperature, etc.) discussed herein with respect to column **10** in FIG. **3**. In addition, the column **40** may have any number of stages, and in an

embodiment, the column **40** may have a number of stages as described with respect to column **10** in FIG. **3**.

[0073] As schematically illustrated in FIG. **6**, the reactive distillation column **70** has two feeds **80**, **82** and uses two catalyst zones, identified as an upper zone **72** containing Catalyst A **74** and a lower catalyst zone **76** containing Catalyst B **78**. Ethanol feed **80** is fed to the upper part of the column **70** (upper feed). Hydrogen feed **82** is fed to the lower part of the column **70** (lower feed). The molar ratio of ethanol to hydrogen may fall within any of the ranges described above with respect to FIG. **5** (e.g., from about 1:10 to about 1000:1, and all sub-ranges). Ethanol may react over the upper catalyst (Catalyst A **74**) producing ethyl acetate and hydrogen. Examples of suitable upper catalysts are described in more detail herein with respect to the dehydrogenation and dimerization catalysts. As with previous schematic designs shown, the column **70** will usually include a top stage or non-reactive rectifying section **71** and a bottom state or non-reactive stripping section **79**.

[0074] Due to boiling point differences, hydrogen moves towards the top of the column **70** and ethyl acetate moves towards the bottom of the column **70**. Acetaldehyde may be produced during the reaction and may move up in the column **70**. At least a portion of the acetaldehyde, if present, can be condensed in condenser **84** and recycled back to the reaction zone through reflux tank **86**. Byproducts such as n-butyraldehyde and butan-2-one produced in the reaction can have boiling points close to the boiling point of ethyl acetate. The lower hydrogen feed is useful in hydrogenating the by-products over the lower catalyst (Catalyst B) to produce components that can be separated easily from ethyl acetate. Examples of hydrogenation catalysts (Catalyst B) are described in more detail herein. A product stream **88** comprising hydrogen from the reaction leaves at the top of the column **70**. A portion of the bottom draw is taken out as the ethyl acetate product stream **92**, while the remaining portion is passed through reboiler **90** to be recycled to the column **70**. In an embodiment, the bottom draw may be passed through a reboiler (e.g., similar to reboiler **90**) and optionally passed to a separator where the vapor portion may pass to the column **70** while at least a portion of the remainder is taken out as the ethyl acetate product stream **92**. The stream passing through the reboiler **90** provides the evaporation effect and vapor flow for operating the column **70**. The product stream **92** may comprise the ethyl acetate produced in the column along with unreacted ethanol and potentially any side products produced by the reaction. Subsequent purification of product stream **92** comprising ethyl acetate may be needed to remove the hydrogenated byproducts from the ethyl acetate, e.g., using a separator such as that as shown in FIG. **4** as separator **32**, which in an embodiment may comprise a distillation column.

[0075] In an embodiment, the column **70** may operate at any of the conditions (e.g., operating pressure, operating temperature, etc.) discussed herein with respect to column **10** in FIG. **3**. In addition, the column **70** may have any number of stages, and in an embodiment have any number of stages as described with respect to column **10** in FIG. **3**.

[0076] In the dual feed systems described above with respect to FIGS. **5** and **6**, the hydrogen feed should be at a sufficiently low level that it does not significantly adversely affect the dehydrogenation of ethanol in the zone above, while being effective to hydrogenate the undesirable close boiling point byproducts. Feed rates of hydrogen can be adjusted empirically to optimize this balance. Commonly, the

ratio of ethanol:hydrogen will be in a range of about 500:1 to 1:1 molar ratio, more commonly about 500:1 to 10:1 or 500:1 to 100:1.

[0077] In an embodiment, side reactors can be connected to a reactive distillation column to increase the catalyst holdup for improved reactant conversion. In the side reactor embodiment, the side reactor feed is withdrawn from the distillation column and the reactor effluent is returned back to the same column. An adequate amount of catalyst may be arranged in a side reactor system where traditional reactor types and catalyst structures can be used. Also, the reaction conditions within the side reactor such as temperature can be adjusted independently of those prevailing in the distillation column by appropriate heat exchange. In some embodiments, only the side reactor may comprise one or more catalysts, and the column may operate to separate the outlet of the side reactors. In this embodiment, the column may not contain a dehydrogenation catalyst, or in some embodiments, any catalyst at all.

[0078] Schematics for a side reactor reactive distillation column with a single catalyst are shown in FIG. **7**. A single side reactor is shown, however, multiple side reactors along the length of the reactive distillation column can be used. FIG. **7**(*a*) shows a configuration where the feed **93** to the side reactor **94** is bottom up and vapor phase. The outlet from side reactor **94** is stream **95** which is sent back to the distillation column **40** at any location in the column **40** above the location of feed **93**. FIG. **7**(*b*) shows a configuration where the feed **96** to the side reactor **97** is top down and liquid phase. The outlet from side reactor **97** is stream **98** which is sent back to the distillation column **40** at any location in the column **40** below the location of feed **96**. The side reactors **94** and **97** each contain catalyst for converting ethanol into ethyl acetate. Examples of suitable catalysts are described in more detail herein.

[0079] The use of a side reactor using a liquid feed may allow for the reaction to occur in the liquid phase. While not intending to be limited by theory, it is believed that the dehydrogenative dimerization of ethanol to ethyl acetate may occur over the dehydrogenation and dimerization catalysts described herein in the liquid phase. As noted above, it has not been previously recognized that the dehydrogenation and dimerization conversion of ethanol to ethyl acetate would occur in the liquid phase. The use of a liquid phase reaction may allow for reactive distillation to be effectively used for converting ethanol into ethyl acetate and hydrogen.

[0080] While illustrated as a bottom up vapor phase design and a top down liquid phase design in FIGS. **7**(*a*) and **7**(*b*), the side reactors **94**, **97** may also operate bottom up using a liquid phase draw from the column **40** and top down using a vapor phase draw from the column with the appropriate equipment such as pumps, compressors, valves, piping, etc. In an embodiment, the side reactors **94**, **97** may be implemented as a single reactor vessel, or as a plurality of reactor vessels arranged in series and/or parallel. In an embodiment, a plurality of side reactors may be implemented as shown in FIGS. **7**(*a*) and **7**(*b*) along the length of the column as needed. In addition, the catalyst in both the column **40** and the side reactor **94** may convert ethanol into ethyl acetate, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **40** and the side reactor **94**, **97** may be the same or different. Suitable catalysts for converting ethanol into ethyl acetate

may be selected based on the expected operating conditions, which may vary between the column **40** and the side reactor **94**, **97**.

[0081] Schematics for a side reactor reactive distillation with two feeds and using two distinct catalyst zones are shown in FIG. **8**. A single side reactor is shown for each catalyst zone in the reactive distillation column **70**, however, multiple side reactors along the length of the reactive distillation column **70** can be used for each catalyst zone. FIG. **8** (*a*) shows a configuration where the top zone feed **99** to the side reactor **100** is bottom up and vapor phase. The bottom zone feed **102** to another side reactor **103** is also bottom up and vapor phase. The outlet from side reactor **100** is stream **101** which is sent back to the distillation column at any location in the column above the location of feed **99**. The outlet from side reactor **103** is stream **104** which is sent back to the distillation column at any location in the column above the location of feed **102**. FIG. **8** (*b*) shows a configuration where the top zone feed **105** to the side reactor **106** is top down and liquid phase. The bottom zone feed **108** to another side reactor **109** is also top down and liquid phase. The outlet from side reactor **106** is stream **107** which is sent back to the distillation column at any location in the column below the location of feed **105**. The outlet from side reactor **109** is stream **110** which is sent back to the distillation column at any location in the column below the location of feed **108**. Examples of suitable catalysts for side reactors **100** and **106** may include any of the dehydrogenation and dimerization catalysts described in more detail herein. Examples of hydrogenation catalysts for side reactors **103** and **109** include any of the hydrogenation catalysts described in more detail herein.

[0082] While illustrated as a bottom up vapor phase design and a top down liquid phase design in FIGS. **8**(*a*) and **8**(*b*), the side reactors **100**, **103**, **106**, **109** may also operate bottom up using a liquid phase draw from the column **70** and top down using a vapor phase draw from the column **70** with the appropriate equipment such as pumps, compressors, valves, piping, etc. In an embodiment, the side reactors **100**, **103**, **106**, **109** may be implemented as a single reactor vessel, or as a plurality of reactor vessels arranged in series and/or parallel. In an embodiment, a plurality of side reactors may be implemented as shown in FIGS. **8**(*a*) and **8**(*b*) along the length of the column as needed. In addition, the respective catalysts in the column **70** and/or the side reactors **100**, **106** may convert ethanol into ethyl acetate, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **40** and the side reactors **100**, **106** may be the same or different. Suitable catalysts for converting ethanol into ethyl acetate may be selected based on the expected operating conditions, which may vary between the column **40** and the side reactors **100**, **106**. Similarly, the respective catalysts in the column **70** and/or the side reactors **103**, **109** may comprise hydrogenation catalysts, though the specific catalysts (e.g., catalyst compositions, catalyst forms, and/or catalyst component loadings) in each of the column **70** and the side reactors **103**, **109** may be the same or different. Suitable hydrogenation catalysts may be selected based on the expected operating conditions, which may vary between the column **70** and the side reactors **100**, **106**.

[0083] As schematically illustrated in FIG. **9**, an ethyl acetate production system **200** may comprise a products separation and/or purification section **212** for use in removing a portion of any byproducts or impurities from the product

stream. In some embodiments, the ethyl acetate product stream produced in the processes and systems described herein may comprise one or more impurities. In some embodiments, the ethyl acetate product stream produced in the reactive distillation systems described with respect to FIG. **3-8** may comprise less than about 10 wt. %, less than about 8 wt. %, less than about 6 wt. %, less than about 4 wt. %, less than about 2 wt. %, or less than about 1.5 wt. % impurities, and in some embodiments, more than about 0.01 wt. %, more than about 0.1 wt. %, more than about 0.5 wt. %, or more than about 1 wt. %. The products separation section **212** may be configured to provide at least one product stream **216** comprising ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight. At least one additional stream **218** may be produced comprising the remaining components of the product stream **210** from the ethyl acetate production process **206** (e.g., a reactive distillation column as described above). In an embodiment, a plurality of streams can be produced in the separation section comprising a stream **216** predominantly comprising ethyl acetate, and a stream **218** predominantly comprising the impurities removed from the ethyl acetate. In some embodiments, the product stream **216** may undergo further processing to remove one or more impurities. For example, an optional dehydration process may be carried out to remove any water present in the product stream **216**.

[0084] As schematically illustrated in FIG. **9**, a system **200** for producing ethyl acetate may comprise a feed stream **202** comprising ethanol that can be fed to the reactive distillation system **206**. In an embodiment, the reactive distillation system **206** may comprise any of the reactive distillation systems described with respect to FIG. **3-8** herein. The reactive distillation system may produce an overhead product stream **208** and a bottoms product stream **210**. The overhead product stream **208** may comprise hydrogen along with trace amounts of other light components (e.g., ethanol, etc.) and may generally correspond to any of the streams **19**, **59**, and/or **88** as illustrated in FIGS. **3-8**. Similarly, the bottoms product stream **210** may comprise ethyl acetate, at least a portion of any unreacted ethanol, and/or additional reaction products (e.g., byproducts, impurities, etc.), and the bottoms product stream **210** may generally correspond to any of the streams **22**, **36**, **58**, and/or **92** as illustrated in FIGS. **3-8**.

[0085] A products separation section **212** may receive the bottoms product stream **210** from the reactive distillation system **206**. The products separation section **212** may comprise any number or type of separation units, which may employ pressure- or temperature-swing distillation, pressure- or temperature-swing adsorption, membrane-based separation, cryogenic distillation, extraction, and/or any other suitable separation technology, all of which may be used to generate a desired product distribution. The products separation section **212** may generally produce an ethyl acetate product stream **216**. The ethyl acetate product stream **216** may comprise ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight. In addition to the ethyl acetate product stream **216**, one or more additional streams may be produced by the products separation section **212**. In an embodiment, an impurities stream **218** may be produced. The impurities stream **218** may comprise

one or more reaction products (e.g., butanol, one or more aldehydes and/or ketones, etc.). Each of the potential product streams **216**, **218** may exit the system as separate product streams and/or exit the system **200** for use as fuel and/or as a feed to additional downstream processes. While illustrated as separate streams **216**, **218** one or more of these streams may exit the system **200** as a combined product stream.

[0086]   In an embodiment as shown in FIG. **10**, the separation section **212** may comprise an extraction process **300** for removing a portion of the impurities in the product stream **210**. For example, an extraction process **300** may be used to separate at least a portion of one or more byproducts from the ethyl acetate in the product stream **210**, thereby improving the quality and value of the ethyl acetate product stream. In this embodiment, the separation section **212** used to carry out the extraction process **300** may be the same or similar to the separation section described above with respect to FIG. **9**. The extraction process **300** generally comprises an extraction section **250** in which the product stream **210** is contacted with a solvent in a solvent stream **254** to transfer or remove at least a portion of the impurities from the product. The extract stream **256** comprising the impurities transferred from the product can then be regenerated in a stripping section **252**, which generally involves separating the impurities from the solvent to allow the impurities to be removed from the system and the solvent to be recycled.

[0087]   The extraction process **300** may receive the bottoms product stream **210** from a reactive distillation system, which may comprise any of the reactive distillation systems described with respect to FIG. **3-8** herein. The extraction process **300** may comprise the extraction section **250** in which the bottoms product stream **210** is contacted with a solvent in a solvent stream **254**. In an embodiment, the extraction section **250** comprises a liquid-liquid contact vessel suitable for contacting two liquid streams. Suitable vessels and extraction section **250** configurations are described in more detail herein. The solvent may draw a portion of one or more impurities from the bottoms product stream **210** into the solvent phase. The bottoms product stream **210** having the portion of the impurities removed may then exit the extraction section **250** as a purified product stream **216**. The extract comprising the solvent and the portion of the impurity compound transferred from the bottoms product stream **210** may then exit the extraction section **250** as an extract stream **256**.

[0088]   An optional drying section **258** may serve to remove any remaining solvent or a component of a solvent (e.g., water from an aqueous solvent) from the purified product stream **216**. The resulting dried purified product stream **260** may then leave the system as the final product stream. Any suitable drying units may be used to remove at least a portion of the solvent from the purified product stream **216**. Suitable drying units may include, but are not limited to, industrial dehydration units comprising adsorbents such as Zeolites, alumina, silica, and other drying agents arranged in a pressure and/or temperature swing configuration, and/or liquid absorption (e.g., liquid-liquid extraction, gas-liquid extraction, etc.) using a drying agent. The purified product stream **216** and/or the dried purified product stream **260** may comprise ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0089]   In order to separate the impurities from the solvent, the extract stream **256** may be transferred to a stripping sec-

tion **252**. In an embodiment, the impurities may be removed using vapor-liquid stripping, heating, liquid-liquid phase separation, flashing and/or distillation, and/or any other suitable technique. Suitable vessels and stripping section **252** configurations are described in more detail herein. As shown in FIG. **10**, the stripping section **252** may result in the separation of the impurities from the extract stream **256**, thereby producing a liquid impurities stream **218** and/or a vapor impurities stream **262**, and a regenerate solvent stream **254**. In some embodiments, different components of the impurities may leave the separation section **212** as either a vapor or a liquid, including those generated by the solvent and/or any reactions within the separation section **212**. The solvent may be regenerated by removing at least a portion of the impurities in the stripping section **252**. In some embodiments, only a portion of any extracted impurities can be removed in the stripping section **252**, and the resulting regenerated solvent stream **254** may comprise a minor amount of impurities. The regenerated solvent stream **254** may be recycled to the extraction section **250** to serve as the solvent. In some embodiments, a new solvent stream (e.g., a makeup solvent stream) may enter the extraction section separately or with the regenerated solvent stream **254** to serve as the solvent in the extraction section **250**. The liquid impurities stream **218** and/or vapor impurities stream **262** may exit the system for various downstream uses. In an embodiment, the impurities stream may comprise commercially valuable chemicals that can be transferred for sale. In some embodiments, the impurities may be further separated before being sold, or alternatively, the impurities can be used as fuel or any other suitable use.

[0090]   When used with the ethyl acetate production systems and processes describe herein, the solvent used in the extraction process **300** may be selected to remove the expected impurities within the ethyl acetate product stream (e.g., bottoms product stream **210**). As noted above, the synthesis of ethyl acetate by consecutive dehydrogenation and condensation of ethanol to ethyl acetate is accompanied by the formation of relatively small amounts of byproducts. At least a portion of the byproducts comprising various aldehydes, ketones, and the like can be removed to improve the quality and purity of the ethyl acetate. In an embodiment, the extraction process **300** can be used to selectively extract at least a portion of the byproducts that may be present in the ethyl acetate. In an embodiment, the solvent may be configured to selectively react with and extract the impurities in the ethyl acetate. For example, the solvent may comprise one or compounds configured to reversibly react with the impurities, thereby allowing the reaction to remove the impurities from the ethyl acetate in the extraction section **250** and then be reversed to release the impurities in the stripping section **252**.

[0091]   In an embodiment, the solvent may comprise a fluid comprising one or more extracting agents. In an embodiment, the extracting agent may comprise a nucleophilic compound that can react with aldehydes and/or ketones to form a corresponding adduct. The resulting reaction products may have an increased solubility in the aqueous fluid, thereby allowing the adducts to leave the ethyl acetate product stream **210** and enter the solvent stream **254** to form the extract stream **256**. Within the stripping section **252**, the adduct equilibrium may be shifted to release the extracting agents from the impurities. The impurities may then be separated from the solvent comprising the extracting agents using any suitable separation technique such as vaporization and/or liquid-liquid separation.

[0092] Various extracting agents can be used in the aqueous solvent. In an embodiment, the extracting agents can comprise sulfur and/or nitrogen. Suitable extracting agents can include, but are not limited to, hydrazine (N_2H_4), hydroxylamine (NH_2OH), semicarbazide ($H_2NNH(C=O)NH_2$), phenylhydrazine ($C_6H_5N_2H_3$), phenylhydroxylamine (C_6H_5NHOH), sodium hydrogen sulfite ($NaHSO_3$/$Na_2S_2O_5$), sodium sulfite (Na_2SO_3), salts thereof, aqueous solutions thereof, and any combinations thereof. While any of these extracting agents can be used, reference will be made to sodium hydrogen sulfite in the following discussion as an example.

[0093] In an embodiment, an aqueous solution of sodium hydrogen sulfite (which can also be referred to as sodium bisulfite) can be used as the solvent in the extraction process **300**. Sodium hydrogen sulfite can be sourced as a solid, which usually comprises a mixture of $NaHSO_3$ and $Na_2S_2O_5$. An aqueous solution can be made from the salt, and the use of an aqueous solution of sodium hydrogen sulfite provides an inexpensive, low toxicity solution that can serve as the solvent in the extraction process. Additional extracting agents can include sodium sulfite (Na_2SO_3). Sodium sulfite can be used by directly dissolving sodium sulfite in a solvent, or sodium hydroxide (NaOH) can be added to sodium hydrogen sulfite as a solid or in solution. Further a mixture of sodium hydrogen sulfite and sodium sulfite can be used in an ratio. The reactive moiety in the aqueous solution of sodium hydrogen sulfite is the hydrosulfite ion (HSO_3^-/$S_2O_5^{2-}$) and reactive moiety in an aqueous solution of sodium sulfite is the sulfite ion (SO_3^{2-}). Thus any soluble hydrosulfite and/or sulfite compound can also be used in similar manner regardless of the counter ion. For example hydrosulfite compounds including K^+, NH_4^+ salts can also be used along with or in place of sodium hydrogen sulfite.

[0094] The aqueous solution comprising the hydrosulfite ion reacts reversibly with aldehydes and ketones such as 2-butanone, acetone, acetaldehyde, thereby rendering them more water soluble as sodium salts of hydrosulfite adducts of the corresponding compounds. For example, the following reaction may take place when the aqueous solution comprising the hydrosulfite ion is contacted with a fluid comprising a ketone (e.g., 2-butanone) as follows:

$$Na^+ + HSO_3^- + CH_3C(=O)CH_2CH_3 \leftrightarrows CH_3C(OH)(SO_3^-)CH_2CH_3 \cdot Na^+$$
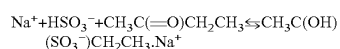
The resulting sodium salt of the 2-butanone sulfonate adduct has higher solubility in water compared to ethyl acetate thus leading to partial extraction of 2-butanone from the organic (ethyl acetate) phase, thereby increasing the ethyl acetate phase purity. The resulting adduct may be formed by various aldehydes and/or ketones, thereby providing for the ability to selectively improve the removal efficiency of the impurities generated in the ethyl acetate production process during the extraction section **250**.

[0095] Within the extraction process **300**, various factors may affect the extraction efficiency of the solvent within the extraction section **250** including the concentration of the extracting agent in the solvent, the ratio of the solvent to the ethyl acetate product, and the temperature at which the extraction takes place. With respect to the concentration of the extracting agent in the solvent, there are several considerations that can have an affect on the concentration of the compound in the solvent. In general, a higher concentration of the extracting agent (e.g., $NaHSO_3$) in the aqueous fluid can reduces the ethyl acetate solubility in the solution. However,

as the concentration of the extracting agent rises above a certain amount, the resulting adduct may precipitate out of solution. Such precipitation may complicate a continuous process in terms of solids handling equipment. In general, the amount of the extracting agent in the aqueous fluid should be sufficient to provide an excess of the ions in solution but less than an amount that would result in precipitation of the resulting adduct in the extract, which indicates that the solubility limit of the adduct has been reached. Thus, the concentration of the extracting agent in the solvent may vary based on the concentration of the impurities in the ethyl acetate product stream. In an embodiment, the concentration of the extracting agent (e.g., sodium hydrogen sulfite) in the aqueous solution can vary. In an embodiment, the extracting agent can comprise sodium hydrogen sulfite, and the amount of sodium hydrogen sulfite in the aqueous solution can vary and may generally range from about 50 grams to about 420 grams, from about 300 grams to about 420 grams of solid (e.g., a mixture of $NaHSO_3$ and $Na_2S_2O_5$) per liter of water. When the extracting agent is sodium hydrogen sulfite, the concentration may generally range from about 5 to about 42 grams per 100 milliliters of solution, or from about 30 to about 42 grams per 100 milliliters of solution at about 68° F. (about 20° C.). In an embodiment, the extracting agent may be provided in the form of sodium sulfite and/or a hydrate thereof, and the concentration may generally range from about 5 to about 68 grams per 100 milliliters of solution when the sodium sulfite is provided as sodium sulfite heptahydrate. The concentration of the extracting agent may vary based on the composition of the extracting agent, the form in which it is provided, the temperature of the solution, the composition of the solution, and the like.

[0096] With respect to the temperature at which the extraction process takes place, it has been discovered that the extraction efficiency of the impurities in the ethyl acetate with the aqueous solvent generally increases at a lower temperature relative to a higher temperature extraction. Accordingly, lowering the temperature of the extraction process may result in a greater amount of the impurities being transferred from the ethyl acetate product to the solvent stream. In general, the extraction section **250** may operate within a temperature of between about 10° C. to about 70° C., from about 15° C. to about 60° C., or from about 20° C. to about 50° C.

[0097] Once the aqueous solvent contacts the ethyl acetate product stream (e.g., bottoms product stream **210**) in the extraction step **250**, the aqueous fluid comprising the adducts can be separated from the organic ethyl acetate phase using liquid-liquid separation. The separated extract stream **256** can then be used to perform an additional extraction of impurities from an ethyl acetate product stream and/or the extract can be transferred to the stripping section **252** for regeneration. In general, the extract stream **256** comprising the adducts can be treated in the stripping section **252** to separate the organic compounds (e.g., the impurities, any dissolved ethyl acetate, etc.) from the aqueous solvent comprising the extracting agent. For example, the extract stream may be heated to reverse the adduct formation, and the organic phase can then be separated from the aqueous solution. In some embodiments, the adducts may be separated by crystallization followed by a subsequent treatment of the precipitated solids.

[0098] When the adducts remains dissolved in the aqueous fluid, the adducts can be decomposed by heating to reverse the equilibrium and release the impurities (e.g., the aldehydes/ketones) while regenerating the aqueous solution comprising

the extracting agent for reuse. The impurities can then be separated using evaporation, distillation, and/or liquid-liquid phase separation. In an embodiment, the aqueous solution (e.g., the extract stream **256**) may comprise the excess of sodium hydrogen sulfite, the dissolved sodium hydrogen sulfite adducts, and some amount dissolved ethyl acetate. The solution can be regenerated by heating the solution to a temperature suitable to reverse the adduct formation equilibrium. In an embodiment in which the nucleophile compound comprises sodium hydrogen sulfite, the regeneration can be achieved by heating the solution to a temperature between about 45° C. and about 100° C. At this temperature, the sodium hydrogen sulfite adduct decomposes to release the impurities and the NaHSO₃. The released impurities and any dissolved ethyl acetate can be separated from the aqueous solution and collected. In some embodiments, the organic compounds can be vaporized (e.g., in a flash tank) or distilled from the aqueous solution, and/or alternatively the organic compounds can be separated based on a liquid-liquid phase separation. The remaining aqueous solution may comprise the regenerated solvent for use in the extraction process **300**. In an embodiment, the separation process within the stripping section **252** may result in some minor amount of the organic compounds remaining in the aqueous solvent.

[0099] During the heating process some amount of the extracting agent may decompose to form an additional impurity. For example, when the extracting agent comprises sodium hydrogen sulfite, heating may result in some sulfur dioxide being lost due to decomposition. The decomposition products can be captured using an aqueous NaHSO₃ solution or an aqueous caustic solution (e.g., NaOH), which may be advantageous in preventing the release of the decomposition products to the atmosphere. The regenerated solvent solution in the stream **354** may have higher or lower extracting agent concentration than desired. The concentration may be adjusted through the addition of water, solid extracting agent, or an extracting agent solution until the desired concentration is reached.

[0100] In some embodiments, the adducts can be removed from the extract stream **256** by crystallization. For example, the adducts can be separated from the extract stream **256** by forming a sodium ketone/aldehyde hydrosulfite adduct crystals. If the adducts are crystallized out of solution, the resulting crystals can be separated physically. The crystals can then be heated to reverse the adduct formation. In an embodiment, the crystals may be dissolved in an aqueous solution prior to heating to reverse the adduct formation. The resulting organic impurities can then be separated from the extracting agent and any aqueous solution.

[0101] The extraction process can be carried out using various configurations and designs. An embodiment of an extraction process **350** is schematically illustrated in FIG. **11**. In this embodiment, a product stream **310** is fed to the extraction section **302**. The product stream may generally correspond to any of the streams **22**, **36**, **58**, and/or **92** as illustrated in FIGS. **3-8**. The product stream **310** may predominantly comprise ethyl acetate, though various byproducts including ketones and/or aldehydes such as 2-butanone, acetone, and/or acetaldehyde may also be present.

[0102] The extraction section **302** may also receive a solvent stream **319**. In an embodiment, the solvent stream **319** may comprise an aqueous fluid and an extracting agent as described above. The solvent comprising the extracting agent may comprise an aqueous solution of hydrazine (N₂H₄),

hydroxylamine (NH₂OH), semicarbazide (H₂NNH(C=O)NH₂), phenylhydrazine (C₆H₅N₂H₃), phenylhydroxylamine (C₆H₅NHOH), sodium hydrogen sulfite (NaHSO₃/Na₂S₂O₅), sodium sulfite (Na₂SO₃), salts thereof, aqueous solutions thereof, and any combination thereof. Additional solvents useful with the extraction process can include dichloromethane-ethanol and methyl isobutyl ketone (MIBK). The extraction section **302** may comprise one or more liquid-liquid contact devices configured to contact the two liquid streams **319**, **310**. Various liquid-liquid contact devices can be used including an extraction column, which may comprise packing material (e.g., structured packing, random packing, trays, etc.) configured to increase mixing and the available contact area for mass transfer between the two liquids. Additional suitable structures can include a series of mixer settlers, sieve trays, a Kerr-McGee extractor, a packed tower, a rotating disk contactor, a Scheibel extractor, a pulsed column, and a centrifugal extractor. The extraction may be carried out in a co-current, counter-current, and/or cross-current flow scheme, each of which is described in more detail below with respect to FIGS. **13**, **14**, and **15**, respectively. In an embodiment, the extraction section can comprises a counter-current flow arrangement between the solvent and product streams.

[0103] A contact device within the extraction section may comprise a number of stages configured to provide the degree of impurity removal from the product stream **310** and/or a desired purity of the purified ethyl acetate product stream. In an embodiment, the contact device, or a plurality of contact devices, can contain between about 1 to about 100 stages, or between about 1 to about 50 stages. The contact device or contact devices may operate at any suitable pressure. In an embodiment, the contact device may operate at a pressure ranging from about 1 atm to about 80 atm, and a temperature of between about 10° C. to about 70° C., from about 15° C. to about 60° C., or from about 20° C. to about 50° C.

[0104] Within the extraction section **302**, at least a portion of the impurities may be transferred to the solvent. In an embodiment, the extracting agent may react with a portion of the impurities in the product stream **310** to form an adduct and improve the solubility of the impurity in the solvent phase. Once the product stream **310** and the solvent stream **319** have been contacted and separated within the extraction section **302**, a purified product stream **216** and an extract stream **256** may exit the extraction section **302**. The purified product stream **216** may have an increased purity of ethyl acetate relative to the entering product stream **310**. As described above, the purified product stream **216** may pass to a drying unit to further remove any solvent to further purify the purified product stream. In an embodiment, the purified product stream **216** and/or a dried, purified product stream may comprise ethyl acetate having a purity of greater than about 90%, greater than about 95%, greater than about 96%, greater than about 97%, greater than about 98%, greater than about 99%, or greater than about 99.5% ethyl acetate by weight.

[0105] The extract stream **256** may comprise the solvent and the impurities removed from the product stream **310**. The extract stream **256** may pass to the stripping section **304**. In an embodiment, the extract stream **256** may comprise a solvent fluid, the adducts formed by the reaction between the extracting agent and the impurities, any excess extracting agent, and potentially some amount of dissolved ethyl acetate. The stripping section **304** may comprise one or more separation devices configured to separate the impurities from the solvent

and any extracting agent. Various separation devices can be used including phase separators and liquid-liquid separators. In an embodiment, the separation device within the stripping section 304 may comprise a flash tank. In this embodiment, the extract stream 256 may enter the flash tank, be heated to a temperature sufficient to dissociate the adduct, and evaporate at least a portion of any impurities and dissolved ethyl acetate. The flash tank may operate at a pressure ranging from about 1 atm to about 80 atm, and a temperature of between about 70° C. to about 120° C., or from about 85° C. to about 100° C. In some embodiments, the separation device may comprise a distillation column. The extract stream 256 can be heated within the distillation column to dissociate the adducts into the impurities and the extracting agent within the solvent. The impurities may then be separated by distillation. The distillation column may comprise about 1 to about 100 stages, or about 1 to about 50 stages. The distillation column may operate at a pressure ranging from about 1 atm to about 80 atm. The temperature and pressure may be selected based on the equilibrium on each stage within the distillation column. In an embodiment, the temperature within the column may range from about 50° C. to about 200° C., or from about 70° C. to about 150° C.

[0106] In an embodiment, the stripping section may operate at a vacuum pressure relative to atmospheric pressure. A lower operating pressure is generally expected to reduce the temperature at which the solvent can be separated from the impurities when the adducts are dissociated. In an embodiment, the stripping section may operate at a pressure ranging from about 0.001 atm to about 1 atm and at a temperature of between about 45° C. and about 100° C. In general, the solvent and/or extracting agent may break down during the heating process in the stripping section, potentially releasing contaminants into the vapor stream. By operating at a reduced pressure, and resulting reduced temperature, the rate of solvent and/or extracting agent loss may be reduced. For example, by lowering the temperature at which the stripping occurs, the rate at which any hydrosulfite/sulfite in solution breaks down to form sulfur dioxide can be reduced or limited.

[0107] When the stripping section 304 comprises a phase separator, an overhead product stream 306 may exit the stripping section 304 and pass to a condenser 308. The overhead stream 306 may comprise the separated impurities, dissolved ethyl acetate, and potentially minor amount of water and decomposition products resulting from a breakdown of the extracting agent. Within the condenser 308, the temperature of the overhead stream 306 may be reduced to condense the impurities into a liquid, which may leave the condenser 308 as an impurities stream 312. The impurities stream 312 may exit the system for sale, for use as fuel, and/or as a feed to one or more suitable downstream processes. Any remaining gases may exit the condenser as an off-gas stream 310. The off-gas stream 310 may comprise a portion of the vaporized impurities, ethyl acetate, and any decomposition products from the solvent. The off-gas stream 310 can be vented to the atmosphere or a flare, or as shown in FIG. 11, recycled to be combined with the regenerated solvent stream 307. The regenerated solvent stream 307 may leave the stripping section 304 as a bottoms stream and pass to the contactor 314. The off-gas stream 310 may then be re-absorbed within the contactor 314. The combined regenerated solvent stream 254 may pass to a heat exchanger 316, which may comprise any of the types of heat exchangers described herein. The regenerated solvent stream 254 may be cooled within the heat

exchanger 316 to a temperature suitable to allow the extracting agent within the solvent to form an adducts with any corresponding impurities in the product stream 310. The cooled, regenerated solvent stream 254 may then be combined with an optional solvent make-up stream 318 to form the solvent stream 319. The make-up stream may include the solvent comprising the extracting agent in any suitable concentration. In an embodiment, the make-up stream may server to adjust the concentration of the extracting agent within the solvent stream 319 to a desired level.

[0108] In some embodiments, the stripping section 304 may comprise a liquid-liquid separator. The liquid-liquid separator may operate at a pressure ranging from about 1 atm to about 80 atm. The extract stream 256 may be heated to a temperature in the range of between about 40° C. to about 120° C., or from about 45° C. to about 100° C. within the separator, which may be sufficient to dissociate the adduct. The impurities may then form an organic liquid phase that is at least partially insoluble in the aqueous solvent. The resulting phases may be separated in a liquid-liquid phase separation device, such as a settling tank or settling tower. Suitable draw points may be used to provide a regenerated solvent stream 307 and an organics stream 306. The organics stream 306 may leave the system without any further separation or processing. The liquid-liquid separator may comprise a gas vent suitable for passing any off-gases back to the contactor 314. The aqueous phase may leave the liquid-liquid separator as the regenerated solvent stream 307 and pass back to the extractor through the contactor 314 and heat exchanger 316 as described above.

[0109] FIG. 12 illustrates an embodiment of a stripping section 354 that is similar to the stripping section 304 described with respect to FIG. 11. In the interest of clarity, similar components will not be described. The stripping section 354 may comprise any of the separation devices operating at any of the operating conditions as described above with respect to FIG. 11, and the stripping section 354 can be used with the remaining components of the extraction process 350 illustrated in FIG. 11. The stripping section 354 differs from the stripping section 304 of FIG. 11 in that a purge gas stream 364 can be introduced into the stripping section 354, which can aid in the extraction of the impurities from the solvent solution. In an embodiment, the purge gas can comprise a gas having a boiling point significantly below that of the impurities, and the purge gas may have a low solubility in the solvent and/or impurities to aid in separation from the solvent and impurities. The purge gas can include, but is not limited to, nitrogen, oxygen, argon, helium, hydrogen, carbon dioxide, and any combination thereof (e.g., air). The use of the purge gas may aid in removing the impurities from the extract stream 256 while maintaining a relatively low stripping temperature. The use of the low temperature may aid in limiting or reducing the breakdown of the solvent and/or extracting agent, which can potentially resulting the generation of pollutants.

[0110] The extract stream 256 can be introduced into the stripping section 354 and can include a solvent fluid, the adducts formed by the reaction between the extracting agent and the impurities, any excess extracting agent, and potentially some amount of dissolved ethyl acetate. As the liquid extract stream 256 flows through the stripping section, a purge gas stream 364 can be introduced into the lower portion of the stripping section 354. The ratio of the purge gas volumetric flow rate to the extract stream volumetric flowrate can

range from about 1,000:1 to about 1:100, and the ratio may be based on the amount of impurities present in the extract stream, the conditions within the stripping section 354, and/or the solubility of the impurities in the purge gas. The extract stream 256 can be heated to a temperature in the range of about 45° C. to about 100° C. before and/or within the stripping section 354, resulting in at least a partial dissociation of the adducts. Vapor-liquid stripping can then take place between the impurities released from the adducts and the purge gas. Since the impurities would generally have a lower boiling point than the solvent, the impurities could expect to be stripped into the purge gas stream.

[0111] The stripping section 354 can have an overhead product stream 356 that can pass to a cooler 358 and into a separator 360. The overhead stream 356 may comprise the purge gas, impurities stripped by the purge gas, and potentially minor amount of solvent, ethyl acetate, and decomposition products resulting from a breakdown of the extracting agent. Within the cooler 358, the temperature of the overhead stream 356 may be reduced to condense the impurities into a liquid, which may then pass to the separator 360 and leave as an impurities stream 362. The impurities stream 362 may exit the system for sale, for use as fuel, and/or as a feed to one or more suitable downstream processes. The purge gas may not condense and may pass out of the separator 360 as the purge gas stream 364 for recycle to the stripping section 354. The purge gas stream 364 may comprise a minor amount of the impurities, the solvent, and the decomposition products, that can reach an equilibrium in the process due to the recycling of the purge gas stream 364. The regenerated solvent stream 307 can be processed and/or recycled as described with respect to the regenerated solvent stream in FIG. 11.

[0112] The extraction section may comprise a number of flow configurations. The extraction may be carried out in a co-current, counter-current, and/or cross-current flow scheme, as schematically illustrated in FIGS. 13, 14, and 15, respectively. An embodiment of a co-current extraction scheme is illustrated in FIG. 13. In this embodiment, the extraction section may comprise a plurality of stages 402, 404, 406. For each stage 402, 404, 406, the product stream 310 and the solvent stream 319 may enter the stage and flow together through the stage. The solvent and product may be separated within the stage, for example using a settler/phase separator. Each phase may then pass to the next stage as separate phases. Alternatively, the combined fluids may pass to the next stage as a single stream. In general, the co-current flow of solvent and product may allow the two streams to reach an equilibrium, and therefore, the co-current flow may only provide an extraction equivalent to a single theoretical stage. However, additional stages may be useful in practice to provide additional residence/contact time to approach the equilibrium concentrations and mass transfer of the impurities from the ethyl acetate product into the solvent phase. The solvent phase may be separated from the product phase within the last stage or within a separator downstream of the last stage to produce the extract stream 256 and the purified product stream 216. While illustrated as separate stages 402, 404, 406, the stages may be present in a single physical vessel. Further, while three stages 402, 404, 406 are shown in FIG. 13, less than three stage or more than three stages may be used. In an embodiment, the number of stages may be between about 1 and about 50 stages.

[0113] An embodiment of a counter-current extraction scheme is illustrated in FIG. 14. In this embodiment, the extraction section may comprise a plurality of stages 408, 410, 412. The product stream 310 may enter at a first of the stages and the solvent stream 319 may enter the last stage and flow countercurrently through each stage. The phases may be arranged to allow the phases to flow countercurrently based on density differences, with the organic product phase flow upwards and the aqueous solvent phase flow downwards. The countercurrent flow of the product and solvent may result in the most efficient extraction and mass transfer of the three flow schemes. The solvent phase may be separated from the product phase within the first stage 408 to allow the extract stream 256 to leave the extraction section 302. Similarly, the product phase may be separated from the solvent phase within the last stage 412 to allow the purified product stream 216 to leave the extraction section 302. While illustrated as separate stages 408, 410, 412, the stages may be present in a single physical vessel. Further, while three stages 408, 410, 412 are shown in FIG. 14, less than three stage or more than three stages may be used. In an embodiment, the number of stages may be between about 1 and about 50 stages.

[0114] An embodiment of a cross-current extraction scheme is illustrated in FIG. 15. In this embodiment, the extraction section may comprise a plurality of stages 414, 416, 418. The product stream 310 may enter at a first of the stages and progress through each stage 414, 416, 418. The solvent stream 319 can be divided into portions 420, 422, 424, which may have the same or different flow rate. The portions 420, 422, 424 may pass to each stage 414, 416, 418, respectively, to contact the product within each stage 414, 416, 418. Within each stage 414, 416, 418, the solvent phase may be separated from the product phase, and the solvent phase portions may be recombined to form extract stream 256. The solvent phase may pass out of the last stage 418 as the purified product stream 216. The use of the cross-current flow configuration may allow the concentration of the impurities in the ethyl acetate product stream to be decreased in each stage. In an embodiment, the cross-current extraction scheme may comprise separate vessels (e.g., contactors, settlers, etc.) for each stage. In some embodiments, the stages may be present in a single physical vessel with internal contactors and separators. Further, while three stages 408, 410, 412 are shown in FIG. 15, less than three stage or more than three stages may be used. In an embodiment, the number of stages may be between about 1 and about 50 stages.

[0115] While described separately, the extraction section 302 may comprise any combination of the extraction schemes illustrated in FIGS. 13, 14, and 15. For example, each stage of the cross-current flow scheme may comprise a co-current or counter-current individual flow scheme. Various other combinations may also be possible.

Dehydrogenation and Dimerization Catalysts

[0116] Suitable dehydrogenation and dimerization catalysts are capable of converting at least a portion of the alcohol (e.g., ethanol) in a feed stream to a higher valued product such as ethyl acetate. Any catalyst capable of carrying out a dehydrogenation and dimerization reaction may be used alone or in combination with additional catalytic materials in the reactors. In an embodiment, suitable dehydrogenation and dimerization catalysts can generally comprise metals and/or oxides of copper, barium, ruthenium, rhodium, platinum, palladium, rhenium, silver, cadmium, zinc, zirconium, gold, thallium, magnesium, manganese, aluminum, chromium, nickel, iron, molybdenum, sodium, strontium, tin, and mixtures thereof.

In many cases, the catalyst material will be provided on a support material. The catalyst can be treated with a carbonate (e.g., sodium carbonate), reduced with hydrogen, and/or other suitable treatments prior to use.

[0117] In certain embodiments, the dehydrogenation and dimerization catalyst may include a catalyst support. The catalyst support stabilizes and supports the catalyst. The type of catalyst support used depends on the chosen catalyst and the reaction conditions. Suitable supports may include, but are not limited to, carbon, silica, silica-alumina, alumina, zirconia, titania, ceria, vanadia, nitride, boron nitride, heteropolyacids, hydroxyapatite, zinc oxide, chromia, zeolites, carbon nanotubes, carbon fullerenes, and any combination thereof.

[0118] The dehydrogenation and dimerization catalyst can be employed in any of the conventional types or structures known to the art. It may be employed in the form of extrudates, pills, pellets, granules, broken fragments, or various special shapes. In an embodiment, consideration of the use of the catalyst in the reactive distillation system and/or as a mass transfer surface within the distillation column may be taken into account when determining a suitable shape. For example, the catalyst may have a shape similar to structured packing material or suitable for insertion in a structured packing. When the hydrogenation catalyst is used with one or more side reactors, the catalyst may be disposed within a reaction zone, and the feed may be passed therethrough in the liquid, vapor, or mixed phase, and in either upward or downward, or inward or outward flow.

[0119] The dehydrogenation and dimerization catalyst may typically have a range of metal loadings. In an embodiment, the catalyst may have a copper oxide weight loading (i.e., weight percentage) of between about 0.5% and about 90%, between about 10% and about 70%, between about 20% and about 65%, between about 30% and about 60%, or about 40% and about 50%. In an embodiment, the catalyst may have a zinc oxide weight loading of between about 20% and about 60%, between about 30% and about 50%, or between about 40% and about 50%. In an embodiment, the catalyst may have a chromium oxide weight loading of between about 20% and about 60%, or between about 30% and about 50%.

[0120] In an embodiment, the catalyst may comprise CuO/ZnO/Al$_2$O$_3$. In this embodiment, the catalyst may have a copper oxide weight loading of between about 0.5% and about 90%, between about 10% and about 70%, between about 20% and about 65%, between about 30% and about 60%, or about 40% and about 50%, and the zinc oxide and alumina may comprise the balance of the weight. In an embodiment, the catalyst may comprise CuO/ZnO/ZrO$_2$/Al$_2$O$_3$, and the catalyst may have a copper oxide weight loading of between about 40% to about 90%, with the remainder of the components forming the balance of the catalyst weight. In an embodiment, the catalyst may comprise CuO/ZnO/ZrO$_2$/Cr$_2$O$_3$, and the catalyst may have a copper oxide weight loading of between about 20% to about 90% and a chromium oxide weight loading between about 30% and about 50%, with the remainder of the components forming the balance of the catalyst weight. In an embodiment, the catalyst may comprise CuO/ZrO$_2$/Al$_2$O$_3$. In an embodiment, the catalyst comprises an alkaline earth metal and/or alkaline earth metal oxide and copper and/or copper oxide on a support. In this embodiment, the support may comprise silica.

[0121] Any of the materials useful as hydrogenation and dimerization catalysts, may be synthesized using a variety of methods. In an embodiment, the dehydrogenation and dimerization catalyst may be prepared via wet impregnation of a catalyst support. Using the wet-impregnation technique, a metal nitrate dissolved in a suitable solvent may be used to prepare the catalyst, however any soluble compound would be suitable. A sufficient amount of solvent should be used to fully dissolve the metal nitrate and appropriately wet the support. In one embodiment, copper nitrate and ethanol and/or water may be mixed in an amount sufficient such that the copper nitrate dissolves. Additional metal nitrates may also be added to provide a catalyst with additional components. The solute may then be combined with a suitable support material of appropriate particle size. The mixture may then be refluxed at a temperature of approximately 100° C. for approximately several hours (e.g., three to five hours) and then allowed to dry at a temperature of about 110° C. The dried material may then be heated to 200° C. to remove the NO$_x$ component, and then the materials may be calcined at about 450° C. to about 550° C. at a heating rate of about one to ten ° C./min. The amount of metal nitrate used in the wet-impregnation technique can be adjusted to achieve a desired final metal weight loading of the catalyst support.

[0122] When multiple components are used to provide a catalyst disposed on a support, each component can be added via the wet-impregnation technique. The appropriate salts can be dissolved and impregnated on a support in a co-impregnation process or a sequential process. In a co-impregnation process, measured amount of the appropriate plurality of metal salts may be dissolved in a suitable solvent and used to wet the desired catalyst support. The impregnated support can then be dried and calcined to provide a final catalyst with a desired weight loading. In the sequential impregnation process, one or more measured amounts of salts may be dissolved in a suitable solvent and used to wet the desired catalyst support. The impregnated support can then be dried and calcined. The resulting material can then be wetted with one or more additional salts that are dissolved in a suitable solvent. The resulting material can then be dried and calcined again. This process may be repeated to provide a final catalyst material with a desired loading of each component. In an embodiment, a single metal may be added with each cycle. The order in which the metals are added in the sequential process can be varied. Various metal weight loadings may be achieved through the wet-impregnation technique. In an embodiment, the wet-impregnation technique may be used to provide a catalyst having a copper weight loading ranging from about 0.5% and about 50%, with one or more additional components having a weight loading between about 0.1% and about 10%.

[0123] The dehydrogenation and dimerization catalysts may also be prepared via a co-precipitation technique. In this technique, a measured amount of one or more appropriate metal nitrates (or other appropriate metal salts) are dissolved in de-ionized water. The total metal concentration can vary and may generally be between about 1 M and about 3 M. The metal-nitrate solution may then be precipitated through the drop-wise addition of the solution to a stirred, equal volume of a sodium hydroxide solution at room temperature. The sodium hydroxide solution may generally have a concentration of about 4M, though other concentrations may also be used as would be known to one of skill in the art with the benefit of this disclosure. After addition of the metal nitrate solution, the resulting suspension can be filtered and washed with de-ionized water. The filtered solids can be dried over-

night, for example, at a temperature of about 110° C. The resulting mixed metal oxide can then be processed to a desired particle size. For example, the resulting mixed metal oxide can be pressed to a desired form, ground, and then sieved to recover a catalyst material with a particle size in a desired range. Catalysts prepared using the co-precipitation technique may have higher metal loadings than the catalysts prepared using the wet-impregnation technique.

[0124] The catalyst prepared via the co-precipitation technique may be used in the prepared form and/or a catalyst binder can be added to impart additional mechanical strength. In an embodiment, the prepared catalyst may be ground to a fine powder and then stirred into a colloidal suspension (e.g., a colloidal suspension of silica and/or alumina) in an aqueous solution. The resulting suspension may be stirred while being heated and allowed to evaporate to dryness. The heating may take place at about 80° C. to about 130° C. The resulting solid can then be processed to a desired particle size. For example, the resulting solid can be pressed to a desired form, ground, and then sieved to recover a catalyst material with a particle size in a desired range. Alternatively, the colloidal suspension may be added to the 4M sodium hydroxide precipitation solution prior to addition of the metal nitrate solution in the co-precipitation technique. Various metal weight loadings may be achieved through the co-precipitation technique. In an embodiment, the co-precipitation technique may be used to provide a catalyst having a copper weight loading ranging from about 2% and about 80%, with one or more additional components having a weight loading between about 2% and about 40%.

[0125] The resulting catalyst from either the wet-impregnation technique and/or the co-precipitation technique may be further treated prior to use in the reactive distillation system disclosed herein. In an embodiment, the catalyst may be treated with a sodium carbonate solution for a period of time to improve the selectivity of the catalyst. In this process, the catalyst may be soaked in an aqueous solution of sodium carbonate for a period of time ranging from about 1 hour to about 48 hours, or alternatively about 2 hours to about 24 hours. In an embodiment, the sodium carbonate solution may have a concentration of about 0.2 M. The catalyst may then be filtered and allowed to dry at about room temperature. In an embodiment, the sodium carbonate may comprise from about 0.2 to about 3.0 weight percent of the catalyst after being contacted with the sodium carbonate solution.

[0126] In another treatment process, the catalyst may be reduced with hydrogen prior to use. In this embodiment, the catalyst may be heated and contacted with hydrogen, which may be flowing over the catalyst, for a period of time sufficient to reduce the catalyst to a desired degree. In an embodiment, the catalyst may be contacted with hydrogen at a temperature of about 190° C. to about 240° C. The hydrogen treatment may be conducted in combination with the sodium carbonate treatment, and may be performed prior to and/or after the sodium carbonate treatment.

[0127] Without intending to be limited by theory, it is believed that the production of hydrogen during the dehydrogenation and dimerization reaction within the process may result in contact between the dehydrogenation and dimerization catalyst and a hydrogen stream sufficient to at least partially reduce the catalyst. Thus, the process described herein may have the potential for the in-situ reduction of the catalyst during use. This may result in an initial break-in period in which the catalyst conversion and selectivity may

change before reaching a steady state conversion and selectivity. This in-situ reduction may be taken into account when considering the degree to which a catalyst should be pre-reduced with hydrogen.

[0128] In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a relatively high conversion and/or selectivity of ethanol to ethyl acetate. As used herein, the "conversion" of ethanol to ethyl acetate refers to the amount of ethanol consumed in the conversion reaction as represented by the formula:

$$X_{ethanol} = 100 \left(\frac{F_{EtOH,0} - F_{EtOH}}{F_{EtOH,0}} \right)$$

where F_{EtOH} represents the molar flow rates of ethanol in the reactor effluent (e.g., the product stream comprising the ethyl acetate), and $F_{EtOH,0}$ represents the molar flow rate of ethanol into the reactor inlet. As used herein, the "selectivity" of the conversion refers to the amount of ethanol that is consumed in the conversion reaction that is converted to ethyl acetate as represented by the formula:

$$S = 100 \left(\frac{2F_{EtOAC} + F_{AcH}}{F_{EtOH,0} - F_{EtOH}} \right)$$

where F_{EtoAc} and F_{AcH} represent the molar flow rate of ethyl acetate and acetaldehyde in the reactor effluent (e.g., the product stream comprising the ethyl acetate), respectively, and the remaining terms are the same as described above with respect to the conversion of ethanol. In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a conversion of ethanol in the reactive distillation process described herein of at least about 10%, at least about 20%, at least about 30%, at least about 40%, or at least about 50%. In an embodiment, the dehydrogenation and dimerization catalyst described herein may be capable of achieving a selectivity of ethyl acetate in the reactive distillation process described herein of at least about 60%, at least about 70%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 96%.

Hydrogenation Catalysts

[0129] The hydrogenation catalyst generally can include a Group VIII metal and/or a Group VI metal. Examples of such a catalyst can include, but is not limited to, Cu, Re, Ni, Fe, Co, Ru, Pd, Rh, Pt, Os, Ir, and alloys or any combination thereof, either alone or with promoters such as W, Mo, Au, Ag, Cr, Zn, Mn, Sn, B, P, Bi, and alloys or any combination thereof. Other effective hydrogenation catalyst materials include either supported nickel or ruthenium modified with rhenium. In an embodiment, the hydrogenation catalyst also includes any one of the supports described below, depending on the desired functionality of the catalyst. The hydrogenation catalysts may be prepared by methods known to those of ordinary skill in the art.

[0130] In an embodiment, the hydrogenation catalyst includes a supported Group VIII metal catalyst and a metal sponge material (e.g., a sponge nickel catalyst). Raney nickel provides an example of an activated sponge nickel catalyst suitable for use in this invention. In an embodiment, the

hydrogenation reaction in the invention is performed using a catalyst comprising a nickel-rhenium catalyst or a tungsten-modified nickel catalyst. One example of a suitable catalyst for the hydrogenation reaction of the invention is a carbon-supported nickel-rhenium catalyst.

[0131] In an embodiment, a suitable Raney nickel catalyst may be prepared by treating an alloy of approximately equal amounts by weight of nickel and aluminum with an aqueous alkali solution, e.g., containing about 25 weight % of sodium hydroxide. The aluminum is selectively dissolved by the aqueous alkali solution resulting in a sponge shaped material comprising mostly nickel with minor amounts of aluminum. The initial alloy includes promoter metals (e.g., molybdenum or chromium) in the amount such that 1 to 2 weight % remains in the formed sponge nickel catalyst. In another embodiment, the hydrogenation catalyst is prepared using a solution of ruthenium(III) nitrosylnitrate, ruthenium (III) chloride in water to impregnate a suitable support material. The solution is then dried to form a solid having a water content of less than 1% by weight. The solid is then reduced at atmospheric pressure in a hydrogen stream at 300° C. (uncalcined) or 400° C. (calcined) in a rotary ball furnace for 4 hours. After cooling and rendering the catalyst inert with nitrogen, 5% by volume of oxygen in nitrogen is passed over the catalyst for 2 hours.

[0132] In certain embodiments, the hydrogenation catalyst may include a catalyst support, which may be the same or different than a catalyst support used with the dehydrogenation and dimerization catalyst. In an embodiment, any of the catalyst supports discussed herein may be used to support a hydrogenation catalyst. The hydrogenation catalyst can be employed in any of the conventional types or structures known to the art. In an embodiment, any of the catalyst shapes and/or types discussed herein with respect to the dehydrogenation and dimerization catalyst may be used with the hydrogenation catalyst.

Production of Methyl Formate from Methanol

[0133] In addition to use of the systems and methods described herein for converting ethanol to ethyl acetate, those systems can also be used in processes with methanol as a feed instead of ethanol, with the production of methyl formate and H_2 as products according to the following formula:

$$2CH_3OH \longleftrightarrow HCOOCH_3 + 2H_2$$
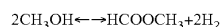
[0134] Such a system and method can utilize selections from the catalysts indicated for use with the ethanol feed. Products can be withdrawn in similar manner as described for the ethanol to ethyl acetate process.

EXAMPLES

[0135] The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

Example 1

Production of Ethyl Acetate from Ethanol

[0136] A 10 cm diameter distillation column is used, which has been rendered adiabatic by heating casings with temperatures controlled in such a way that the temperature gradient in

the column is reproduced. Over a height of 3.5 m, the column is comprised of rectification zone with 8 stages each with a catalytic cell consisting of a cylindrical container with a flat bottom. The bottom of the container is equipped with a grid for retaining the catalyst and also can act as a gas and liquid distributor. The stripping zone is comprised of 12 stages, also with catalyst-containing cells. The rectification section is considered to be above the feed stage and the stripping section is considered to be below the feed stage. Each catalyst cell contains CuO/ZnO/Al$_2$O$_3$. 200 proof ethanol is fed to the 13th stage of the column, starting from the bottom.

[0137] The column is regulated by establishing a reflux ratio which is equal to 0.8, reboil ratio which is equal to 4 and controlling the base temperature to 211° C. and the absolute pressure to 20 bar. The reflux stream is mostly ethanol with small amounts of acetaldehyde. Under stabilized conditions, a bottoms stream and a distillate stream are collected with respective throughputs of about 170 g/h and 4 g/h. The bottoms product gives ethyl acetate purity of 98.5% with small amounts of n-butyraldehyde and butan-2-one.

Example 2

Selective Hydrogenation of n-butyraldehyde and butan-2-one

[0138] Selective hydrogenation of n-butyraldehyde and butan-2-one in the presence of ethyl acetate was conducted over a hydrogenation catalyst. The reactor was filled with 20 g of 0.1 wt % Pd on silica catalyst. Before the selective hydrogenation reaction, the catalyst was reduced at a temperature of 250° C. for 30 minutes. The catalyst reduction was conducted at atmospheric pressure by delivering hydrogen using a mass flow controller. At the end of this procedure, the catalyst was fully reduced.

[0139] The bottoms product from the reactive distillation column, whose composition is given in Table 2, was introduced to a heater at a rate of 30 g/h and mixed with hydrogen prior to admission to the selective hydrogenation reactor. The reaction product was cooled using a jacketed condenser and the liquid condensate was analyzed by gas chromatography. The results are summarized in Table 2, showing n-butyraldehyde and butan-2-one reduced to trace levels.

TABLE 2

Hydrogenation Feed and Products		
Temperature	250° C.	
Pressure	20 atm	
	Weight %	
Component	Feed	Products
Ethyl acetate	93	92.9
Ethanol	2	2.1
Iso-propanol	3	3
n-butyraldehyde	1.5	trace
butan-2-one	0.5	trace
2-butanol	0	0.48
n-butanol	0	1.52

Example 3

Wet-Impregnation Catalyst Preparation

[0140] Various catalysts including CuO/SiO$_2$, CuO/SiO$_2$—Al$_2$O$_3$, CuO/ZnO, CuO/ZrO$_2$, CuO/SiO$_2$—ZrO$_2$,

$CuO/ZnO/Al_2O_3$, $CuO/Cr_2O_3/BaO$, CuO/Cr_2O_3 and CuO/Al_2O_3 were prepared via impregnation of the corresponding oxide catalyst support. The preparation involved dissolving 4 grams (g) of $Cu(NO_3)_2.2.5H_2O$ in 30 mL of de-ionized water, which was then added to 30 g of the appropriate oxide support and stirred until well mixed. The impregnated support was then dried in air at 110° C., followed by calcination in air at 450° C. The amount of $Cu(NO_3)_2.2.5H_2O$ was adjusted to achieve a desired final Cu weight loading. Enough water was used to wet the entire oxide support. Copper loadings between 0.5% and 20% by weight were achieved.

Example 4

Co-Impregnation and Sequential Impregnation Catalyst Preparation

[0141] Various catalysts including $CuO/ZnO/SiO_2$, $CuO/ZrO_2/SiO_2$, $CuO/MgO/SiO_2$, $CuO/CaO/SiO_2$, $CuO/SrO/SiO_2$, $CuO/BaO/SiO_2$, and $CuO/Na_2O/SiO_2$ were prepared via co-impregnation and sequential impregnation of a silica catalyst support. For the co-impregnation, measured amounts of $Cu(NO_3)_2.2.5H_2O$ and $M(NO_3)_x.YH_2O$ (M=Zn, Zr, Mg, Ca, Sr, Ca, or Na; X=1, 2, 4; Y=2-6) were dissolved in de-ionized water. The solution was added to the silica support and stirred until well mixed. The impregnated silica was dried in air at 110° C., followed by calcination in air at 450° C.

[0142] For the sequential impregnation, a measured amount of $M(NO_3)_x.YH_2O$ (M=Mg, Ca, Sr, Ca, or Na; X=1 or 2; Y=2-6) was dissolved in de-ionized water. The solution was then added to the silica support and mixed well. The silica was dried at 110° C. and then calcined at 450° C. in air. This procedure was then repeated using $Cu(NO_3)_2.2.5H_2O$ in place of the first metal nitrate. Copper loadings between 0.5% and 20% by weight and an addition metal loading between 0.1% and 10% by weight were achieved.

Example 5

Co-Precipitation Catalyst Preparation

[0143] Mixed-metal oxide catalysts were prepared via co-precipitation from nitrate solutions. In the co-precipitation synthesis, a measured amount of the appropriate metal nitrate (Cu, Zn, Zr, Al, Cr, Fe, Ni, and/or Ba) were dissolved in de-ionized water (total metal concentration ranges from 1-3 M). The metal-nitrate solution was then precipitated by drop-wise addition to a stirred, equal volume of 4 M aqueous NaOH at room temperature. After addition of all the metal nitrate solution, the suspension was stirred for an additional hour to ensure complete precipitation of the metals. The precipitated solid was then filtered and washed with excess de-ionized water. The solids were then dried overnight at 110° C. The resulting mixed metal oxide was then pressed, ground, and sieved to recover a catalyst with particle sizes between 450 and 850 µm. Catalysts prepared in this manner had copper oxide loadings between 40% and 80% by weight. The loadings of other metal oxides ranged from 2% to 40% by weight. In particular, $CuO/ZnO/ZrO_2/Al_2O_3$, and $CuO/ZnO/ZrO_2/Cr_2O_3$ catalysts were found to be especially active and selective for the dehydrogenative dimerization of ethanol, as illustrated below in Example 6.

[0144] In addition to the catalysts prepare above, various catalysts were prepared via co-precipitation and then a binder was incorporated. The catalyst binder was added to the mixed-metal oxide prepared as described above by first grinding the mixed-metal oxide to a fine powder and then stirring it into a colloidal suspension of silica or alumina in water. The resulting suspension was stirred while heating at 80-130° C. to dryness. The resulting solid was then be pressed, ground, and sieved to appropriate particle sizes.

Example 6

Dehydrogenative Dimerization of Ethanol

[0145] A portion of the catalysts prepared as described in Examples 3 to 5 were treated with a Na_2CO_3 solution by soaking the catalyst in a 0.2 M aqueous solution of Na_2CO_3 for 2-24 hrs. The catalyst was then filtered and allowed to dry in air at room temperature. Another portion of the catalysts prepared as described in Examples 3 to 5 were reduced in a hydrogen environment at 175-240° C. for a period of 4-12 hours. These catalysts were then tested in ethanol dehydrogenation reactions. Conversion and selectivity for gas phase reactions were determined from use in a fixed bed reactor operating at 190-240° C. and 1-24 atm. Pure ethanol was fed to the reactor with a weight hourly space velocity (WHSV) between 0.1-1.5 hr^{-1}. Conversion and selectivity for liquid phase and mixed liquid/vapor phase reactions were determined in a fixed bed reactor, operating at 190-240° C. and at pressures above 25 atm. Liquid phase reactions were also conducted in a batch reactor at 180-200° C. and 20-31 atm (the reactor pressure was maintained above the vapor pressure of ethanol at the operating temperature).

[0146] Table 3 shows the conversion and selectivity of the catalysts in a dehydrogenative dimerization reaction conducted in a fixed bed reactor. Conversion (X) and selectivity (S) were calculated from the composition of the reactor effluent as

$$X_{ethanol} = 100 \left(\frac{F_{EtOH,0} - F_{EtOH}}{F_{EtOH,0}} \right)$$

$$S = 100 \left(\frac{2F_{EtOAC} + F_{AcH}}{F_{EtOH,0} - F_{EtOH}} \right)$$

where F_{EtOH}, F_{EtOAc}, and F_{AcH} represent the molar flow rates of ethanol, ethyl acetate, and acetaldehyde in the reactor effluent, respectively, and F_{Etwo} represents the molar flow rate of ethanol into the reactor inlet. Acetaldehyde is a reaction intermediate and so was included in the selectivity calculation.

TABLE 3

Conversion and Selectivity for selected catalysts in a fixed bed reactor at 220° C. and 1 atm				
	As prepared/received		Reduced in H_2	
Catalyst sample	X	S	X	S
Pellet catalysts				
$CuO/ZnO/Al_2O_3$	18.9	92.4	35.0	89.7
$CuO/Cr_2O_3/BaO$	43.5	89.4	36.0	74.6
Impregnated catalysts				
CuO/SiO_2	19.6	96.2	22.5	80.9
CuO/SiO_2—Al_2O_3	43.0	17.0		
CuO/Al_2O_3	50.2	47.3		

TABLE 3-continued

Conversion and Selectivity for selected catalysts
in a fixed bed reactor at 220° C. and 1 atm

Catalyst sample	As prepared/received		Reduced in H$_2$	
	X	S	X	S
CuO/ZnO	19.7	65.5		
CuO/ZrO$_2$	41.5	63.4		
CuO/SiO$_2$—ZrO$_2$	40.0	59.7		
CuO/MgO/SiO$_2$	37.9	70.0	32.1	65.7
CuO/CaO/SiO$_2$	33.3	73.4	29.0	42.7
CuO/SrO/SiO$_2$	25.1	77.2	31.5	69.6
CuO/BaO/SiO$_2$	31.0	73.2	33.6	73.6
CuO/Na$_2$O/SiO$_2$	19.4	95.9		
CuO/ZrO$_2$/SiO$_2$	39.1	58.7	54.0	61.6
Co-precipitation catalysts				
CuO/ZnO/ZrO$_2$/Al$_2$O$_3$	8.7	83.6	21.4	72.6
CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Na$_2$CO$_3$	26.1	40.1	39.0	86.1
CuO/ZnO/ZrO$_2$/Cr$_2$O$_3$	28.8	92.0	20.9	80.9
CuO/ZnO/ZrO$_2$/Cr$_2$O$_3$/Na$_2$CO$_3$	37.0	90.2	35.9	87.5
CuO/ZnO/ZrO$_2$/Fe$_2$O$_3$	34.1	92.1	17.0	94.2
CuO/ZnO/ZrO$_2$/Fe$_2$O$_3$/Na$_2$CO$_3$	30.7	72.6		
CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Cr$_2$O$_3$	24.5	88.4	18.5	79.4
CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Cr$_2$O$_3$/Na$_2$CO$_3$	33.2	86.3		

Example 7

Pressure Effects on the Conversion

[0147] A fixed bed reactor operated under similar conditions to those described with respect to Example 6 was used to test the reaction conversion and selectivity of a catalyst under varying reaction pressures. Table 4 shows a typical trend in the conversion and selectivity of these catalysts when operated at elevated pressures. Similar trends were seen for all catalysts tested at elevated pressures.

TABLE 4

Conversion and Selectivity for CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Na$_2$CO$_3$
(reduced at 240° C. in H$_2$) in a fixed bed reactor at 220° C.

Pressure (atm)	X	S
1	39.0	86.1
9.4	43.6	96.1
14.5	43.3	96.4
21.4	39.3	97.4

[0148] As seen by the results in Table 4, operation of catalysts at higher pressures increases the selectivity of the catalyst significantly. Increasing the pressure had little effect on the conversion achieved by the catalysts.

Example 8

Liquid Phase Reaction

[0149] The dehydrogenative dimerization of ethanol was also conducted in the liquid phase. Reaction temperatures ranged from 180 to 200° C. and pressures were kept above the vapor pressure of ethanol at the reaction temperature (25-36 atm). Liquid phase reactions were conducted in both a fixed bed reactor and batch reactor. Table 5 shows the results for a CuO/ZnO/Al$_2$O3 catalyst in a batch reactor operating in the liquid phase. During a typical batch reaction, the pressure

initially reached the vapor pressure of ethanol and then slowly increased beyond that pressure as the reaction generated H$_2$ gas. The batch reactor results demonstrated that the dehydrogenative dimerization reaction occurs in the liquid phase.

TABLE 5

Conversion and Selectivity for CuO/ZnO/Al$_2$O$_3$ (reduced
at 240° C. in H$_2$) after 2 hrs in a batch reactor.

Temperature (° C.)	X	S
180	4.4	84.1
190	6.1	81.5
200	13.0	96.1

[0150] Based on the results of Examples 3 through 8, it can be seen that a high selectivity to ethyl acetate using the dehydrogenation and dimerization catalysts described herein (e.g., CuO/ZnO/ZrO$_2$/Al$_2$O$_3$/Na$_2$CO$_3$ and/or CuO/ZnO/Al$_2$O$_3$) should enable the use of the system embodiments as illustrated in FIGS. 3, 5 and 7 of the present disclosure. For catalysts where 2-butanone is produced above acceptable levels, the use of the system embodiments as illustrated in FIGS. 4, 6 and 8 of the present disclosure may be used.

Example 9

Effect of Water in the Ethanol Feed

[0151] In this example, the effect of water in the ethanol feed was investigated. A 4 wt % water in ethanol solution was fed to a CuO/ZnO/Al$_2$O$_3$ catalyst in a fixed bed reactor to demonstrate the water tolerance of the catalyst. The reactor was maintained at 21.4 atm and the catalyst was heated to 200-240° C. Table 6 compares the conversion and selectivity achieved for both the 4 wt % water in ethanol and a pure ethanol feed.

TABLE 6

Conversion and selectivity for CuO/ZnO/Al$_2$O$_3$ in a fixed bed reactor
operating at 21.4 atm for ethanol feeds with and without water.

Temperature (° C.)	Pure Ethanol Feed		4% Water in Ethanol Feed	
	Conversion	Selectivity	Conversion	Selectivity
200	23.2	98.1	14.2	99.2
220	37.9	97.1	29.2	98.6
240	47.9	94.4	42.6	98.0

Example 10

Impregnated Catalysts

[0152] A catalyst comprising CuO/ZrO$_2$/Al$_2$O$_3$ was prepared via co-impregnation of an alumina support. As in a typical co-impregnation, measured amounts of Cu(NO$_3$)$_2$.2.5H$_2$O and ZrO(NO$_3$)$_2$.6H$_2$O were dissolved in an appropriate amount of de-ionized water to fill the pore volume of the alumina support. The solution was added to the alumina support and agitated until the liquid was fully absorbed by the alumina. The impregnated alumina was dried in air at 110° C., followed by calcination in air at 400-600° C. for 2-10 hours. Typical catalyst loadings ranged from 1-50 wt % CuO and 2-40 wt % ZrO$_2$, and some of the catalyst weight loadings were about 13 wt % CuO and about 7 wt % ZrO$_2$.

[0153] The supported CuO/ZrO₂/Al₂O₃ could be treated with a base such as sodium carbonate after the calcination to improve catalyst selectivity. For these catalysts, a volume of an aqueous sodium carbonate solution sufficient to fully submerge the supported catalyst was prepared (0.1-1.0 M). The catalyst was then added to the solution and allowed to cure for 2-12 hours at room temperature. The catalyst was then filtered and washed to remove the excess base, then dried prior to use in a reaction. Bases other than sodium carbonate that could be used include K_2CO_3, Li_2CO_3, Cs_2CO_3, NaOH, $Ca(OH)_2$, KOH, CsOH, $Ba(OH)_2$.

[0154] The results of the impregnated catalyst are shown below in Table 7, wherein X and S are based on the formulas provided above in Example 6.

TABLE 7

Conversion and Selectivity for selected supported catalysts in a fixed bed reactor operating at 200° C. and 33 atm with an LHSV = 0.5 hr⁻¹.		
Catalyst sample	As prepared	
Impregnated catalyst	X	S
CuO/ZrO₂ on Al₂O₃	13.8	95.1

Example 11

Co-Precipitation Catalyst Preparation

[0155] Mixed-metal oxide catalysts comprising CuO/ZrO₂/Al₂O₃ and CuO/ZrO₂ were prepared via co-precipitation from nitrate solutions. As in a typical co-precipitation synthesis, a measured amount of the appropriate metal nitrates were dissolved in de-ionized water (total metal concentration ranges from 0.5-3 M). The metal-nitrate solution was then precipitated by drop-wise addition into a stirred, equal volume of 1-4 M aqueous NaOH. The NaOH solution could be at room temperature or heated up to near boiling. After addition of all the metal nitrate solution, the suspension was stirred for 2-24 hours to ensure complete precipitation of the metal oxides. The precipitated solid was then filtered and washed with excess de-ionized water. The solids were then dried at 110° C., followed by calcination at 220-500° C. Catalysts prepared in this manner had CuO loadings between about 40 to about 80 wt %. The loadings of other metal oxides range from about 2 to about 40 wt %. Other metal salts, such as acetates and carbonates, could be used in place of the nitrates.

[0156] A catalyst binder could be added to the mixed-metal oxide to impart additional mechanical strength. The metal oxide catalyst would be ground to a fine powder and then stirred into a suspension of the binder. The resulting slurry could then be extruded or pressed, ground, and sieved to appropriate particle sizes. An alternative could include adding the binder material to the NaOH precipitation solution prior to addition of the metal nitrate solution. Binders can include SiO₂, Al₂O₃, bentonite and other clays, hydrotalcite, and Al(OH)₃.

[0157] The results of the co-precipitation catalyst are shown below in Table 8, wherein X and S are based on the formulas provided above in Example 6.

TABLE 8

Conversion and Selectivity for selected supported catalysts in a fixed bed reactor operating at 200° C. and 33 atm with an LHSV = 0.5 hr⁻¹.		
Catalyst sample	As prepared	
Co-Precipitation Catalyst	X	S
CuO/ZrO₂	17.2	96.2
Cu/O/ZrO₂/Al₂O₃	17.8	98.6

Example 12

[0158] In order to demonstrate the extraction of impurities from ethyl acetate using an aqueous solution comprising an extracting agent, a solution of sodium hydrogen sulfite (NaHSO₃) was prepare using 30 grams of sodium hydrogen sulfite per 100 milliliters of water. A product stream was simulated by preparing an ethyl acetate solution containing 1.6 wt. % 2-butanone. The extraction was first conducted by sequentially contact 100 milliliters of the ethyl acetate with 25 milliliters of the aqueous solution at a time. For each extraction, the ethyl acetate solution was mixed with the 25 milliliters of the aqueous NaHSO₃ solution. The separation funnel was vigorously shaken several times at room temperature then allowed to rest and let the ethyl acetate-water phase separation take place. The heavier, aqueous phase was drained and replaced with same amount of fresh NaHSO₃ solution, and the procedure was repeated as needed until the 2-butanone level drops below the desired level. The residual concentration of the 2-butanone was tracked with a GC analysis after each extraction step. The results of the analysis are illustrated in FIG. 16.

[0159] The results demonstrate that 3 consecutive washes resulted in a final 2-butanone concentration below 0.1 wt. %. Similar behavior would be expected for other ketones and aldehydes such as acetone and acetaldehyde.

Example 13

[0160] The effect of the extraction efficiency with respect to the volume and concentration of the solvent was explored in this example. In this example, the effects on the 2-butanone concentration in the ethyl acetate solution were determined using different volumes of solvent as well as different concentrations of the extracting agent in the solvent. The same ethyl acetate solution comprising 1.6 wt. % 2-butanone was prepared as in Example 12. The starting solvent solution included 30 grams of sodium hydrogen sulfite per 100 milliliters of water. A volume of 75 milliliters of the ethyl acetate solution was first contacted with 25 milliliters of the solvent solution in multiple extraction steps that were carried out as described above in Example 12. The concentration of the 2-butanone was measured after each step and the results are shown in FIG. 17. Another volume of 75 milliliters of the ethyl acetate solution was then contacted with 15 milliliters of the solvent solution in multiple extraction steps. A fresh volume of 75 milliliters of the ethyl acetate solution was then contacted in multiple extraction steps with 25 milliliters of the solvent solution that was prepared by diluting 15 milliliters of the original solvent solution (30 grams of sodium hydrogen sulfite per 100 milliliters of water) with 10 milliliters of water. The concentration of the 2-butanone was measured after each step and the results are shown in FIG. 17.

[0161] The results indicate that smaller volumes with the same concentration of NaHSO₃ (15 ml extraction volumes) is less efficient than larger ones (25 ml as shown in FIG. **16**). Furthermore, a dilution of the NaHSO₃ solution yielded improved removal efficiency and reduced tendency to form crystals (FIG. **17**). This unexpected results is likely due to the higher solubility of the sodium sulfite 2-butanone adduct in a less concentrated aqueous NaHSO₃ salt solution. Thus we discovered that optimal removal rates are not achieved by excessively high concentrations of NaHSO₃ or small extraction volumes but with concentration that is high enough to provide NaHSO₃ excess but not suppress the removal of the sodium sulfite 2-butanone adduct which has to dissolve in the aqueous phase.

Example 14

[0162] The effect of the extraction temperature explored in this example. In this example, an identical amount of ethyl acetate was treated with the same amount and the same concentration of the aqueous NaHSO₃ (30 grams of sodium hydrogen sulfite per 100 milliliters of water). The first sample was kept cooled for 2 hours at approximately 4° C. The final concentration of the 2-butanone in the sample maintained at 4° C. was measured by a gas chromatograph analysis as 0.08 wt. %. The sample maintained at room temperature (approximately 25° C.) had a final concentration of about 0.18%. Thus, a greater amount of the 2-butanone was transferred from the ethyl acetate sample into the solvent solution in the sample maintained at 4° C. than the sample maintained at room temperature.

Example 15

[0163] The effect of the use of mixtures of sodium sulfite and sodium hydrogen sulfite was explored in this example. The sodium sulfite solution (Na₂SO₃) was prepared in situ by the addition of NaOH to a solution of NaHSO₃. A stoichiometric amount of NaOH can be used to completely convert an amount of NaHSO₃ into Na₂SO₃. A less than stoichiometric amount of NaOH can be used to create a mixture of Na₂SO₃ and NaHSO₃. Tests were performed with a solution of NaHSO₃ that was neutralized with NaOH to a 50% solution (corresponding to a mixture of 50% NaHSO₃ and 50% Na₂SO₃) as well as a solution of NaHSO₃ that was neutralized with NaOH to a 100% solution (corresponding to substantially pure aqueous Na₂SO₃). Several multi-step extractions were performed on a solution comprising ethyl acetate solution comprising 1.86 wt. % 2-butanone. The results are presented in FIG. **18**.

[0164] As shown in FIG. **18**, each point on the graph represents an extraction, wherein the x-axis represents the cumulative amount of extractant solution used. The starting solution of NaHSO₃ contained approximately 30 grams of NaHSO₃/100 ml. The exact concentration was determined by iodometric titration and the solution was adjusted with 4 M NaOH as needed to achieve the desired neutralization level. Although the tests demonstrate that the performance of the Na₂SO₃ containing extraction was slightly lower, the regeneration of Na₂SO₃ solution is expected to be much more reproducible and with lower potential release of SO₂ gas. A similar performance is expected from corresponding mixtures of NaHSO₃ and Na₂SO₃.

ADDITIONAL EMBODIMENTS

[0165] Having described the systems and methods, various embodiments may include, but are not limited to:

[0166] In a first embodiment, a method of purifying an ethyl acetate stream comprises contacting an inlet stream with a solvent, transferring at least a portion of the impurity compound from the inlet stream into the solvent to form an extract and a purified product, separating the extract from the purified product, separating the portion of the impurity compound from the extract, forming an impurities stream and a regenerated solvent, and recycling at least a portion of the regenerated solvent to contact the inlet stream. The inlet stream comprises ethyl acetate and an impurity compound, and the extract comprises the solvent and the portion of the impurity compound transferred from the inlet stream. In a second embodiment, the solvent of the first embodiment may comprise an aqueous fluid. In a third embodiment, the method of the first or second embodiment can also include heating the extract after separating the extract from the purified product. Heating the extract can include heating the extract to a temperature between about 85 45° C. and about 100° C. In a fourth embodiment, the solvent of any of the first to third embodiments can also include an extracting agent, and the extracting agent may be configured to increase the solubility of the impurity compound in the solvent. In a fifth embodiment, the extracting agent of the fourth embodiment may comprise sodium hydrogen sulfite. In a sixth embodiment, the extracting agent of the fourth embodiment may comprise a compound selected from the group consisting of: hydrosulfite ion, sulfite ion, hydrazine, hydroxylamine, semicarbazide, phenylhydrazine, phenylhydroxylamine, salts thereof, aqueous solutions thereof, and any combination thereof. In a seventh embodiment, the method of any of the fourth to sixth embodiments can also include reacting the extracting agent and the impurity compound to form an adduct in response to contacting the inlet stream with the solvent. In an eighth embodiment, separating the portion of the impurity compound from the extract in the seventh embodiment may comprise dissociating the adduct. In a ninth embodiment, the impurity compound of any of the first to eighth embodiments may comprise at least one of a ketone, an aldehyde, or any combination thereof. In a tenth embodiment, the method of any of the first to ninth embodiments may comprise drying the purified product. In an eleventh embodiment, the purified product of any of the first to tenth embodiments may comprise at least about 90% ethyl acetate by weight. In a twelfth embodiment, contacting the inlet stream with the solvent in any of the first to eleventh embodiments may comprise at least one of contacting the inlet stream with the solvent in a counter-current flow, or contacting the inlet stream with the solvent in a cross-current flow. In a thirteenth embodiment, the method of any of the first to twelfth embodiments can also include feeding a feed stream comprising ethanol to a reactive distillation column, contacting the ethanol with a catalyst, dehydrogenating ethanol over the catalyst, removing ethyl acetate during the distillation process as a liquid bottoms product, removing hydrogen during the distillation process as a gaseous top product, and providing the ethyl acetate as the inlet stream. In a fourteenth embodiment, the catalyst of the thirteenth embodiment may be disposed in a side reactor, and the side reactor may be in fluid communication with the reactive distillation column. In a fifteenth embodiment, the catalyst of the fourteenth embodiment may be disposed in the reactive distillation column. In a sixteenth embodiment, sepa-

rating the portion of the impurity compound from the extract in any of the first to fifteenth embodiments may comprise contacting the extract with a purge gas, transferring at least a portion of the impurity compound from the extract to the purge gas, and separating the purge gas from at least the portion of the impurity compound. In a seventeenth embodiment, separating the portion of the impurity compound from the extract in any of the first to sixteenth embodiments may occur at a pressure of between about 0.001 atm and about 1 atm.

[0167] In an eighteenth embodiment, a reactive distillation system for producing high purity ethyl acetate from ethanol comprises a reactive distillation column, an extraction unit, and a stripping unit. The reactive distillation column comprises a dehydrogenation catalyst, an ethanol inlet configured to pass an ethanol feed over the dehydrogenation catalyst, a top product gaseous hydrogen removal passage, and a bottoms product liquid ethyl acetate removal passage. The extraction unit is configured to receive a liquid ethyl acetate product stream from the reactive distillation column through the bottoms product liquid ethyl acetate removal passage, contact a liquid solvent feed stream with the liquid ethyl acetate product stream, provide an extract stream comprising a portion of any impurities in the liquid ethyl acetate product stream, and provide a purified product stream. The stripping unit is configured to receive the extract stream from the extraction unit, separate the portion of the impurities from the extract stream, provide an outlet impurities stream, and provide a regenerated solvent stream back to the extraction unit as at least a portion of the liquid solvent feed stream. In a nineteenth embodiment, the system of the eighteenth embodiment can also include a drying unit, and the drying unit can be configured to receive the purified product stream from the extraction unit, remove at least a portion of any water in the purified product stream, and provide a dried purified product stream. In a twentieth embodiment, the extraction unit of the eighteenth or nineteenth embodiments may be configured to contact the liquid solvent feed stream with the liquid ethyl acetate product stream using a counter-current flow. In a twenty first embodiment, the extraction unit of the eighteenth or nineteenth embodiments may be configured to contact the liquid solvent feed stream with the liquid ethyl acetate product stream using a cross-current flow. In a twenty second embodiment, the extraction unit of any of the eighteenth to twenty first embodiments may comprise a liquid-liquid contact vessel. In a twenty third embodiment, the liquid-liquid contact vessel of the twenty second embodiment may comprise packing. In a twenty fourth embodiment, the stripping unit of any of the eighteenth to twenty third embodiments may comprise a distillation column. In a twenty fifth embodiment, the distillation column of the twenty fourth embodiment may comprise between about 1 and about 50 stages. In a twenty sixth embodiment, the system of any of the eighteenth to twenty fifth embodiments can also include a cooler, and the cooler can be configured to receive the regenerated solvent stream, cool the regenerated solvent stream, and provide the cooled regenerated solvent stream back to the extraction unit. In a twenty seventh embodiment, the system of any of the eighteenth to twenty sixth embodiments may also include at least one side reactor in fluid communication with the reactive distillation column. In a twenty eighth embodiment, the system of the twenty seventh embodiment may also include a second catalyst disposed in the at least one

side reactor, wherein the catalyst comprises at least one of a dehydrogenation catalyst or a hydrogenation catalyst.

[0168] In a twenty ninth embodiment, a reactive distillation process producing high purity ethyl acetate from ethanol comprises feeding a feed stream comprising ethanol to a reactive distillation column, contacting the ethanol with a catalyst, dehydrogenating ethanol over the catalyst in the liquid phase during the distillation process, removing ethyl acetate during the distillation process as a bottoms product, and removing hydrogen during the distillation process as a top product. In a thirtieth embodiment, the reactive distillation process of the twenty ninth embodiment may also include contacting the bottoms stream with a hydrogenation catalyst and hydrogen, hydrogenating at least a portion of a contaminant in the bottoms stream, and separating the hydrogenated portion of the contaminant from the bottoms stream. In a thirty first embodiment, separating the hydrogenated portion of the contaminant from the bottoms stream in the thirtieth embodiment comprises distilling the hydrogenated portion of the contaminant from the bottoms stream. In a thirty second embodiment, the contacting, the hydrogenating, and the separating in the thirtieth or thirty first embodiments may occur downstream of the reactive distillation column. In a thirty third embodiment, the contaminant of any of the thirtieth to thirty second embodiments may comprise a ketone or an aldehyde. In a thirty fourth embodiment, the reactive distillation process of any of the twenty ninth to thirty third embodiments may also include extracting at least a portion of a contaminant in the bottoms stream using a solvent to produce an extract stream and a purified product stream, and stripping the portion of the contaminant from the extract stream to produce a contaminant stream and regenerate the solvent stream. In a thirty fifth embodiment, the reactive distillation process of any of the twenty ninth to thirty fourth embodiments may also include contacting a first fluid drawn from the reactive distillation column with the catalyst in a side reactor, and introducing the second fluid to the reactive distillation column during the distillation process. The first fluid may react in the presence of the catalyst to produce a reaction product comprising a second fluid. In a thirty sixth embodiment, the reactive distillation process of the thirty fifth embodiment may also include increasing a contact time between the ethanol and the catalyst, and improving a conversion of ethanol to ethyl acetate in response to increasing the contact time between the ethanol and the catalyst. In a thirty seventh embodiment, the reactive distillation process of the thirty fifth to thirty sixth embodiments may also include contacting the bottoms stream with a hydrogenation catalyst and hydrogen, hydrogenating at least a portion of a contaminant in the bottoms stream, and separating the hydrogenated portion of the contaminant from the bottoms stream. In a thirty eighth embodiment, the bottoms product of any of the twenty ninth to thirty seventh embodiments may comprise at least about 90% ethyl acetate. In a thirty ninth embodiment, the feed stream comprising ethanol of any of the twenty ninth to thirty eighth embodiments may be the only feed stream fed to the reactive distillation column. In a fortieth embodiment, the catalyst of any of the twenty ninth to thirty ninth embodiments may be disposed within the reactive distillation column. In a forty first embodiment, the reactive distillation process of any of the twenty ninth to fortieth embodiments may also include introducing a second feed stream to the reactive distillation column, and contacting the second feed

stream with a hydrogenation catalyst during the distillation process. The second feed stream may comprise hydrogen.

[0169] In the preceding discussion and in the claims, the terms "including" and "comprising" are used in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to . . . ". At least one embodiment is disclosed and variations, combinations, and/or modifications of the embodiment(s) and/or features of the embodiment(s) made by a person having ordinary skill in the art are within the scope of the disclosure. Alternative embodiments that result from combining, integrating, and/or omitting features of the embodiment(s) are also within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, R_1, and an upper limit, R_u, is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R = R_1 + k^*(R_u - R_1)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, . . . , 50 percent, 51 percent, 52 percent, . . . , 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element of a claim means that the element is required, or alternatively, the element is not required, both alternatives being within the scope of the claim. Use of broader terms such as comprises, includes, and having should be understood to provide support for narrower terms such as consisting of, consisting essentially of, and comprised substantially of. Accordingly, the scope of protection is not limited by the description set out above but is defined by the claims that follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated as further disclosure into the specification and the claims are embodiment(s) of the present invention.

What is claimed is:

1. A method of purifying an ethyl acetate stream comprising:

contacting an inlet stream with a solvent, wherein the inlet stream comprises ethyl acetate and an impurity compound;

transferring at least a portion of the impurity compound from the inlet stream into the solvent to form an extract and a purified product, wherein the extract comprises the solvent and the portion of the impurity compound transferred from the inlet stream;

separating the extract from the purified product;

separating the portion of the impurity compound from the extract;

forming an impurities stream and a regenerated solvent; and

recycling at least a portion of the regenerated solvent to contact the inlet stream.

2. The method of claim 1, wherein the solvent comprises an aqueous fluid

3. The method of claim 1, wherein the solvent further comprises an extracting agent, wherein the extracting agent is configured to increase the solubility of the impurity compound in the solvent.

4. The method of claim 3, wherein the extracting agent comprises sodium hydrogen sulfite.

5. The method of claim 3, wherein the extracting agent comprises a compound selected from the group consisting of: hydrosulfite ion, sulfite ion, hydrazine, hydroxylamine, semi-carbazide, phenylhydrazine, phenylhydroxylamine, salts thereof, aqueous solutions thereof, and any combination thereof.

6. The method of claim 3, further comprising reacting the extracting agent and the impurity compound to form an adduct in response to contacting the inlet stream with the solvent.

7. The method of claim 6, wherein separating the portion of the impurity compound from the extract comprises dissociating the adduct.

8. The method of claim 1, wherein the impurity compound comprises at least one of a ketone, an aldehyde, or any combination thereof.

9. The method of claim 1, wherein the purified product comprises at least about 90% ethyl acetate by weight.

10. The method of claim 1, wherein contacting the inlet stream with the solvent comprises at least one of contacting the inlet stream with the solvent in a counter-current flow, or contacting the inlet stream with the solvent in a cross-current flow.

11. The method of claim 1, further comprising:

feeding a feed stream comprising ethanol to a reactive distillation column;

contacting the ethanol with a catalyst;

dehydrogenating ethanol over the catalyst;

removing ethyl acetate during the distillation process as a liquid bottoms product;

removing hydrogen during the distillation process as a gaseous top product; and

providing the ethyl acetate as the inlet stream.

12. The method of claim 11, wherein the catalyst is disposed in a side reactor, and wherein the side reactor is in fluid communication with the reactive distillation column.

13. The method of claim 1, wherein separating the portion of the impurity compound from the extract comprises: contacting the extract with a purge gas, transferring at least a portion of the impurity compound from the extract to the purge gas, and separating the purge gas from at least the portion of the impurity compound.

14. The method of claim 1, wherein separating the portion of the impurity compound from the extract occurs at a pressure of between about 0.001 atm and about 1 atm.

15. A reactive distillation system for producing high purity ethyl acetate from ethanol, the system comprising:

a reactive distillation column comprising: a dehydrogenation catalyst, an ethanol inlet configured to pass an ethanol feed over the dehydrogenation catalyst, a top product gaseous hydrogen removal passage, and a bottoms product liquid ethyl acetate removal passage;

an extraction unit configured to receive a liquid ethyl acetate product stream from the reactive distillation column through the bottoms product liquid ethyl acetate removal passage, contact a liquid solvent feed stream with the liquid ethyl acetate product stream, provide an extract stream comprising a portion of any impurities in

the liquid ethyl acetate product stream, and provide a purified product stream; and

a stripping unit configured to receive the extract stream from the extraction unit, separate the portion of the impurities from the extract stream, provide an outlet impurities stream, and provide a regenerated solvent stream back to the extraction unit as at least a portion of the liquid solvent feed stream.

16. The system of claim **15**, further comprising a drying unit, wherein the drying unit is configured to receive the purified product stream from the extraction unit, remove at least a portion of any water in the purified product stream, and provide a dried purified product stream.

17. The system of claim **15**, wherein the extraction unit comprises a liquid-liquid contact vessel.

18. The system of claim **15**, wherein the stripping unit comprises a distillation column.

19. A reactive distillation process producing high purity ethyl acetate from ethanol, comprising:

feeding a feed stream comprising ethanol to a reactive distillation column;

contacting the ethanol with a catalyst;

dehydrogenating ethanol over the catalyst in the liquid phase during the distillation process;

removing ethyl acetate during the distillation process as a bottoms product; and

removing hydrogen during the distillation process as a top product.

20. The reactive distillation process of claim **19**, further comprising:

contacting the bottoms stream with a hydrogenation catalyst and hydrogen;

hydrogenating at least a portion of a contaminant in the bottoms stream; and

separating the hydrogenated portion of the contaminant from the bottoms stream.

21. The reactive distillation process of claim **20**, wherein the contacting, the hydrogenating, and the separating occur downstream of the reactive distillation column.

22. The reactive distillation process of claim **19**, further comprising:

extracting at least a portion of a contaminant in the bottoms stream using a solvent to produce an extract stream and a purified product stream; and

stripping the portion of the contaminant from the extract stream to produce a contaminant stream and regenerate the solvent stream.

23. The reactive distillation process of claim **19**, further comprising:

contacting a first fluid drawn from the reactive distillation column with the catalyst in a side reactor, wherein the first fluid reacts in the presence of the catalyst to produce a reaction product comprising a second fluid; and

introducing the second fluid to the reactive distillation column during the distillation process.

24. The reactive distillation process of claim **23**, further comprising:

increasing a contact time between the ethanol and the catalyst; and

improving a conversion of ethanol to ethyl acetate in response to increasing the contact time between the ethanol and the catalyst.

25. The reactive distillation process of claim **23**, further comprising:

contacting the bottoms stream with a hydrogenation catalyst and hydrogen;

hydrogenating at least a portion of a contaminant in the bottoms stream; and

separating the hydrogenated portion of the contaminant from the bottoms stream.

26. The reactive distillation process of claim **19**, wherein the bottoms product comprises at least about 90% ethyl acetate.

* * * * *

ThermoFisher
SCIENTIFIC

SAFETY DATA SHEET

Creation Date 09-Jul-2009	**Revision Date** 18-Jan-2018	**Revision Number** 4

1. Identification

Product Name   **Ethanol, Anhydrous (Histological)**

Cat No. :   **A405-20; A405F-1GAL; A405P-4**

Synonyms   Grain alcohol, denatured; Ethyl alcohol, denatured; Ethyl hydroxide, denatured.

Recommended Use   Laboratory chemicals.
Uses advised against   Not for food, drug, pesticide or biocidal product use

Details of the supplier of the safety data sheet

Company
Fisher Scientific
One Reagent Lane
Fair Lawn, NJ 07410
Tel: (201) 796-7100

Emergency Telephone Number
CHEMTREC®, Inside the USA: 800-424-9300
CHEMTREC®, Outside the USA: 001-703-527-3887

2. Hazard(s) identification

Classification
This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Flammable liquids	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Specific target organ toxicity (single exposure)	Category 1
Target Organs - Central nervous system (CNS), Optic nerve, Respiratory system.	
Specific target organ toxicity - (repeated exposure)	Category 1
Target Organs - Kidney, Liver, spleen, Blood.	

Label Elements

Signal Word
Danger

Hazard Statements
Highly flammable liquid and vapor
Causes serious eye irritation
Causes damage to organs
Causes damage to organs through prolonged or repeated exposure

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Page   1 / 10

233

Precautionary Statements
Prevention
Obtain special instructions before use
Do not handle until all safety precautions have been read and understood
Use personal protective equipment as required
Wash face, hands and any exposed skin thoroughly after handling
Wear eye/face protection
Do not breathe dust/fume/gas/mist/vapors/spray
Do not eat, drink or smoke when using this product
Keep away from heat/sparks/open flames/hot surfaces. - No smoking
Keep container tightly closed
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting/equipment
Use only non-sparking tools
Take precautionary measures against static discharge
Response
IF exposed: Call a POISON CENTER or doctor/physician
Skin
IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower
Eyes
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention
Fire
In case of fire: Use CO2, dry chemical, or foam for extinction
Storage
Store locked up
Store in a well-ventilated place. Keep cool
Disposal
Dispose of contents/container to an approved waste disposal plant
Hazards not otherwise classified (HNOC)
Repeated exposure may cause skin dryness or cracking
Other hazards
Poison, may be fatal or cause blindness if swallowed. Vapor harmful. Cannot be made non-poisonous.
WARNING. Cancer and Reproductive Harm - https://www.p65warnings.ca.gov/.

3. Composition/Information on Ingredients

Component	CAS-No	Weight %
Ethyl alcohol	64-17-5	91-92
Methyl alcohol	67-56-1	<5
Methylisobutyl ketone	108-10-1	1.0 - 2.0
Ethyl acetate	141-78-6	1-2
Hexane	110-54-3	<1
Toluene	108-88-3	<0.1
Ligroine	8032-32-4	<0.1

4. First-aid measures

General Advice   If symptoms persist, call a physician.

Eye Contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.
Skin Contact	Wash off immediately with plenty of water for at least 15 minutes. If skin irritation persists, call a physician.
Inhalation	Move to fresh air. If not breathing, give artificial respiration. Get medical attention if symptoms occur.
Ingestion	Clean mouth with water and drink afterwards plenty of water.
Most important symptoms and effects	None reasonably foreseeable. Breathing difficulties. Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting
Notes to Physician	Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media	Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.
Unsuitable Extinguishing Media	Water may be ineffective, Do not use a solid water stream as it may scatter and spread fire

Flash Point	13.9 °C / 57 °F
Method -	No information available
Autoignition Temperature	362.8 °C / 685 °F

Explosion Limits
Upper	18.0 vol %
Lower	3.3 vol %
Sensitivity to Mechanical Impact	No information available
Sensitivity to Static Discharge	No information available

Specific Hazards Arising from the Chemical
Flammable. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back. Containers may explode when heated. Vapors may form explosive mixtures with air.

Hazardous Combustion Products
Carbon monoxide (CO) Carbon dioxide (CO_2)

Protective Equipment and Precautions for Firefighters
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
3	3	0	N/A

6. Accidental release measures

Personal Precautions	Use personal protective equipment. Ensure adequate ventilation.
Environmental Precautions	Should not be released into the environment. See Section 12 for additional ecological information.
Methods for Containment and Clean Up	Soak up with inert absorbent material. Keep in suitable, closed containers for disposal.

7. Handling and storage

Handling	Wear personal protective equipment. Ensure adequate ventilation. Do not get in eyes, on skin, or on clothing. Avoid ingestion and inhalation.

Storage   Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from heat
                                         and sources of ignition.

8. Exposure controls / personal protection

__Exposure Guidelines__

Component	ACGIH TLV	OSHA PEL	NIOSH IDLH	Mexico OEL (TWA)
Ethyl alcohol	STEL: 1000 ppm	(Vacated) TWA: 1000 ppm (Vacated) TWA: 1900 mg/m³ TWA: 1000 ppm TWA: 1900 mg/m³	IDLH: 3300 ppm TWA: 1000 ppm TWA: 1900 mg/m³	TWA: 1000 ppm TWA: 1900 mg/m³
Methyl alcohol	TWA: 200 ppm STEL: 250 ppm Skin	(Vacated) TWA: 200 ppm (Vacated) TWA: 260 mg/m³ (Vacated) STEL: 250 ppm (Vacated) STEL: 325 mg/m³ Skin TWA: 200 ppm TWA: 260 mg/m³	IDLH: 6000 ppm TWA: 200 ppm TWA: 260 mg/m³ STEL: 250 ppm STEL: 325 mg/m³	TWA: 200 ppm TWA: 260 mg/m³ STEL: 250 ppm STEL: 310 mg/m³
Methylisobutyl ketone	TWA: 20 ppm STEL: 75 ppm	(Vacated) TWA: 50 ppm (Vacated) TWA: 205 mg/m³ (Vacated) STEL: 75 ppm (Vacated) STEL: 300 mg/m³ TWA: 100 ppm TWA: 410 mg/m³	IDLH: 500 ppm TWA: 50 ppm TWA: 205 mg/m³ STEL: 75 ppm STEL: 300 mg/m³	TWA: 50 ppm TWA: 205 mg/m³ STEL: 75 ppm STEL: 307 mg/m³
Ethyl acetate	TWA: 400 ppm	(Vacated) TWA: 400 ppm (Vacated) TWA: 1400 mg/m³ TWA: 400 ppm TWA: 1400 mg/m³	IDLH: 2000 ppm TWA: 400 ppm TWA: 1400 mg/m³	TWA: 400 ppm TWA: 1400 mg/m³
Hexane	TWA: 50 ppm Skin	(Vacated) TWA: 50 ppm (Vacated) TWA: 180 mg/m³ TWA: 500 ppm TWA: 1800 mg/m³	IDLH: 1100 ppm TWA: 50 ppm TWA: 180 mg/m³	TWA: 50 ppm TWA: 176 mg/m³
Toluene	TWA: 20 ppm	(Vacated) TWA: 100 ppm (Vacated) TWA: 375 mg/m³ Ceiling: 300 ppm (Vacated) STEL: 150 ppm (Vacated) STEL: 560 mg/m³ TWA: 200 ppm	IDLH: 500 ppm TWA: 100 ppm TWA: 375 mg/m³ STEL: 150 ppm STEL: 560 mg/m³	TWA: 50 ppm TWA: 188 mg/m³
Ligroine		(Vacated) TWA: 300 ppm (Vacated) TWA: 1350 mg/m³ (Vacated) STEL: 400 ppm (Vacated) STEL: 1800 mg/m³	TWA: 350 mg/m³ Ceiling: 1800 mg/m³	TWA: 300 ppm TWA: 1350 mg/m³ STEL: 400 ppm STEL: 1800 mg/m³

Legend

ACGIH - American Conference of Governmental Industrial Hygienists
OSHA - Occupational Safety and Health Administration
NIOSH IDLH: The National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

Engineering Measures   Ensure adequate ventilation, especially in confined areas. Use explosion-proof
                                        electrical/ventilating/lighting/equipment. Ensure that eyewash stations and safety showers
                                        are close to the workstation location.

__Personal Protective Equipment__

  Eye/face Protection   Wear appropriate protective eyeglasses or chemical safety goggles as described by
                                        OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard
                                        EN166.

  Skin and body protection   Long sleeved clothing.

Respiratory Protection   Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard
EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if
exposure limits are exceeded or if irritation or other symptoms are experienced.

Hygiene Measures   Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Liquid
Appearance	Clear
Odor	Alcohol-like
Odor Threshold	No information available
pH	No information available
Melting Point/Range	< -90 °C / -130 °F
Boiling Point/Range	No information available 77.1 °C / 170.8 °F
Flash Point	13.9 °C / 57 °F
Evaporation Rate	3.6 (Butyl acetate = 1.0)
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	18.0 vol %
Lower	3.3 vol %
Vapor Pressure	48 mmHg
Vapor Density	1.5
Specific Gravity	0.785 - 0.792
Solubility	Soluble in water
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	362.8 °C / 685 °F
Decomposition Temperature	No information available
Viscosity	No information available

10. Stability and reactivity

Reactive Hazard   None known, based on information available

Stability   Stable under normal conditions.

Conditions to Avoid   Incompatible products. Excess heat. Keep away from open flames, hot surfaces and
sources of ignition.

Incompatible Materials   Strong oxidizing agents, Acids, Acid anhydrides, Acid chlorides, Peroxides, Alkali metals

Hazardous Decomposition Products Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazardous Polymerization   Hazardous polymerization does not occur.

Hazardous Reactions   None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information
Oral LD50   Based on ATE data, the classification criteria are not met. ATE > 2000 mg/kg.
Dermal LD50   Based on ATE data, the classification criteria are not met. ATE > 2000 mg/kg.
Vapor LC50   Based on ATE data, the classification criteria are not met. ATE > 20 mg/l.
Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Ethyl alcohol	3450 mg/kg (Mouse)	Not listed	20000 ppm/10H (Rat)
Methyl alcohol	**Calc. ATE 60 mg/kg** LD50 > 1187 – 2769 mg/kg (Rat)	**Calc. ATE 60 mg/kg** LD50 = 17100 mg/kg (Rabbit)	**Calc. ATE 0.6 mg/L (vapours) or** **0.5 mg/L (mists)** LC50 = 128.2 mg/L (Rat) 4 h

Methylisobutyl ketone	LD50 = 2080 mg/kg (Rat)	LD50 = 3000 mg/kg (Rabbit)	LC50 = 8.2 mg/L (Rat) 4 h
Ethyl acetate	10,200 mg/kg (Rat)	> 20 mL/kg (Rabbit) > 18000 mg/kg (Rabbit)	58 mg/l (rat; 8 h)
Hexane	LD50 = 25 g/kg (Rat)	LD50 = 3000 mg/kg (Rabbit)	LC50 = 48000 ppm (Rat) 4 h
Toluene	> 5000 mg/kg (Rat)	LD50 = 12000 mg/kg (Rabbit)	26700 ppm (Rat) 1 h
Ligroine	Not listed	Not listed	LC50 = 3400 ppm (Rat) 4 h

Toxicologically Synergistic Products   No information available

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Irritation   Severe eye irritant

Sensitization   No information available

Carcinogenicity   The table below indicates whether each agency has listed any ingredient as a carcinogen.

Component	CAS-No	IARC	NTP	ACGIH	OSHA	Mexico
Ethyl alcohol	64-17-5	Group 1	Known	A3	X	Not listed
Methyl alcohol	67-56-1	Not listed	Not listed	Not listed	Not listed	Not listed
Methylisobutyl ketone	108-10-1	Group 2B	Not listed	A3	X	Not listed
Ethyl acetate	141-78-6	Not listed	Not listed	Not listed	Not listed	Not listed
Hexane	110-54-3	Not listed	Not listed	Not listed	Not listed	Not listed
Toluene	108-88-3	Not listed	Not listed	Not listed	Not listed	Not listed
Ligroine	8032-32-4	Not listed	Not listed	Not listed	Not listed	A3

IARC: (International Agency for Research on Cancer)   *IARC: (International Agency for Research on Cancer)*
Group 1 - Carcinogenic to Humans
Group 2A - Probably Carcinogenic to Humans
Group 2B - Possibly Carcinogenic to Humans
NTP: (National Toxicity Program)   *NTP: (National Toxicity Program)*
Known - Known Carcinogen
Reasonably Anticipated - Reasonably Anticipated to be a Human Carcinogen
ACGIH: (American Conference of Governmental Industrial Hygienists)   *A1 - Known Human Carcinogen*
A2 - Suspected Human Carcinogen
A3 - Animal Carcinogen
ACGIH: (American Conference of Governmental Industrial Hygienists)
Mexico - Occupational Exposure Limits - Carcinogens   *Mexico - Occupational Exposure Limits - Carcinogens*
A1 - Confirmed Human Carcinogen
A2 - Suspected Human Carcinogen
A3 - Confirmed Animal Carcinogen
A4 - Not Classifiable as a Human Carcinogen
A5 - Not Suspected as a Human Carcinogen

Mutagenic Effects   Mutagenic effects have occurred in experimental animals.

Reproductive Effects   No information available.

Developmental Effects   No information available.

Teratogenicity   No information available.

STOT - single exposure   Central nervous system (CNS) Optic nerve Respiratory system
STOT - repeated exposure   Kidney Liver spleen Blood

Aspiration hazard   No information available

Symptoms / effects,both acute and delayed   Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting

Endocrine Disruptor Information   No information available

Other Adverse Effects   The toxicological properties have not been fully investigated.

12. Ecological information

Ecotoxicity

Contains a substance which is:. Toxic to aquatic organisms. The product contains following substances which are hazardous for the environment.

Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
Ethyl alcohol	EC50 (72h) = 275 mg/l (Chlorella vulgaris)	Fathead minnow (Pimephales promelas) LC50 = 14200 mg/l/96h	Photobacterium phosphoreum:EC50 = 34634 mg/L/30 min Photobacterium phosphoreum:EC50 = 35470 mg/L/5 min	EC50 = 9268 mg/L/48h EC50 = 10800 mg/L/24h
Methyl alcohol	Not listed	Pimephales promelas: LC50 > 10000 mg/L 96h	EC50 = 39000 mg/L 25 min EC50 = 40000 mg/L 15 min EC50 = 43000 mg/L 5 min	EC50 > 10000 mg/L 24h
Methylisobutyl ketone	EC50: 400 mg/L/96h	LC50: 496 - 514 mg/L, 96h flow-through (Pimephales promelas)	EC50 = 79.6 mg/L 5 min	EC50: 4280.0 mg/L/24h EC50: 170 mg/L/48h EC50: 4280.0 mg/L/24h
Ethyl acetate	EC50 = 3300 mg/L/48h	Fathead minnow: LC50: 230 mg/l/ 96h Gold orfe: LC50: 270 mg/L/48h	EC50 = 1180 mg/L 5 min EC50 = 1500 mg/L 15 min EC50 = 5870 mg/L 15 min EC50 = 7400 mg/L 2 h	EC50 = 717 mg/L/48h
Hexane	Not listed	LC50: 2.1 - 2.98 mg/L, 96h flow-through (Pimephales promelas)	Not listed	EC50: 3.87 mg/L/48h
Toluene	EC50: = 12.5 mg/L, 72h static (Pseudokirchneriella subcapitata) EC50: > 433 mg/L, 96h (Pseudokirchneriella subcapitata)	50-70 mg/L LC50 96 h 5-7 mg/L LC50 96 h 15-19 mg/L LC50 96 h 28 mg/L LC50 96 h 12 mg/L LC50 96 h	EC50 = 19.7 mg/L 30 min	EC50: = 11.5 mg/L, 48h (Daphnia magna) EC50: 5.46 - 9.83 mg/L, 48h Static (Daphnia magna)
Ligroine	EC50: = 4700 mg/L, 72h (Pseudokirchneriella subcapitata)	Not listed	Not listed	Not listed

Persistence and Degradability   Persistence is unlikely based on information available.

Bioaccumulation/ Accumulation   No information available.

Mobility   Will likely be mobile in the environment due to its volatility.

Component	log Pow
Ethyl alcohol	-0.32
Methyl alcohol	-0.74
Methylisobutyl ketone	1.19
Ethyl acetate	0.6
Hexane	4.11
Toluene	2.7

13. Disposal considerations

Waste Disposal Methods   Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

Component	RCRA - U Series Wastes	RCRA - P Series Wastes
Methyl alcohol - 67-56-1	U154	-
Methylisobutyl ketone - 108-10-1	U161	-

Ethyl acetate - 141-78-6	U112	-
Toluene - 108-88-3	U220	-

14. Transport information

DOT
    UN-No   UN1170
    Proper Shipping Name   ETHANOL
    Hazard Class   3
    Packing Group   II
TDG
    UN-No   UN1170
    Proper Shipping Name   ETHANOL
    Hazard Class   3
    Packing Group   II
IATA
    UN-No   UN1170
    Proper Shipping Name   ETHANOL
    Hazard Class   3
    Packing Group   II
IMDG/IMO
    UN-No   UN1170
    Proper Shipping Name   ETHANOL
    Hazard Class   3
    Packing Group   II

15. Regulatory information

All of the components in the product are on the following Inventory lists: Australia Complete Regulatory Information contained in following SDS's X = listed China Canada The product is classified and labeled according to EC directives or corresponding national laws The product is classified and labeled in accordance with Directive 1999/45/EC Europe TSCA Korea Philippines U.S.A. (TSCA) Canada (DSL/NDSL) Europe (EINECS/ELINCS/NLP) Australia (AICS) Korea (ECL) China (IECSC) Japan (ENCS) Philippines (PICCS)

International Inventories

Component	TSCA	DSL	NDSL	EINECS	ELINCS	NLP	PICCS	ENCS	AICS	IECSC	KECL
Ethyl alcohol	X	X	-	200-578-6	-		X	X	X	X	X
Methyl alcohol	X	X	-	200-659-6	-		X	X	X	X	X
Methylisobutyl ketone	X	X	-	203-550-1	-		X	X	X	X	X
Ethyl acetate	X	X	-	205-500-4	-		X	X	X	X	X
Hexane	X	X	-	203-777-6	438-390 -3		X	X	X	X	X
Toluene	X	X	-	203-625-9	-		X	X	X	X	X
Ligroine	X	X	-	232-453-7	-		X	-	X	X	X

Legend:
X - Listed
E - Indicates a substance that is the subject of a Section 5(e) Consent order under TSCA.
F - Indicates a substance that is the subject of a Section 5(f) Rule under TSCA.
N - Indicates a polymeric substance containing no free-radical initiator in its inventory name but is considered to cover the designated polymer made with any free-radical initiator regardless of the amount used.
P - Indicates a commenced PMN substance
R - Indicates a substance that is the subject of a Section 6 risk management rule under TSCA.
S - Indicates a substance that is identified in a proposed or final Significant New Use Rule
T - Indicates a substance that is the subject of a Section 4 test rule under TSCA.
XU - Indicates a substance exempt from reporting under the Inventory Update Rule, i.e. Partial Updating of the TSCA Inventory Data Base Production and Site Reports (40 CFR 710(B).
Y1 - Indicates an exempt polymer that has a number-average molecular weight of 1,000 or greater.
Y2 - Indicates an exempt polymer that is a polyester and is made only from reactants included in a specified list of low concern reactants that comprises one of the eligibility criteria for the exemption rule.

U.S. Federal Regulations

TSCA 12(b)   Not applicable

SARA 313

Component	CAS-No	Weight %	SARA 313 - Threshold Values %
Methyl alcohol	67-56-1	<5	1.0
Methylisobutyl ketone	108-10-1	1.0 - 2.0	1.0
Hexane	110-54-3	<1	1.0
Toluene	108-88-3	<0.1	1.0

SARA 311/312 Hazard Categories   See section 2 for more information

CWA (Clean Water Act)

Component	CWA - Hazardous Substances	CWA - Reportable Quantities	CWA - Toxic Pollutants	CWA - Priority Pollutants
Toluene	X	1000 lb	X	X

Clean Air Act

Component	HAPS Data	Class 1 Ozone Depletors	Class 2 Ozone Depletors
Methyl alcohol	X		-
Methylisobutyl ketone	X		-
Hexane	X		-
Toluene	X		-

OSHA Occupational Safety and Health Administration
Not applicable

CERCLA

Component	Hazardous Substances RQs	CERCLA EHS RQs
Methyl alcohol	5000 lb	-
Methylisobutyl ketone	5000 lb	-
Ethyl acetate	5000 lb	-
Hexane	5000 lb	-
Toluene	1000 lb 1 lb	-

California Proposition 65   Ethyl alcohol is only a considered a Proposition 65 developmental hazard when it is ingested as an alcoholic beverage This product contains the following proposition 65 chemicals

Component	CAS-No	California Prop. 65	Prop 65 NSRL	Category
Ethyl alcohol	64-17-5	Development (alcoholic beverages only)	-	Developmental Carcinogen
Methyl alcohol	67-56-1	Developmental	-	Developmental
Methylisobutyl ketone	108-10-1	Carcinogen Developmental	-	Developmental Carcinogen
Toluene	108-88-3	Developmental	-	Developmental

U.S. State Right-to-Know Regulations

Component	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
Ethyl alcohol	X	X	X	X	X
Methyl alcohol	X	X	X	X	X
Methylisobutyl ketone	X	X	X	X	X
Ethyl acetate	X	X	X	-	X
Hexane	X	X	X	X	X
Toluene	X	X	X	X	X
Ligroine	-	X	X	-	-

U.S. Department of Transportation

Reportable Quantity (RQ):   N
DOT Marine Pollutant   N
DOT Severe Marine Pollutant   N

U.S. Department of Homeland Security
This product does not contain any DHS chemicals.

Other International Regulations

Mexico - Grade   Serious risk, Grade 3

16. Other information

Prepared By	Regulatory Affairs Thermo Fisher Scientific Email: EMSDS.RA@thermofisher.com
Creation Date	09-Jul-2009
Revision Date	18-Jan-2018
Print Date	18-Jan-2018
Revision Summary	This document has been updated to comply with the US OSHA HazCom 2012 Standard replacing the current legislation under 29 CFR 1910.1200 to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

Disclaimer

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text

End of SDS

SAFETY DATA SHEET

Creation Date 13-October-2009	**Revision Date** 18-January-2018	**Revision Number** 5

1. Identification

Product Name   Ethyl acetate

Cat No. :   BP1125-1; BP1125-4

CAS-No   141-78-6
Synonyms   Acetic acid ethyl ester

Recommended Use   Laboratory chemicals.
Uses advised against   Not for food, drug, pesticide or biocidal product use

Details of the supplier of the safety data sheet

Company

Importer/Distributor
Fisher Scientific
112 Colonnade Road,
Ottawa, ON K2E 7L6,
Canada
Tel: 1-800-234-7437

Manufacturer
Fisher Scientific
One Reagent Lane
Fair Lawn, NJ 07410
Tel: (201) 796-7100

Emergency Telephone Number
CHEMTREC®, Inside the USA: 800-424-9300
CHEMTREC®, Outside the USA: 001-703-527-3887

2. Hazard(s) identification

Classification

WHMIS 2015 Classification   Classified as hazardous under the Hazardous Products Regulations (SOR/2015-17)

Flammable liquids	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Central nervous system (CNS).	
Health Hazards Not Otherwise Classified	Category 1
Prolonged or repeated contact may dry skin and cause irritation or cracking	

Label Elements

Signal Word
Danger

Hazard Statements
Highly flammable liquid and vapor
Causes serious eye irritation
May cause drowsiness and dizziness
Prolonged or repeated contact may dry skin and cause irritation or cracking

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Page 1 / 7

Precautionary Statements
Prevention
Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking
Keep container tightly closed
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting/equipment
Use only non-sparking tools
Take precautionary measures against static discharges
Do not breathe dust/fumes/gas/mist/vapours/spray
Wash face, hands and any exposed skin thoroughly after handling
Use only outdoors or in a well-ventilated area
Wear protective gloves/protective clothing/eye protection/face protection
Response
IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/ shower
IF INHALED: Remove person to fresh air and keep comfortable for breathing
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
Call a POISON CENTER/ doctor if you feel unwell
In case of fire: Use dry sand, dry chemical or alcohol-resistant foam to extinguish
Storage
Store in a well-ventilated place. Keep container tightly closed
Store locked up
Disposal
Dispose of contents/container to an approved waste disposal plant

3. Composition/Information on Ingredients

Component	CAS-No	Weight %
Ethyl acetate	141-78-6	>95

4. First-aid measures

General Advice	If symptoms persist, call a physician.
Eye Contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.
Skin Contact	Wash off immediately with plenty of water for at least 15 minutes. If skin irritation persists, call a physician.
Inhalation	Move to fresh air. If not breathing, give artificial respiration. Get medical attention if symptoms occur.
Ingestion	Clean mouth with water and drink afterwards plenty of water.
Most important symptoms/effects	Breathing difficulties. May cause central nervous system depression: Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting
Notes to Physician	Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media   Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Unsuitable Extinguishing Media   Water may be ineffective, Do not use a solid water stream as it may scatter and spread fire

Flash Point   -4 °C / 24.8 °F

Method -   Closed cup

Autoignition Temperature   427 °C / 800.6 °F

Explosion Limits
Upper   11.5 vol %
Lower   2.0 vol %
Oxidizing Properties   Not oxidising

Sensitivity to Mechanical Impact No information available
Sensitivity to Static Discharge   No information available

Specific Hazards Arising from the Chemical
Flammable. Risk of ignition. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back.
Containers may explode when heated.

Hazardous Combustion Products
Carbon monoxide (CO) Carbon dioxide (CO_2)
Protective Equipment and Precautions for Firefighters
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full
protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
2	3	0	N/A

6. Accidental release measures

Personal Precautions   Use personal protective equipment. Ensure adequate ventilation.
Environmental Precautions   Should not be released into the environment. See Section 12 for additional ecological
                                  information.

Methods for Containment and Clean Soak up with inert absorbent material. Keep in suitable, closed containers for disposal.
Up

7. Handling and storage

Handling   Ensure adequate ventilation. Wear personal protective equipment. Do not get in eyes, on
                      skin, or on clothing. Avoid ingestion and inhalation.

Storage   Flammables area. Keep away from heat and sources of ignition. Keep container tightly
                      closed in a dry and well-ventilated place.

8. Exposure controls / personal protection

Exposure Guidelines

Component	Alberta	British Columbia	Ontario TWAEV	Quebec	ACGIH TLV	OSHA PEL	NIOSH IDLH
Ethyl acetate	TWA: 400 ppm TWA: 1440 mg/m³	TWA: 150 ppm	TWA: 400 ppm	TWA: 400 ppm TWA: 1440 mg/m³	TWA: 400 ppm	(Vacated) TWA: 400 ppm (Vacated) TWA: 1400 mg/m³ TWA: 400 ppm	IDLH: 2000 ppm TWA: 400 ppm TWA: 1400 mg/m³

Page 3 / 7

						TWA: 1400 mg/m³	

Legend

ACGIH - American Conference of Governmental Industrial Hygienists

OSHA - Occupational Safety and Health Administration

NIOSH IDLH: The National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

Engineering Measures

Ensure adequate ventilation, especially in confined areas. Use explosion-proof electrical/ventilating/lighting/equipment. Ensure that eyewash stations and safety showers are close to the workstation location.

Wherever possible, engineering control measures such as the isolation or enclosure of the process, the introduction of process or equipment changes to minimise release or contact, and the use of properly designed ventilation systems, should be adopted to control hazardous materials at source

Personal protective equipment

Eye Protection	Goggles
Hand Protection	Wear appropriate protective gloves and clothing to prevent skin exposure.

Glove material	Breakthrough time	Glove thickness	Glove comments
Butyl rubber	> 120 minutes	0.5 - 0.7 mm	Permeation rate 8 µg/cm2/min
Nitrile rubber	< 200 minutes		As tested under EN374-3 Determination of Resistance to Permeation by Chemicals

Inspect gloves before use. observe the instructions regarding permeability and breakthrough time which are provided by the supplier of the gloves. (Refer to manufacturer/supplier for information) gloves are suitable for the task: Chemical compatability, Dexterity, Operational conditions, User susceptibility, e.g. sensitisation effects, also take into consideration the specific local conditions under which the product is used, such as the danger of cuts, abrasion. gloves with care avoiding skin contamination.

Respiratory Protection

No protective equipment is needed under normal use conditions.

Environmental exposure controls

No information available.

Hygiene Measures

Handle in accordance with good industrial hygiene and safety practice. Keep away from food, drink and animal feeding stuffs. Do not eat, drink or smoke when using this product. Remove and wash contaminated clothing before re-use. Wash hands before breaks and at the end of workday.

9. Physical and chemical properties

Physical State	Liquid
Appearance	Colorless
Odor	sweet
Odor Threshold	50 ppm
pH	No information available
Melting Point/Range	-83.5 °C / -118.3 °F
Boiling Point/Range	75 - 78 °C / 167 - 172.4 °F
Flash Point	-4 °C / 24.8 °F
Method -	Closed cup
Evaporation Rate	6.2
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	11.5 vol %
Lower	2.0 vol %

Vapor Pressure	103 mbar @ 20°C
Vapor Density	3.04
Specific Gravity	0.902
Solubility	Slightly soluble in water
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	427 °C / 800.6 °F
Decomposition Temperature	No information available
Viscosity	0.45 cP @ 20 °C
Molecular Formula	C4 H8 O2
Molecular Weight	88.11
Surface tension	24 mN/m @ 20°C

10. Stability and reactivity

Reactive Hazard   None known, based on information available

Stability   Stable under normal conditions.

Conditions to Avoid   Incompatible products. Keep away from open flames, hot surfaces and sources of ignition.

Incompatible Materials   Strong oxidizing agents, Strong acids, Amines, Peroxides

Hazardous Decomposition Products Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazardous Polymerization   Hazardous polymerization does not occur.

Hazardous Reactions   None under normal processing.

11. Toxicological information

__Acute Toxicity__

Product Information
Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Ethyl acetate	10,200 mg/kg (Rat)	> 20 mL/kg (Rabbit) > 18000 mg/kg (Rabbit)	58 mg/l (rat; 8 h)

Toxicologically Synergistic   No information available
Products
__Delayed and immediate effects as well as chronic effects from short and long-term exposure__

Irritation   Irritating to eyes

Sensitization   No information available

Carcinogenicity   The table below indicates whether each agency has listed any ingredient as a carcinogen.

Component	CAS-No	IARC	NTP	ACGIH	OSHA	Mexico
Ethyl acetate	141-78-6	Not listed	Not listed	Not listed	Not listed	Not listed

Mutagenic Effects   No information available

Reproductive Effects   No information available.

Developmental Effects   No information available.

Teratogenicity   No information available.

STOT - single exposure   Central nervous system (CNS)
STOT - repeated exposure   None known

Aspiration hazard	No information available
Symptoms / effects,both acute and delayed	May cause central nervous system depression: Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting
Endocrine Disruptor Information	No information available
Other Adverse Effects	The toxicological properties have not been fully investigated.

12. Ecological information

Ecotoxicity
Do not empty into drains.

Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
Ethyl acetate	EC50 = 3300 mg/L/48h	Fathead minnow: LC50: 230 mg/l/ 96h Gold orfe: LC50: 270 mg/L/48h	EC50 = 1180 mg/L 5 min EC50 = 1500 mg/L 15 min EC50 = 5870 mg/L 15 min EC50 = 7400 mg/L 2 h	EC50 = 717 mg/L/48h

Persistence and Degradability	Persistence is unlikely based on information available.
Bioaccumulation/ Accumulation	No information available.
Mobility	Will likely be mobile in the environment due to its volatility.

Component	log Pow
Ethyl acetate	0.6

13. Disposal considerations

Waste Disposal Methods	Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

Component	RCRA - U Series Wastes	RCRA - P Series Wastes
Ethyl acetate - 141-78-6	U112	-

14. Transport information

DOT
   UN-No UN1173
   Proper Shipping Name ETHYL ACETATE
   Hazard Class 3
   Packing Group II
TDG
   UN-No UN1173
   Proper Shipping Name ETHYL ACETATE
   Hazard Class 3
   Packing Group II
IATA
   UN-No UN1173
   Proper Shipping Name ETHYL ACETATE
   Hazard Class 3
   Packing Group II
IMDG/IMO
   UN-No UN1173
   Proper Shipping Name ETHYL ACETATE
   Hazard Class 3
   Packing Group II

15. Regulatory information

All of the components in the product are on the following Inventory lists: X = listed

International Inventories

Component	DSL	NDSL	TSCA	EINECS	ELINCS	NLP	PICCS	ENCS	AICS	IECSC	KECL
Ethyl acetate	X	-	X	205-500-4	-		X	X	X	X	X

Canada

SDS in compliance with provisions of information as set out in Canadian Standard - Part 4, Schedule 1 and 2 of the Hazardous Products Regulations (HPR) and meets the requirements of the HPR (Paragraph 13(1)(a) of the Hazardous Products Act (HPA)).

Component	Canada - National Pollutant Release Inventory (NPRI)	Canadian Environmental Protection Agency (CEPA) - List of Toxic Substances	Canada's Chemicals Management Plan (CEPA)
Ethyl acetate	Part 5, Individual Substances		

16. Other information

Prepared By	Regulatory Affairs Thermo Fisher Scientific Email: EMSDS.RA@thermofisher.com
Creation Date	13-October-2009
Revision Date	18-January-2018
Print Date	18-January-2018
Revision Summary	This document has been updated to comply with the requirements of WHMIS 2015 to align with the Globally Harmonised System (GHS) for the Classification and Labelling of Chemicals.

Disclaimer

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End of SDS

Praxair Material Safety Data Sheet
(See section 15, under TSCA, for important restrictions on product use.)

1. Chemical Product and Company Identification

Product Name: Hydrogen, compressed (MSDS No. P-4604-G)	**Trade Names:** Hydrogen
Chemical Name: Hydrogen	**Synonyms:** Dihydrogen, parahydrogen, refrigerant gas R702, water gas
Chemical Family: Permanent gas	**Product Grades:** Industrial, 4.5, 4.5-Zero, 4.5 TOC, 5.0-UHP, 5.0-SPG, 5.5-SPG, 6.0-SPG, 6.0-UHP, and 6.0-Research

Telephone: Emergencies: 1-800-645-4633*   **Company Name:** Praxair, Inc.
                    CHEMTREC: 1-800-424-9300*   39 Old Ridgebury Road
                    Routine: 1-800-PRAXAIR   Danbury, CT 06810-5113
  *Call emergency numbers 24 hours a day only for spills, leaks, fire, exposure, or accidents
  involving this product. For routine information, contact your supplier, Praxair sales
  representative, or call 1-800-PRAXAIR (1-800-772-9247).

2. Hazards Identification

EMERGENCY OVERVIEW

DANGER! Flammable high-pressure gas.
Can form explosive mixtures with air.
May ignite if valve is opened to air.
Burns with invisible flame.
May cause dizziness and drowsiness.
Self-contained breathing apparatus may be required by rescue workers.
Under ambient conditions, this is a colorless, odorless, tasteless gas.

OSHA REGULATORY STATUS: This material is considered hazardous by the OSHA Hazard Communications Standard (29 CFR 1910.1200).

POTENTIAL HEALTH EFFECTS:

Effects of a Single (Acute) Overexposure

Inhalation. Asphyxiant. Effects are due to lack of oxygen. Moderate concentrations may cause headache, drowsiness, dizziness, excitation, excess salivation, vomiting, and unconsciousness. Lack of oxygen can kill.

Skin Contact. No harm expected.

Swallowing. An unlikely route of exposure; this product is a gas at normal temperature and pressure.

Eye Contact. No harm expected.

Effects of Repeated (Chronic) Overexposure. No harm expected.

A vertical line in the left margin indicates revised or new material.

Other Effects of Overexposure. Hydrogen is an asphyxiant. Lack of oxygen can kill.

Medical Conditions Aggravated by Overexposure. The toxicology and the physical and chemical properties of hydrogen suggest that overexposure is unlikely to aggravate existing medical conditions.

CARCINOGENICITY: This product is not listed by NTP, OSHA, or IARC

POTENTIAL ENVIRONMENTAL EFFECTS: None known. For further information, see section 12, Ecological Information.

---

3. Composition/Information on Ingredients

See section 16 for important information about mixtures.

COMPONENT	CAS NUMBER	CONCENTRATION
Hydrogen	1333-74-0	>99%*

The symbol > means "greater than."

---

4. First Aid Measures

INHALATION: Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, qualified personnel may give oxygen. Call a physician.

SKIN CONTACT: An unlikely route of exposure. This product is a gas at normal temperature and pressure.

SWALLOWING: An unlikely route of exposure. This product is a gas at normal temperature and pressure.

EYE CONTACT: An unlikely route of exposure. This product is a gas at normal temperature and pressure.

NOTES TO PHYSICIAN: There is no specific antidote. Treatment of overexposure should be directed at the control of symptoms and the clinical condition of the patient.

---

5. Fire Fighting Measures

FLAMMABLE PROPERTIES: Flammable gas. Flame is nearly invisible. Escaping gas may ignite spontaneously. Hydrogen has a low ignition energy. Fireball forms if gas cloud ignites immediately after release. Forms explosive mixtures with air and oxidizing agents.

SUITABLE EXTINGUISHING MEDIA: CO_2, dry chemical, water spray, or fog

PRODUCTS OF COMBUSTION: Water (H_2O)

PROTECTION OF FIREFIGHTERS: DANGER! Flammable high-pressure gas. Evacuate all personnel from danger area. Immediately deluge cylinders with water from maximum distance until cool; then move them away from fire area if without risk. Continue cooling water spray while moving cylinders. Do not extinguish flames emitted from cylinders; allow them to burn out. Self-contained breathing apparatus may be required by rescue workers. On-site fire brigades must comply with OSHA 29 CFR 1910.156.

Specific Physical and Chemical Hazards. Heat of fire can build pressure in cylinder and cause it to rupture. Hydrogen cylinders are equipped with a pressure relief device. (Exceptions may exist where authorized by DOT.) No part of a cylinder should be subjected to a temperature higher than 125°F (52°C). If venting or leaking hydrogen catches fire, do not

extinguish flames. Flammable gas may spread from leak, creating an explosive re-ignition hazard. Vapors can be ignited by pilot lights, other flames, smoking, sparks, heaters, electrical equipment, static discharge, or other ignition sources at locations distant from product handling point. Explosive atmospheres may linger. Before entering area, especially confined areas, check atmosphere with approved explosion meter.

Protective Equipment and Precautions for Firefighters. Firefighters should wear self-contained breathing apparatus and full fire-fighting turnout gear.

6. Accidental Release Measures

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:

DANGER! Flammable high-pressure gas.

Personal Precautions. Forms explosive mixtures with air. (See section 5.) Immediately evacuate all personnel from danger area. Use self-contained breathing apparatus where needed. Approach suspected leak area with caution. Remove all sources of ignition if without risk. Reduce gas with fog or fine water spray. Shut off flow if without risk. Ventilate area or move cylinder to a well-ventilated area. Flammable gas may spread from leak. Before entering area, especially confined areas, check atmosphere with an appropriate device.

Environmental Precautions. Prevent waste from contaminating the surrounding environment. Keep personnel away. Discard any product, residue, disposable container, or liner in an environmentally acceptable manner, in full compliance with federal, state, and local regulations. If necessary, call your local supplier for assistance.

7. Handling and Storage

PRECAUTIONS TO BE TAKEN IN HANDLING: *Keep away from heat, sparks, and open flame.* Use only spark-proof tools and explosion-proof equipment. *Protect cylinders from damage.* Use a suitable hand truck to move cylinders; do not drag, roll, slide, or drop. *Hydrogen is the lightest known gas.* It may leak out of systems that are air-tight for other gases and may collect in poorly ventilated upper reaches of buildings. Leak check system with soapy water; never use a flame. *All piped hydrogen systems and associated equipment must be grounded.* Electrical equipment must be non-sparking or explosion-proof. *Do not crack or open hydrogen cylinder valves unless connected to utilization equipment;* escaping gas may ignite spontaneously. Open valve slowly. If valve is hard to open, discontinue use and contact your supplier. Close cylinder valve after each use; keep closed even when empty. *Never attempt to lift a cylinder by its cap;* the cap is intended solely to protect the valve. Never insert an object (e.g., wrench, screwdriver, pry bar) into cap openings; doing so may damage the valve and cause a leak. Use an adjustable strap wrench to remove over-tight or rusted caps. For other precautions in using hydrogen, see section 16.

PRECAUTIONS TO BE TAKEN IN STORAGE: *Store and use with adequate ventilation.* Store only where temperature will not exceed 125°F (52°C). *Separate hydrogen cylinders from oxygen, chlorine, and other oxidizers* by at least 20 ft (6.1 m), or use a barricade of noncombustible material. This barricade should be at least 5 ft (1.53 m) high and have a fire resistance rating of at least ½ hour. *Always secure cylinders upright to keep them from falling or being knocked over.* Install valve protection cap, if provided, firmly in place by hand when the cylinder is not in use. *Post "No Smoking or Open Flames" signs in storage and use areas.* There must be no sources of ignition. All electrical equipment in storage areas must be explosion-proof. Storage areas must meet national electric codes for Class 1

hazardous areas. ***Store full and empty cylinders separately.*** Use a first-in, first-out inventory system to prevent storing full cylinders for long periods.

RECOMMENDED PUBLICATIONS: For further information on storage, handling, and use, see Praxair publication P-14-153, *Guidelines for Handling Gas Cylinders and Containers*. Obtain from your local supplier. For further information specific to hydrogen, see NFPA 50A, *Standard for Gaseous Hydrogen Systems at Consumer Sites*, published by the National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101; 1-800-344-3555; www.nfpa.org.

8. Exposure Controls/Personal Protection

COMPONENT	OSHA PEL	ACGIH TLV-TWA (2007)
Hydrogen	N.E.*	Simple asphyxiant

*N.E.–Not Established.

IDLH = Not applicable.

ENGINEERING CONTROLS:

Local Exhaust. An explosion-proof local exhaust system is acceptable. See SPECIAL.

Mechanical (General). Inadequate; see special.

Special. Use only in a closed system.

Other. See special.

PERSONAL PROTECTIVE EQUIPMENT:

Skin Protection. Wear work gloves for cylinder handling and metatarsal shoes for cylinder handling. Select in accordance with OSHA 29 CFR 1910.132 and 1910.133. Regardless of protective equipment, never touch live electrical parts.

Eye/Face Protection. Select in accordance with OSHA 29 CFR 1910.133.

Respiratory Protection. None required under normal use. An air-supplied respirator must be used in confined spaces. Respiratory protection must conform to OSHA rules as specified in 29 CFR 1910.134. Select per OSHA 29 CFR 1910.134 and ANSI Z88.2.

9. Physical and Chemical Properties

APPEARANCE:	Colorless gas
ODOR:	Odorless
ODOR THRESHOLD:	Not applicable.
PHYSICAL STATE:	Gas at normal temperature and pressure
pH:	Not applicable.
MELTING POINT at 1 atm**:**	-434.56°F (-259.2°C)
BOILING POINT at 1 atm**:**	-422.97°F (-252.76°C)
FLASH POINT (test method)**:**	Not available.
EVAPORATION RATE (Butyl Acetate = 1)**:**	Not applicable.
FLAMMABILITY:	Flammable
FLAMMABLE LIMITS IN AIR, % by volume**:**	**LOWER:** 4.0% **UPPER:** 75.0%

LIQUID DENSITY at boiling point and 1 atm**:**	4.43 lb/ft^3 (70.96 kg/m^3)
VAPOR PRESSURE at 68°F (20°C)**:**	Not applicable.
VAPOR DENSITY at 70°F (21.1°C) and 1 atm**:**	0.0052 lb/ft^3 (0.083 kg/m^3)
SPECIFIC GRAVITY (H$_2$O = 1) at 19.4°F (-7°C)**:**	Not available.
SPECIFIC GRAVITY (Air = 1) at 32°F (0°C) and 1 atm**:**	0.07
SOLUBILITY IN WATER vol/vol at 60°F (15.6°C) and 1 atm**:**	0.019
PARTITION COEFFICIENT: n-octanol/water:	Not available.
AUTOIGNITION TEMPERATURE:	932°F (500°C)
DECOMPOSITION TEMPERATURE:	Not available.
PERCENT VOLATILES BY VOLUME:	100
MOLECULAR WEIGHT:	2.016
MOLECULAR FORMULA:	H$_2$

10. Stability and Reactivity

CHEMICAL STABILITY: ☐ Unstable   ☒ Stable

CONDITIONS TO AVOID: None known.

INCOMPATIBLE MATERIALS: Oxidizing agents, lithium, halogens

HAZARDOUS DECOMPOSITION PRODUCTS: None

POSSIBILITY OF HAZARDOUS REACTIONS: ☒ May Occur   ☐ Will Not Occur

Flammable gas. Forms explosive mixtures with air and oxidizing agents.

11. Toxicological Information

ACUTE DOSE EFFECTS: Hydrogen is a simple asphyxiant.

STUDY RESULTS: None known.

12. Ecological Information

ECOTOXICITY: No adverse ecological effects expected.

OTHER ADVERSE EFFECTS: Hydrogen does not contain any Class I or Class II ozone-depleting chemicals.

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13. Disposal Considerations

WASTE DISPOSAL METHOD: Do not attempt to dispose of residual or unused quantities. Return cylinder to supplier.

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14. Transport Information

DOT/IMO SHIPPING NAME: Hydrogen, compressed

HAZARD CLASS: 2.1	**PACKING GROUP/Zone:** NA*	**IDENTIFICATION NUMBER:** UN1049	**PRODUCT RQ:** None
SHIPPING LABEL(s):	FLAMMABLE GAS		
PLACARD (when required):	FLAMMABLE GAS		

*NA-Not applicable.

SPECIAL SHIPPING INFORMATION: Cylinders should be transported in a secure position, in a well-ventilated vehicle. Cylinders transported in an enclosed, nonventilated compartment of a vehicle can present serious safety hazards.

Shipment of compressed gas cylinders that have been filled without the owner's consent is a violation of federal law [49 CFR 173.301(b)].

MARINE POLLUTANTS: Hydrogen is not listed as a marine pollutant by DOT.

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15. Regulatory Information

The following selected regulatory requirements may apply to this product. Not all such requirements are identified. Users of this product are solely responsible for compliance with all applicable federal, state, and local regulations.

U.S. FEDERAL REGULATIONS:

EPA (ENVIRONMENTAL PROTECTION AGENCY)

CERCLA: COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT OF 1980 (40 CFR Parts 117 and 302):

Reportable Quantity (RQ): None

SARA: SUPERFUND AMENDMENT AND REAUTHORIZATION ACT:

SECTIONS 302/304: Require emergency planning based on Threshold Planning Quantity (TPQ) and release reporting based on Reportable Quantities (RQ) of Extremely Hazardous Substances (EHS) (40 CFR Part 355):

TPQ: None
EHS RQ (40 CFR 355): None

SECTIONS 311/312: Require submission of MSDSs and reporting of chemical inventories with identification of EPA hazard categories. The hazard categories for this product are as follows:

IMMEDIATE: No	**PRESSURE:** Yes
DELAYED: No	**REACTIVITY:** No
	FIRE: Yes

SECTION 313: Requires submission of annual reports of release of toxic chemicals that appear in 40 CFR Part 372.

Hydrogen is not subject to reporting under Section 313.

40 CFR 68: RISK MANAGEMENT PROGRAM FOR CHEMICAL ACCIDENTAL RELEASE PREVENTION: Requires development and implementation of risk management programs at facilities that manufacture, use, store, or otherwise handle regulated substances in quantities that exceed specified thresholds.

> Hydrogen is listed as a regulated substance in quantities of 10,000 lb (4536 kg) or greater.

TSCA: TOXIC SUBSTANCES CONTROL ACT: Hydrogen is listed on the TSCA inventory.

OSHA: OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION:

29 CFR 1910.119: PROCESS SAFETY MANAGEMENT OF HIGHLY HAZARDOUS CHEMICALS: Requires facilities to develop a process safety management program based on Threshold Quantities (TQ) of highly hazardous chemicals.

> Hydrogen is not listed in Appendix A as a highly hazardous chemical. However, any process that involves a flammable gas on site in one location in quantities of 10,000 lb (4536 kg) or greater is covered under this regulation unless the gas is used as a fuel.

STATE REGULATIONS:

CALIFORNIA: Hydrogen is not listed by California under the SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 (Proposition 65).

PENNSYLVANIA: Hydrogen is subject to the PENNSYLVANIA WORKER AND COMMUNITY RIGHT-TO-KNOW ACT (35 P.S. Sections 7301-7320).

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16. Other Information

Be sure to read and understand all labels and instructions supplied with all containers of this product.

OTHER HAZARDOUS CONDITIONS OF HANDLING, STORAGE, AND USE: *Flammable high-pressure gas. Use only in a closed system. Use piping and equipment adequately designed to withstand pressures and temperatures to be encountered.* Use a backflow prevention device in the piping. *Gas can cause rapid suffocation due to oxygen deficiency.* Store and use with adequate ventilation. *Never work on a pressurized system.* If there is a leak, close the cylinder valve. Blow the system down in a safe and environmentally sound manner in compliance with all federal, state, and local laws; then repair the leak. *Never place a compressed gas cylinder where it may become part of an electrical circuit.*

Mixtures. When you mix two or more gases or liquefied gases, you can create additional, unexpected hazards. Obtain and evaluate the safety information for each component before you produce the mixture. Consult an industrial hygienist or other trained person when you evaluate the end product. Remember, gases and liquids have properties that can cause serious injury or death.

HAZARD RATING SYSTEMS:

NFPA RATINGS:		HMIS RATINGS:	
HEALTH	= 0	HEALTH	= 0
FLAMMABILITY	= 4	FLAMMABILITY	= 4
INSTABILITY	= 0	PHYSICAL HAZARD	= 3
SPECIAL	= None		

STANDARD VALVE CONNECTIONS FOR U.S. AND CANADA:

THREADED:	0-3000 psig	CGA-350
	3301-5500 psig	CGA-695
	5501-7500 psig	CGA-703
PIN-INDEXED YOKE:	Not applicable.	
ULTRA-HIGH-INTEGRITY CONNECTION:	CGA-724	

Use the proper CGA connections. **DO NOT USE ADAPTERS.** Additional limited-standard connections may apply. See CGA pamphlet V-1 listed below.

Ask your supplier about free Praxair safety literature as referred to in this MSDS and on the label for this product. Further information can be found in the following materials published by the Compressed Gas Association, Inc. (CGA), 4221 Walney Road, 5th Floor, Chantilly, VA 20151-2923; telephone (703) 788-2700, http://www.cganet.com/Publication.asp.

AV-1   *Safe Handling and Storage of Compressed Gases*
G-5   *Hydrogen*
G-5.3   *Commodity Specification for Hydrogen*
P-1   *Safe Handling of Compressed Gases in Containers*
SB-2   *Oxygen-Deficient Atmospheres*
V-1   *Compressed Gas Cylinder Valve Inlet and Outlet Connections*
—   *Handbook of Compressed Gases, Fourth Edition*

Praxair asks users of this product to study this MSDS and become aware of product hazards and safety information. To promote safe use of this product, a user should (1) notify employees, agents, and contractors of the information in this MSDS and of any other known product hazards and safety information, (2) furnish this information to each purchaser of the product, and (3) ask each purchaser to notify its employees and customers of the product hazards and safety information.

The opinions expressed herein are those of qualified experts within Praxair, Inc. We believe that the information contained herein is current as of the date of this Material Safety Data Sheet. Since the use of this information and the conditions of use of the product are not within the control of Praxair, Inc., it is the user's obligation to determine the conditions of safe use of the product.

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PRAXAIR

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Printed in USA

Eastman(TM) Acetaldehyde

Version 2.2 PRD	Revision Date: 02/20/2019	SDS Number: 150000000122 SDSUS / Z8 / 0001	Date of last issue: 11/26/2018 Date of first issue: 09/06/2016

SECTION 1. IDENTIFICATION

Product name	:	Eastman(TM) Acetaldehyde
Product code	:	00160-00, P0016000, P0016001, E0016002, E0016001

Manufacturer or supplier's details

Company name of supplier	:	Eastman Chemical Company
Address	:	200 South Wilcox Drive Kingsport TN 37660-5280
Telephone	:	(423) 229-2000
Emergency telephone	:	CHEMTREC: +1-800-424-9300, +1-703-527-3887 CCN7321

Recommended use of the chemical and restrictions on use

Recommended use	:	Chemical intermediate
Restrictions on use	:	None known.

SECTION 2. HAZARDS IDENTIFICATION

GHS classification in accordance with 29 CFR 1910.1200

Flammable liquids	:	Category 1
Acute toxicity (Oral)	:	Category 4
Eye irritation	:	Category 2A
Carcinogenicity	:	Category 2
Specific target organ systemic toxicity - single exposure	:	Category 3 (Respiratory system)

GHS label elements

Hazard pictograms	:	
Signal Word	:	Danger
Hazard Statements	:	H224 Extremely flammable liquid and vapor. H302 Harmful if swallowed. H319 Causes serious eye irritation. H335 May cause respiratory irritation.

SAFETY DATA SHEET

EASTMAN

Eastman(TM) Acetaldehyde

| Version 2.2 PRD | Revision Date: 02/20/2019 | SDS Number: 150000000122 SDSUS / Z8 / 0001 | Date of last issue: 11/26/2018 Date of first issue: 09/06/2016 |

H351 Suspected of causing cancer.

Precautionary Statements :

Prevention:

P201 Obtain special instructions before use.
P202 Do not handle until all safety precautions have been read and understood.
P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.
P233 Keep container tightly closed.
P240 Ground/bond container and receiving equipment.
P241 Use explosion-proof electrical/ ventilating/ lighting/ equipment.
P242 Use only non-sparking tools.
P243 Take precautionary measures against static discharge.
P261 Avoid breathing dust/ fume/ gas/ mist/ vapors/ spray.
P264 Wash skin thoroughly after handling.
P270 Do not eat, drink or smoke when using this product.
P271 Use only outdoors or in a well-ventilated area.
P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.

Response:

P301 + P312 + P330 IF SWALLOWED: Call a POISON CENTER/doctor if you feel unwell. Rinse mouth.
P303 + P361 + P353 IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.
P304 + P340 + P312 IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER/doctor if you feel unwell.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P308 + P313 IF exposed or concerned: Get medical advice/ attention.
P337 + P313 If eye irritation persists: Get medical advice/ attention.
P370 + P378 In case of fire: Use dry sand, dry chemical or alcohol-resistant foam to extinguish.

Storage:

P403 + P233 Store in a well-ventilated place. Keep container tightly closed.
P403 + P235 Store in a well-ventilated place. Keep cool.
P405 Store locked up.

Disposal:

P501 Dispose of contents/ container to an approved waste disposal plant.

Other hazards

May polymerize resulting in hazardous condition.
May form peroxides of unknown stability.

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Ingredients

Chemical name	CAS-No.	Concentration (% w/w)
acetaldehyde	75-07-0	100

SECTION 4. FIRST AID MEASURES

If inhaled	:	Move to fresh air. Treat symptomatically. If symptoms persist, call a physician.
In case of skin contact	:	Wash off with soap and water. Remove contaminated clothing and shoes. Get medical attention if symptoms occur.
In case of eye contact	:	Remove contact lenses, if present and easy to do. Continue rinsing. If eye irritation persists: Get medical advice/ attention.
If swallowed	:	Seek medical advice.
Most important symptoms and effects, both acute and delayed	:	Harmful if swallowed. Causes serious eye irritation. May cause respiratory irritation. Suspected of causing cancer.
Notes to physician	:	Treat symptomatically.

SECTION 5. FIRE-FIGHTING MEASURES

Suitable extinguishing media	:	Alcohol-resistant foam Carbon dioxide (CO2) Dry chemical Water spray
Unsuitable extinguishing media	:	Water spray jet
Specific hazards during fire fighting	:	Water may be ineffective. The product will float on water and can be reignited on surface water.
Further information	:	Highly flammable liquid and vapor. Use water spray to cool unopened containers.
Special protective equipment for fire-fighters	:	Wear an approved positive pressure self-contained breathing apparatus in addition to standard fire fighting gear.

SECTION 6. ACCIDENTAL RELEASE MEASURES

Eastman(TM) Acetaldehyde

Personal precautions, protective equipment and emergency procedures	:	Wear appropriate personal protective equipment. Local authorities should be advised if significant spillages cannot be contained.	
Environmental precautions	:	Avoid release to the environment.	
Methods and materials for containment and cleaning up	:	Contain spillage, soak up with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and transfer to a container for disposal according to local / national regulations (see section 13). After cleaning, flush away traces with water. Eliminate all ignition sources if safe to do so.	

SECTION 7. HANDLING AND STORAGE

Advice on protection against fire and explosion	:	None known.
Advice on safe handling	:	Do not get in eyes. Avoid contact with skin, eyes and clothing. Do not swallow. Wash thoroughly after handling. Keep away from fire (No Smoking). Keep away from fire, sparks and heated surfaces. Do not use sparking tools.
Conditions for safe storage	:	Keep container closed when not in use. Store locked up.

SECTION 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Ingredients with workplace control parameters

Ingredients	CAS-No.	Value type (Form of exposure)	Control parameters / Permissible concentration	Basis
acetaldehyde	75-07-0	C	25 ppm	ACGIH
		TWA	200 ppm 360 mg/m3	OSHA Z-1
		TWA	100 ppm 180 mg/m3	OSHA P0
		STEL	150 ppm 270 mg/m3	OSHA P0

Engineering measures : Ensure adequate ventilation.

Personal protective equipment

Respiratory protection	:	Use respiratory protection unless adequate local exhaust ventilation is provided or exposure assessment demonstrates that exposures are within recommended exposure guidelines.
Hand protection		

Version 2.2 PRD	Revision Date: 02/20/2019	SDS Number: 150000000122 SDSUS / Z8 / 0001	Date of last issue: 11/26/2018 Date of first issue: 09/06/2016

Remarks	:	Wear suitable gloves.
Eye protection	:	Wear safety glasses with side shields (or goggles). Face-shield Always wear eye protection when the potential for inadvertent eye contact with the product cannot be excluded.
Protective measures	:	Remove respiratory and skin/eye protection only after vapors have been cleared from the area. Ensure that eye flushing systems and safety showers are located close to the working place. Use personal protective equipment as required.
Hygiene measures	:	Handle in accordance with good industrial hygiene and safety practice.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	:	liquid
Color	:	colorless
Odor	:	pungent
Odor Threshold	:	0.05 ppm
pH	:	not determined
Melting point/range	:	-189 °F / -123 °C
Boiling point/boiling range	:	70 °F / 21 °C
Flash point	:	-38 °F / -39 °C Method: Tag closed cup
Evaporation rate	:	not determined
Vapor pressure	:	532 mbar (41 °F / 5 °C)
Relative vapor density	:	1.5
Relative density	:	0.788 (68 °F / 20 °C)
Solubility(ies) Water solubility	:	completely soluble
Partition coefficient: n-octanol/water	:	Pow: 2.7 log Pow: 0.43
Autoignition temperature	:	300 °F / 149 °C Method: ASTM D2155

264

SAFETY DATA SHEET

![EASTMAN]

Eastman(TM) Acetaldehyde

Version 2.2 PRD	Revision Date: 02/20/2019	SDS Number: 150000000122 SDSUS / Z8 / 0001	Date of last issue: 11/26/2018 Date of first issue: 09/06/2016

Decomposition temperature	:	Thermal stability not tested. Low stability hazard expected at normal operating temperatures.
Viscosity		
Viscosity, dynamic	:	not determined
Viscosity, kinematic	:	not determined
Explosive properties	:	No data available
Oxidizing properties	:	No data available

SECTION 10. STABILITY AND REACTIVITY

Reactivity	:	Stable
Chemical stability	:	Stable under normal conditions.
Possibility of hazardous reactions	:	Stable
Conditions to avoid	:	Heat, flames and sparks.
Incompatible materials	:	Strong oxidizing agents
Hazardous decomposition products	:	Carbon dioxide (CO2) Carbon monoxide

SECTION 11. TOXICOLOGICAL INFORMATION

Acute toxicity
Harmful if swallowed.

Product:

Acute oral toxicity	:	Remarks: No data available
Acute inhalation toxicity	:	Remarks: No data available
Acute dermal toxicity	:	Remarks: No data available

Ingredients:

acetaldehyde:

Acute oral toxicity	:	LD50 Oral (Rat): 1,930 mg/kg
		LD50 Oral (Rat): 661 mg/kg
Acute inhalation toxicity	:	LC50 (Rat): 13300 ppm Exposure time: 4 h
Acute dermal toxicity	:	LD50 Dermal (Rabbit): 3,540 mg/kg

SAFETY DATA SHEET

EASTMAN

Eastman(TM) Acetaldehyde

Version 2.2 PRD	Revision Date: 02/20/2019	SDS Number: 150000000122 SDSUS / Z8 / 0001	Date of last issue: 11/26/2018 Date of first issue: 09/06/2016

Skin corrosion/irritation

Not classified based on available information.

Product:

Remarks	:	No data available

Ingredients:

acetaldehyde:

Species	:	Rabbit
Exposure time	:	24 h
Result	:	slight

Serious eye damage/eye irritation

Causes serious eye irritation.

Product:

Remarks	:	No data available

Ingredients:

acetaldehyde:

Species	:	Rabbit
Result	:	Moderate

Respiratory or skin sensitization

Skin sensitization

Not classified based on available information.

Respiratory sensitization

Not classified based on available information.

Product:

Remarks	:	No data available

Ingredients:

acetaldehyde:

Species	:	Guinea pig
Result	:	negative

Germ cell mutagenicity

Not classified based on available information.

Carcinogenicity

Suspected of causing cancer.
IARC	Group 2B: Possibly carcinogenic to humans	
	acetaldehyde	75-07-0

SAFETY DATA SHEET

EASTMAN

Eastman(TM) Acetaldehyde

| Version 2.2 PRD | Revision Date: 02/20/2019 | SDS Number: 150000000122 SDSUS / Z8 / 0001 | Date of last issue: 11/26/2018 Date of first issue: 09/06/2016 |

OSHA	No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.
NTP	Reasonably anticipated to be a human carcinogen

acetaldehyde   75-07-0

Reproductive toxicity

Not classified based on available information.

Product:

Effects on fertility   :   Remarks: No data available

STOT-single exposure

May cause respiratory irritation.

Product:

Remarks   :   No data available

STOT-repeated exposure

Not classified based on available information.

Product:

Remarks   :   No data available

Aspiration toxicity

Not classified based on available information.

Product:

No data available

No aspiration toxicity classification

Information on likely routes of exposure

Product:

Inhalation   :   Remarks: Irritating to respiratory system.

Skin contact   :   Remarks: None known.

Eye contact   :   Remarks: Causes serious eye irritation.

Ingestion   :   Remarks: Harmful if swallowed.

Further information

Product:

Remarks   :   None known.

267

Eastman(TM) Acetaldehyde

SECTION 12. ECOLOGICAL INFORMATION

Ecotoxicity

Ingredients:

acetaldehyde:

Toxicity to fish	:	LC50 (Lepomis macrochirus (Bluegill sunfish)): 53 mg/l Exposure time: 96 h
		LC50 (golden orfe): 124 - 140 mg/l Exposure time: 48 h
Toxicity to daphnia and other aquatic invertebrates	:	EC50 (daphnid): 57.4 mg/l Exposure time: 48 h
Toxicity to algae	:	EC50 (Pseudokirchneriella subcapitata (algae)): > 100 mg/l Exposure time: 72 h

Persistence and degradability

Ingredients:

acetaldehyde:

Biochemical Oxygen Demand (BOD)	:	127 - 130 mg/g Incubation time: 5 d

Bioaccumulative potential
No data available

Mobility in soil
No data available

Other adverse effects
No data available

SECTION 13. DISPOSAL CONSIDERATIONS

Disposal methods

Waste from residues	:	Dispose of in accordance with local regulations.

SECTION 14. TRANSPORT INFORMATION

International Regulations

IATA-DGR
Not permitted for transport

IMDG-Code

UN number	:	UN 1089
Proper shipping name	:	ACETALDEHYDE

SAFETY DATA SHEET

Eastman(TM) Acetaldehyde

| Version 2.2 PRD | Revision Date: 02/20/2019 | SDS Number: 150000000122 SDSUS / Z8 / 0001 | Date of last issue: 11/26/2018 Date of first issue: 09/06/2016 |

Class	:	3
Packing group	:	I
Labels	:	3
EmS Code	:	F-E, S-D
Marine pollutant	:	no

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code

Not applicable for product as supplied.

Domestic regulation

49 CFR

UN/ID/NA number	:	UN 1089
Proper shipping name	:	Acetaldehyde
Class	:	3
Packing group	:	I
Labels	:	Class 3 - Flammable Liquid
ERG Code	:	129
Marine pollutant	:	no

Special precautions for user

The transport classification(s) provided herein are for informational purposes only, and solely based upon the properties of the unpackaged material as it is described within this Safety Data Sheet. Transportation classifications may vary by mode of transportation, package sizes, and variations in regional or country regulations.

SECTION 15. REGULATORY INFORMATION

EPCRA - Emergency Planning and Community Right-to-Know

CERCLA Reportable Quantity

Ingredients	CAS-No.	Component RQ (lbs)	Calculated product RQ (lbs)
acetaldehyde	75-07-0	1000	1000

SARA 304 Extremely Hazardous Substances Reportable Quantity

This material does not contain any components with a section 304 EHS RQ.

SARA 302 Extremely Hazardous Substances Threshold Planning Quantity

This material does not contain any components with a section 302 EHS TPQ.

SARA 311/312 Hazards	:	Flammable (gases, aerosols, liquids, or solids) Acute toxicity (any route of exposure) Serious eye damage or eye irritation Specific target organ toxicity (single or repeated exposure) Carcinogenicity
SARA 313	:	The following components are subject to reporting levels established by SARA Title III, Section 313:
		acetaldehyde 75-07-0

SAFETY DATA SHEET

EASTMAN

Eastman(TM) Acetaldehyde

Version	Revision Date:	SDS Number:	Date of last issue: 11/26/2018
2.2	02/20/2019	150000000122	Date of first issue: 09/06/2016
PRD		SDSUS / Z8 / 0001	

California Prop. 65

WARNING: This product can expose you to chemicals including acetaldehyde, which is/are known to the State of California to cause cancer. For more information go to www.P65Warnings.ca.gov.

The ingredients of this product are reported in the following inventories:

TSCA	:	On TSCA Inventory
DSL	:	All components of this product are on the Canadian DSL
AICS	:	On the inventory, or in compliance with the inventory
ENCS	:	On the inventory, or in compliance with the inventory
ISHL	:	On the inventory, or in compliance with the inventory
KECI	:	On the inventory, or in compliance with the inventory
PICCS	:	On the inventory, or in compliance with the inventory
IECSC	:	On the inventory, or in compliance with the inventory

TSCA list

No substances are subject to a Significant New Use Rule.

The following substance(s) is/are subject to TSCA 12(b) export notification requirements:
acetaldehyde   75-07-0

SECTION 16. OTHER INFORMATION

Further information

NFPA 704:

Flammability

Health

Instability

Special hazard.
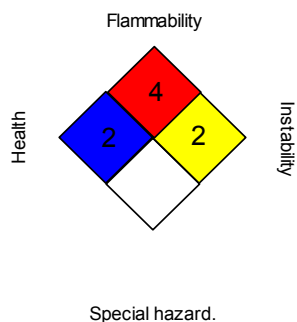
HMIS® IV:

HEALTH	*	2
FLAMMABILITY		4
PHYSICAL HAZARD		2

HMIS® ratings are based on a 0-4 rating scale, with 0 representing minimal hazards or risks, and 4 representing significant hazards or risks. The "*" represents a chronic hazard, while the "/" represents the absence of a chronic hazard.

Full text of other abbreviations

ACGIH	:	USA. ACGIH Threshold Limit Values (TLV)

OSHA P0	:	USA. OSHA - TABLE Z-1 Limits for Air Contaminants - 1910.1000
OSHA Z-1	:	USA. Occupational Exposure Limits (OSHA) - Table Z-1 Limits for Air Contaminants
ACGIH / C	:	Ceiling limit
OSHA P0 / TWA	:	8-hour time weighted average
OSHA P0 / STEL	:	Short-term exposure limit
OSHA Z-1 / TWA	:	8-hour time weighted average

AICS - Australian Inventory of Chemical Substances; ASTM - American Society for the Testing of Materials; bw - Body weight; CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act; CMR - Carcinogen, Mutagen or Reproductive Toxicant; DIN - Standard of the German Institute for Standardisation; DOT - Department of Transportation; DSL - Domestic Substances List (Canada); ECx - Concentration associated with x% response; EHS - Extremely Hazardous Substance; ELx - Loading rate associated with x% response; EmS - Emergency Schedule; ENCS - Existing and New Chemical Substances (Japan); ErCx - Concentration associated with x% growth rate response; ERG - Emergency Response Guide; GHS - Globally Harmonized System; GLP - Good Laboratory Practice; HMIS - Hazardous Materials Identification System; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; IBC - International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk; IC50 - Half maximal inhibitory concentration; ICAO - International Civil Aviation Organization; IECSC - Inventory of Existing Chemical Substances in China; IMDG - International Maritime Dangerous Goods; IMO - International Maritime Organization; ISHL - Industrial Safety and Health Law (Japan); ISO - International Organisation for Standardization; KECI - Korea Existing Chemicals Inventory; LC50 - Lethal Concentration to 50 % of a test population; LD50 - Lethal Dose to 50% of a test population (Median Lethal Dose); MARPOL - International Convention for the Prevention of Pollution from Ships; MSHA - Mine Safety and Health Administration; n.o.s. - Not Otherwise Specified; NFPA - National Fire Protection Association; NO(A)EC - No Observed (Adverse) Effect Concentration; NO(A)EL - No Observed (Adverse) Effect Level; NOELR - No Observable Effect Loading Rate; NTP - National Toxicology Program; NZIoC - New Zealand Inventory of Chemicals; OECD - Organization for Economic Co-operation and Development; OPPTS - Office of Chemical Safety and Pollution Prevention; PBT - Persistent, Bioaccumulative and Toxic substance; PICCS - Philippines Inventory of Chemicals and Chemical Substances; (Q)SAR - (Quantitative) Structure Activity Relationship; RCRA - Resource Conservation and Recovery Act; REACH - Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; RQ - Reportable Quantity; SADT - Self-Accelerating Decomposition Temperature; SARA - Superfund Amendments and Reauthorization Act; SDS - Safety Data Sheet; TCSI - Taiwan Chemical Substance Inventory; TSCA - Toxic Substances Control Act (United States); UN - United Nations; UNRTDG - United Nations Recommendations on the Transport of Dangerous Goods; vPvB - Very Persistent and Very Bioaccumulative

Revision Date   :   02/20/2019

US / Z8

ThermoFisher SCIENTIFIC

SAFETY DATA SHEET

Creation Date 13-Apr-2009   **Revision Date** 17-Jan-2018   **Revision Number** 6

1. Identification

Product Name   **Methyl Ethyl Ketone**

Cat No. :   **M209-1, M209-20, M209-200, M209-4, M209-500, M209S-4, M209FB-19, M209FB-50, M209FB-115, M209FB-200, M209RB-115, M209RS-19, M209RS-28, M209RS-50, M209RS-200, M209SS-28, M209SS-50, M209SS-115, M209SS-200**

CAS-No   78-93-3
Synonyms   2-Butanone; MEK; Ethyl methyl ketone

Recommended Use   Laboratory chemicals.
Uses advised against   Not for food, drug, pesticide or biocidal product use

Details of the supplier of the safety data sheet

Company
Fisher Scientific
One Reagent Lane
Fair Lawn, NJ 07410
Tel: (201) 796-7100

Emergency Telephone Number
CHEMTREC®, Inside the USA: 800-424-9300
CHEMTREC®, Outside the USA: 001-703-527-3887

2. Hazard(s) identification

Classification
This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Flammable liquids	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Central nervous system (CNS).	
Specific target organ toxicity - (repeated exposure)	Category 2
Target Organs - Kidney, Liver.	

Label Elements

Signal Word
Danger

Hazard Statements
Highly flammable liquid and vapor
Causes serious eye irritation
May cause drowsiness or dizziness
May cause damage to organs through prolonged or repeated exposure

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Page 1 / 8

272

Precautionary Statements
Prevention
Wash face, hands and any exposed skin thoroughly after handling
Do not breathe dust/fume/gas/mist/vapors/spray
Use only outdoors or in a well-ventilated area
Keep away from heat/sparks/open flames/hot surfaces. - No smoking
Keep container tightly closed
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting/equipment
Use only non-sparking tools
Take precautionary measures against static discharge
Wear protective gloves/protective clothing/eye protection/face protection
Keep cool
Response
Get medical attention/advice if you feel unwell
Inhalation
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Call a POISON CENTER or doctor/physician if you feel unwell
Skin
IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower
Eyes
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention
Fire
In case of fire: Use CO2, dry chemical, or foam for extinction
Storage
Store in a well-ventilated place. Keep container tightly closed
Store locked up
Disposal
Dispose of contents/container to an approved waste disposal plant
Hazards not otherwise classified (HNOC)
Repeated exposure may cause skin dryness or cracking

3. Composition/Information on Ingredients

Component	CAS-No	Weight %
Methyl ethyl ketone	78-93-3	>95

4. First-aid measures

Eye Contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.
Skin Contact	Wash off immediately with plenty of water for at least 15 minutes. Get medical attention if symptoms occur.
Inhalation	Move to fresh air. Get medical attention if symptoms occur. If not breathing, give artificial respiration.

Ingestion	Do not induce vomiting. Obtain medical attention.
Most important symptoms and effects	Breathing difficulties. Symptoms of overexposure may be headache, dizziness, tiredness, nausea and vomiting: Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting
Notes to Physician	Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media	CO_2, dry chemical, dry sand, alcohol-resistant foam. Cool closed containers exposed to fire with water spray.
Unsuitable Extinguishing Media	Water may be ineffective
Flash Point	-7 °C / 19.4 °F
Method -	Closed cup
Autoignition Temperature	404 °C / 759.2 °F

Explosion Limits
Upper   11.4 vol %
Lower   1.4 vol %
Oxidizing Properties   Not oxidising

Sensitivity to Mechanical Impact No information available
Sensitivity to Static Discharge   No information available

Specific Hazards Arising from the Chemical
Flammable. Risk of ignition. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back. Containers may explode when heated. Thermal decomposition can lead to release of irritating gases and vapors. Keep product and empty container away from heat and sources of ignition.

Hazardous Combustion Products
Carbon monoxide (CO) Carbon dioxide (CO_2)
Protective Equipment and Precautions for Firefighters
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
2	3	1	N/A

6. Accidental release measures

Personal Precautions	Use personal protective equipment. Remove all sources of ignition. Take precautionary measures against static discharges. Avoid contact with skin, eyes and clothing. Ensure adequate ventilation.
Environmental Precautions	Avoid release to the environment. See Section 12 for additional ecological information.
Methods for Containment and Clean Up	Remove all sources of ignition. Soak up with inert absorbent material. Keep in suitable, closed containers for disposal. Use spark-proof tools and explosion-proof equipment.

7. Handling and storage

Handling	Wear personal protective equipment. Ensure adequate ventilation. Use spark-proof tools and explosion-proof equipment. Avoid contact with skin, eyes and clothing. Avoid ingestion and inhalation. Keep away from open flames, hot surfaces and sources of ignition. Take precautionary measures against static discharges. Use only non-sparking tools. To avoid ignition of vapors by static electricity discharge, all metal parts of the equipment must be grounded.

Storage   Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from heat and sources of ignition. Flammables area.

8. Exposure controls / personal protection

Exposure Guidelines

Component	ACGIH TLV	OSHA PEL	NIOSH IDLH	Mexico OEL (TWA)
Methyl ethyl ketone	TWA: 200 ppm STEL: 300 ppm	(Vacated) TWA: 200 ppm (Vacated) TWA: 590 mg/m³ (Vacated) STEL: 300 ppm (Vacated) STEL: 885 mg/m³ TWA: 200 ppm TWA: 590 mg/m³	IDLH: 3000 ppm TWA: 200 ppm TWA: 590 mg/m³ STEL: 300 ppm STEL: 885 mg/m³	TWA: 200 ppm TWA: 590 mg/m³ STEL: 300 ppm STEL: 885 mg/m³

Legend

ACGIH - American Conference of Governmental Industrial Hygienists
OSHA - Occupational Safety and Health Administration
NIOSH IDLH: The National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

Engineering Measures   Ensure adequate ventilation, especially in confined areas. Use explosion-proof electrical/ventilating/lighting/equipment. Ensure that eyewash stations and safety showers are close to the workstation location.

Personal Protective Equipment

    Eye/face Protection   Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

    Skin and body protection   Wear appropriate protective gloves and clothing to prevent skin exposure.

    Respiratory Protection   Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

    Hygiene Measures   Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Liquid
Appearance	Colorless
Odor	Characteristic - sweet
Odor Threshold	No information available
pH	No information available
Melting Point/Range	-87 °C / -124.6 °F
Boiling Point/Range	80 °C / 176 °F
Flash Point	-7 °C / 19.4 °F
Method -	Closed cup
Evaporation Rate	3.7
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	11.4 vol %
Lower	1.4 vol %
Vapor Pressure	105 mbar @ 20 °C
Vapor Density	2.41
Specific Gravity	0.806
Solubility	Soluble in water
Partition coefficient; n-octanol/water	No data available

Autoignition Temperature	404 °C / 759.2 °F
Decomposition Temperature	No information available
Viscosity	0.42 mPa.s @ 15°C
Molecular Formula	C4 H8 O
Molecular Weight	72.11

10. Stability and reactivity

Reactive Hazard   None known, based on information available

Stability   Hygroscopic.

Conditions to Avoid   Incompatible products. Excess heat. Keep away from open flames, hot surfaces and sources of ignition. Exposure to moist air or water.

Incompatible Materials   Strong oxidizing agents, Strong acids, Strong bases, Strong reducing agents, Ammonia, copper, Amines

Hazardous Decomposition Products Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazardous Polymerization Hazardous polymerization does not occur.

Hazardous Reactions   None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information
Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Methyl ethyl ketone	LD50 = 2483 mg/kg (Rat) LD50 = 2737 mg/kg (Rat)	LD50 = 5000 mg/kg (Rabbit) LD50 = 6480 mg/kg (Rabbit)	LC50 = 11700 ppm (Rat) 4 h

Toxicologically Synergistic   No information available
Products
Delayed and immediate effects as well as chronic effects from short and long-term exposure

Irritation   Irritating to eyes

Sensitization   No information available

Carcinogenicity   The table below indicates whether each agency has listed any ingredient as a carcinogen.

Component	CAS-No	IARC	NTP	ACGIH	OSHA	Mexico
Methyl ethyl ketone	78-93-3	Not listed	Not listed	Not listed	Not listed	Not listed

Mutagenic Effects   Not mutagenic in AMES Test

Reproductive Effects   No information available.

Developmental Effects   No information available.

Teratogenicity   No information available.

STOT - single exposure   Central nervous system (CNS)
STOT - repeated exposure Kidney Liver

Aspiration hazard   No information available

Symptoms / effects,both acute and   Symptoms of overexposure may be headache, dizziness, tiredness, nausea and vomiting:
delayed   Inhalation of high vapor concentrations may cause symptoms like headache, dizziness,

Page 5 / 8

tiredness, nausea and vomiting

Endocrine Disruptor Information   No information available

Other Adverse Effects   The toxicological properties have not been fully investigated.

12. Ecological information

Ecotoxicity

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Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
Methyl ethyl ketone	Not listed	Lepomis macrochirus: LC50=3,22 g/L 96 h	EC50 = 3403 mg/L 30 min EC50 = 3426 mg/L 5 min	EC50: 4025 - 6440 mg/L, 48h Static (Daphnia magna) EC50: = 5091 mg/L, 48h (Daphnia magna) EC50: > 520 mg/L, 48h (Daphnia magna)

Persistence and Degradability   Persistence is unlikely based on information available.

Bioaccumulation/ Accumulation   No information available.

Mobility   Will likely be mobile in the environment due to its volatility.

Component	log Pow
Methyl ethyl ketone	0.29

13. Disposal considerations

Waste Disposal Methods   Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

Component	RCRA - U Series Wastes	RCRA - P Series Wastes
Methyl ethyl ketone - 78-93-3	U159	-

14. Transport information

DOT
    UN-No   UN1193
    Proper Shipping Name   Ethyl methyl ketone
    Hazard Class   3
    Packing Group   II
TDG
    UN-No   UN1193
    Proper Shipping Name   ETHYL METHYL KETONE
    Hazard Class   3
    Packing Group   II
IATA
    UN-No   UN1193
    Proper Shipping Name   Methyl ethyl ketone
    Hazard Class   3
    Packing Group   II
IMDG/IMO
    UN-No   UN1193
    Proper Shipping Name   Ethyl methyl ketone (Methyl ethyl ketone)
    Hazard Class   3
    Packing Group   II

15. Regulatory information

All of the components in the product are on the following Inventory lists: X = listed

277

International Inventories

Component	TSCA	DSL	NDSL	EINECS	ELINCS	NLP	PICCS	ENCS	AICS	IECSC	KECL
Methyl ethyl ketone	X	X	-	201-159-0	-		X	X	X	X	X

Legend:
X - Listed
E - Indicates a substance that is the subject of a Section 5(e) Consent order under TSCA.
F - Indicates a substance that is the subject of a Section 5(f) Rule under TSCA.
N - Indicates a polymeric substance containing no free-radical initiator in its inventory name but is considered to cover the designated polymer made with any free-radical initiator regardless of the amount used.
P - Indicates a commenced PMN substance
R - Indicates a substance that is the subject of a Section 6 risk management rule under TSCA.
S - Indicates a substance that is identified in a proposed or final Significant New Use Rule
T - Indicates a substance that is the subject of a Section 4 test rule under TSCA.
XU - Indicates a substance exempt from reporting under the Inventory Update Rule, i.e. Partial Updating of the TSCA Inventory Data Base Production and Site Reports (40 CFR 710(B).
Y1 - Indicates an exempt polymer that has a number-average molecular weight of 1,000 or greater.
Y2 - Indicates an exempt polymer that is a polyester and is made only from reactants included in a specified list of low concern reactants that comprises one of the eligibility criteria for the exemption rule.

U.S. Federal Regulations

TSCA 12(b)   Not applicable

SARA 313   Not applicable

SARA 311/312 Hazard Categories   See section 2 for more information

CWA (Clean Water Act)   Not applicable

Clean Air Act   Not applicable

OSHA Occupational Safety and Health Administration
Not applicable

CERCLA   This material, as supplied, contains one or more substances regulated as a hazardous
                                      substance under the Comprehensive Environmental Response Compensation and Liability
                                      Act (CERCLA) (40 CFR 302)

Component	Hazardous Substances RQs	CERCLA EHS RQs
Methyl ethyl ketone	5000 lb	-

California Proposition 65   This product does not contain any Proposition 65 chemicals

U.S. State Right-to-Know
Regulations

Component	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
Methyl ethyl ketone	X	X	X	X	X

U.S. Department of Transportation

Reportable Quantity (RQ):   Y
DOT Marine Pollutant   N
DOT Severe Marine Pollutant   N

U.S. Department of Homeland Security
This product does not contain any DHS chemicals.

Other International Regulations

Mexico - Grade   Serious risk, Grade 3

Methyl Ethyl Ketone   **Revision Date** 17-Jan-2018

16. Other information

Prepared By	Regulatory Affairs Thermo Fisher Scientific Email: EMSDS.RA@thermofisher.com
Creation Date	13-Apr-2009
Revision Date	17-Jan-2018
Print Date	17-Jan-2018
Revision Summary	This document has been updated to comply with the US OSHA HazCom 2012 Standard replacing the current legislation under 29 CFR 1910.1200 to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

End of SDS

n-**Butyraldehyde** **CAS No 123-72-8**	**MATERIAL SAFETY DATA SHEET** **SDS/MSDS**

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1   Product identifiers
Product name   :   n-**Butyraldehyde**

CAS-No.   :   123-72-8

1.2   Relevant identified uses of the substance or mixture and uses advised against

Identified uses   :   Laboratory chemicals, Industrial & for professional use only.

1.3   Details of the supplier of the safety data sheet
Company   :   Central Drug House (P) Ltd
                                            7/28 Vardaan House
                                            New Delhi-10002
                                            INDIA

Telephone   :   +91 11 49404040
Email   :   care@cdhfinechemical.com

1.4   Emergency telephone number
Emergency Phone #   :   +91 11 49404040 (9:00am - 6:00 pm) [Office hours]

SECTION 2: Hazards identification

2.1   Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Flammable liquids (Category 2), H225
Eye irritation (Category 2), H319

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2   Label elements

Labelling according Regulation (EC) No 1272/2008
Pictogram

Signal word   Danger

Hazard statement(s)
H225   Highly flammable liquid and vapour.
H319   Causes serious eye irritation.

Precautionary statement(s)
P210   Keep away from heat/sparks/open flames/hot surfaces. No smoking.

| P305 + P351 + P338 | IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. |
| Supplemental Hazard Statements | none |

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.1 Substances

Synonyms	:	Butanal
Formula	:	C_4H_8O
Molecular weight	:	72.11 g/mol
CAS-No.	:	123-72-8
EC-No.	:	204-646-6
Index-No.	:	605-006-00-2

Hazardous ingredients according to Regulation (EC) No 1272/2008

Component			Classification	Concentration
Butyraldehyde				
CAS-No.	123-72-8		Flam. Liq. 2; Eye Irrit. 2; H225,	<= 100 %
EC-No.	204-646-6		H319	
Index-No.	605-006-00-2			

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first aid measures

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2   Special hazards arising from the substance or mixture
Carbon oxides

5.3   Advice for firefighters
Wear self-contained breathing apparatus for firefighting if necessary.

5.4   Further information
Use water spray to cool unopened containers.

SECTION 6: Accidental release measures

6.1   Personal precautions, protective equipment and emergency procedures
Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.
For personal protection see section 8.

6.2   Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

6.3   Methods and materials for containment and cleaning up
Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations (see section 13).

6.4   Reference to other sections
For disposal see section 13.

SECTION 7: Handling and storage

7.1   Precautions for safe handling
Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.
Keep away from sources of ignition - No smoking.Take measures to prevent the build up of electrostatic charge.
For precautions see section 2.2.

7.2   Conditions for safe storage, including any incompatibilities
Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Stench. Dry residue is explosive.
Storage class (TRGS 510): Flammable Liquids

7.3   Specific end use(s)
Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1   Control parameters

8.2   Exposure controls

Appropriate engineering controls
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Body Protection
Impervious clothing, Flame retardant antistatic protective clothing., The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use (US) or type ABEK (EN 14387) respirator cartridges as a backup to enginee protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

SECTION 9: Physical and chemical properties

9.1   Information on basic physical and chemical properties

a)	Appearance	Form: clear, liquid Colour: colourless
b)	Odour	pungent
c)	Odour Threshold	No data available
d)	pH	6.0 - 7.0 at 71 g/l at 20 °C
e)	Melting point/freezing point	Melting point/range: -96 °C - lit.
f)	Initial boiling point and boiling range	75 °C - lit.
g)	Flash point	-5 °C - closed cup
h)	Evaporation rate	No data available
i)	Flammability (solid, gas)	No data available
j)	Upper/lower flammability or explosive limits	Upper explosion limit: 8 %(V) Lower explosion limit: 1.8 %(V)
k)	Vapour pressure	90 mmHg at 20 °C
l)	Vapour density	2.49 - (Air = 1.0)
m)	Relative density	0.8 g/cm3 at 25 °C
n)	Water solubility	50 g/l at 20 °C - OECD Test Guideline 105 - soluble
o)	Partition coefficient: n-octanol/water	log Pow: 0.79
p)	Auto-ignition temperature	190 °C at 1013.0 hPa
q)	Decomposition temperature	No data available
r)	Viscosity	No data available
s)	Explosive properties	No data available
t)	Oxidizing properties	No data available

9.2   Other safety information

Surface tension	70 mN/m at 20 °C
Relative vapour density	2.49 - (Air = 1.0)

SECTION 10: Stability and reactivity

10.1 Reactivity
No data available

10.2 Chemical stability
Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions
No data available

10.4 Conditions to avoid
Heat, flames and sparks. Extremes of temperature and direct sunlight.

10.5 Incompatible materials
Oxidizing agents, Strong bases, Strong reducing agents, Strong acids

10.6 Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides
Other decomposition products - No data available
In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - Rat - male and female - 5,890 mg/kg(Butyraldehyde)
(OECD Test Guideline 401)
LC50 Inhalation - Rat - male and female - 4 h - > 5.46 mg/l(Butyraldehyde)
(OECD Test Guideline 403)
LD50 Dermal - Rabbit - 3,560 mg/kg(Butyraldehyde)

Skin corrosion/irritation
Skin - Rabbit(Butyraldehyde)
Result: No skin irritation - 4 h
(OECD Test Guideline 404)

Serious eye damage/eye irritation
Eyes - Rabbit(Butyraldehyde)
Result: Irritating to eyes. - 24 h
(Directive 67/548/EEC, Annex V, B.5.)

Respiratory or skin sensitisation
Buehler Test - Guinea pig(Butyraldehyde)

Result: Does not cause skin sensitisation.
(OECD Test Guideline 406)

Germ cell mutagenicity

No data available(Butyraldehyde)
Ames test(Butyraldehyde)
S. typhimurium
Result: negative
(Butyraldehyde)
Drosophila melanogaster - male
Result: negative

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as
          probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity

No data available(Butyraldehyde)

Specific target organ toxicity - single exposure
No data available(Butyraldehyde)

Specific target organ toxicity - repeated exposure
No data available

Aspiration hazard
No data available(Butyraldehyde)

Additional Information
RTECS: ES2275000

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.(Butyraldehyde)

SECTION 12: Ecological information

12.1 Toxicity

Toxicity to fish	static test LC50 - Pimephales promelas (fathead minnow) - 25.8 mg/l - 96 h(Butyraldehyde)
Toxicity to daphnia and other aquatic invertebrates	static test EC50 - Daphnia magna (Water flea) - 195 mg/l - 24 h(Butyraldehyde) (DIN 38412)
Toxicity to bacteria	EC50 - Photobacterium phosphoreum - 99.1 mg/l - 25 min(Butyraldehyde)

12.2 Persistence and degradability

Biodegradability	aerobic - Exposure time 5 d(Butyraldehyde) Result: 46 - 57 % - Readily biodegradable (OECD Test Guideline 301C)
Ratio BOD/ThBOD	28 - 43 %(Butyraldehyde)

12.3 Bioaccumulative potential
No bioaccumulation is to be expected (log Pow <= 4).

12.4 Mobility in soil
No data available(Butyraldehyde)

12.5 Results of PBT and vPvB assessment
This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Other adverse effects
Harmful to aquatic life.

SECTION 13: Disposal considerations

13.1 Waste treatment methods

Product
Burn in a chemical incinerator equipped with an afterburner and scrubber b highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

SECTION 14: Transport information

14.1 UN number
ADR/RID: 1129   IMDG: 1129   IATA: 1129

14.2 UN proper shipping name
ADR/RID: BUTYRALDEHYDE
IMDG: BUTYRALDEHYDE
IATA: Butyraldehyde

14.3 Transport hazard class(es)
ADR/RID: 3   IMDG: 3   IATA: 3

14.4 Packaging group
ADR/RID: II   IMDG: II   IATA: II

14.5 Environmental hazards
ADR/RID: no   IMDG Marine pollutant: no   IATA: no

14.6 Special precautions for user
No data available

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture
This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.
15.2 Chemical safety assessment
For this product a chemical safety assessment was not carried out

SECTION 16: Other information

Full text of H-Statements referred to under sections 2 and 3.

H225   Highly flammable liquid and vapour.
H319   Causes serious eye irritation.

Further information
The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Central Drug House (P) Ltd and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.cdhfinechemical.com for additional terms and conditions of sale.

ThermoFisher
SCIENTIFIC

SAFETY DATA SHEET

Creation Date 21-Jan-2009 **Revision Date** 18-Jan-2018 **Revision Number** 4

1. Identification

Product Name **1-Butanol (Spectranalyzed)**

Cat No. : **A400; A400-4**

CAS-No 71-36-3
Synonyms n-Butanol; n-Butyl alcohol, Butan-1-ol

Recommended Use Laboratory chemicals.
Uses advised against Not for food, drug, pesticide or biocidal product use

Details of the supplier of the safety data sheet

Company
Fisher Scientific
One Reagent Lane
Fair Lawn, NJ 07410
Tel: (201) 796-7100

Emergency Telephone Number
CHEMTREC®, Inside the USA: 800-424-9300
CHEMTREC®, Outside the USA: 001-703-527-3887

2. Hazard(s) identification

Classification
This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Flammable liquids	Category 3
Acute oral toxicity	Category 4
Skin Corrosion/irritation	Category 2
Serious Eye Damage/Eye Irritation	Category 1
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Respiratory system, Central nervous system (CNS).	

Label Elements

Signal Word
Danger

Hazard Statements
Flammable liquid and vapor
Harmful if swallowed
Causes skin irritation
Causes serious eye damage
May cause respiratory irritation
May cause drowsiness or dizziness

Page 1 / 8

287

Precautionary Statements
Prevention
Wash face, hands and any exposed skin thoroughly after handling
Do not eat, drink or smoke when using this product
Wear protective gloves/protective clothing/eye protection/face protection
Do not breathe dust/fume/gas/mist/vapors/spray
Use only outdoors or in a well-ventilated area
Keep away from heat/sparks/open flames/hot surfaces. - No smoking
Keep container tightly closed
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting/equipment
Use only non-sparking tools
Take precautionary measures against static discharge
Keep cool
Response
Get medical attention/advice if you feel unwell
Inhalation
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Call a POISON CENTER or doctor/physician if you feel unwell
Skin
If skin irritation occurs: Get medical advice/attention
IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower
Wash contaminated clothing before reuse
Eyes
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
Immediately call a POISON CENTER or doctor/physician
Ingestion
IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell
Rinse mouth
Fire
In case of fire: Use CO2, dry chemical, or foam for extinction
Storage
Store in a well-ventilated place. Keep container tightly closed
Store locked up
Disposal
Dispose of contents/container to an approved waste disposal plant
Hazards not otherwise classified (HNOC)
None identified

3. Composition/Information on Ingredients

Component	CAS-No	Weight %
n-Butyl alcohol	71-36-3	99

4. First-aid measures

General Advice   If symptoms persist, call a physician.

Eye Contact   Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get

medical attention.

Skin Contact   Wash off immediately with plenty of water for at least 15 minutes. If skin irritation persists, call a physician.

Inhalation   Move to fresh air. If not breathing, give artificial respiration. Get medical attention if symptoms occur.

Ingestion   Clean mouth with water and drink afterwards plenty of water.

Most important symptoms and   Breathing difficulties. Symptoms of overexposure may be headache, dizziness, tiredness,
effects   nausea and vomiting
Notes to Physician   Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media   Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Unsuitable Extinguishing Media   No information available

   Flash Point   35 °C / 95 °F

   Method -   Closed cup

Autoignition Temperature   340 °C / 644 °F

Explosion Limits
   Upper   11.2 vol %
   Lower   1.4 vol %
   Sensitivity to Mechanical Impact No information available
   Sensitivity to Static Discharge No information available

Specific Hazards Arising from the Chemical
Flammable. Risk of ignition. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back. Containers may explode when heated. Thermal decomposition can lead to release of irritating gases and vapors. Keep product and empty container away from heat and sources of ignition.

Hazardous Combustion Products
Carbon monoxide (CO) Carbon dioxide (CO_2)
Protective Equipment and Precautions for Firefighters
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
2	3	0	N/A

6. Accidental release measures

Personal Precautions   Use personal protective equipment. Ensure adequate ventilation.
Environmental Precautions   Should not be released into the environment.

Methods for Containment and Clean Soak up with inert absorbent material. Keep in suitable, closed containers for disposal.
Up

7. Handling and storage

Handling   Wear personal protective equipment. Ensure adequate ventilation. Do not get in eyes, on skin, or on clothing. Avoid ingestion and inhalation.

Storage   Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from heat and sources of ignition. Flammables area.

8. Exposure controls / personal protection

Exposure Guidelines

Component	ACGIH TLV	OSHA PEL	NIOSH IDLH	Mexico OEL (TWA)
n-Butyl alcohol	TWA: 20 ppm	Skin (Vacated) Ceiling: 50 ppm (Vacated) Ceiling: 150 mg/m³ TWA: 100 ppm TWA: 300 mg/m³	IDLH: 1400 ppm Ceiling: 50 ppm Ceiling: 150 mg/m³	Ceiling: 50 ppm Ceiling: 150 mg/m³

Legend

ACGIH - American Conference of Governmental Industrial Hygienists
OSHA - Occupational Safety and Health Administration
NIOSH IDLH: The National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

Engineering Measures	Ensure adequate ventilation, especially in confined areas. Use explosion-proof electrical/ventilating/lighting/equipment. Ensure that eyewash stations and safety showers are close to the workstation location.

Personal Protective Equipment

Eye/face Protection	Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.
Skin and body protection	Long sleeved clothing.
Respiratory Protection	Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.
Hygiene Measures	Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Liquid
Appearance	Colorless
Odor	Alcohol-like
Odor Threshold	No information available
pH	No information available
Melting Point/Range	-89 °C / -128.2 °F
Boiling Point/Range	117.6 °C / 243.7 °F
Flash Point	35 °C / 95 °F
Method -	Closed cup
Evaporation Rate	0.46
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	11.2 vol %
Lower	1.4 vol %
Vapor Pressure	6.7 mbar @ 20 °C
Vapor Density	2.6
Specific Gravity	0.810
Solubility	Slightly soluble in water
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	340 °C / 644 °F
Decomposition Temperature	No information available
Viscosity	2.95 mPa.s (20 °C)

Molecular Formula	C4 H10 O
Molecular Weight	74.12
Refractive index	1.390 - 1.400

10. Stability and reactivity

Reactive Hazard   None known, based on information available

Stability   Stable under normal conditions.

Conditions to Avoid   Keep away from open flames, hot surfaces and sources of ignition. Incompatible products.

Incompatible Materials   Strong oxidizing agents, Reducing agents, Acid chlorides, copper, Copper alloys, Acid anhydrides

Hazardous Decomposition Products Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazardous Polymerization   Hazardous polymerization does not occur.

Hazardous Reactions   None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information
Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
n-Butyl alcohol	LD50 = 700 mg/kg (Rat) LD50 = 790 mg/kg (Rat)	LD50 = 3402 mg/kg (Rabbit) LD50 = 3400 mg/kg (Rabbit)	LC50 > 8000 ppm (Rat) 4 h

Toxicologically Synergistic Products   No information available

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Irritation   Severe eye irritant; Irritating to respiratory system and skin

Sensitization   No information available

Carcinogenicity   The table below indicates whether each agency has listed any ingredient as a carcinogen.

Component	CAS-No	IARC	NTP	ACGIH	OSHA	Mexico
n-Butyl alcohol	71-36-3	Not listed	Not listed	Not listed	Not listed	Not listed

Mutagenic Effects   No information available

Reproductive Effects   No information available.

Developmental Effects   No information available.

Teratogenicity   No information available.

STOT - single exposure   Respiratory system Central nervous system (CNS)
STOT - repeated exposure   None known

Aspiration hazard   No information available

Symptoms / effects,both acute and delayed   Symptoms of overexposure may be headache, dizziness, tiredness, nausea and vomiting

Endocrine Disruptor Information   No information available

Other Adverse Effects   The toxicological properties have not been fully investigated.

12. Ecological information

Ecotoxicity
Do not flush into surface water or sanitary sewer system.

Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
n-Butyl alcohol	EC50: > 500 mg/L, 72h (Desmodesmus subspicatus) EC50: > 500 mg/L, 96h (Desmodesmus subspicatus)	LC50: 100000 - 500000 µg/L, 96h static (Lepomis macrochirus) LC50: = 1740 mg/L, 96h flow-through (Pimephales promelas) LC50: = 1910000 µg/L, 96h static (Pimephales promelas) LC50: 1730 - 1910 mg/L, 96h static (Pimephales promelas)	EC50 = 2041.4 mg/L 5 min EC50 = 2186 mg/L 30 min EC50 = 3980 mg/L 24 h EC50 = 4400 mg/L 17 h	EC50: = 1983 mg/L, 48h (Daphnia magna) EC50: 1897 - 2072 mg/L, 48h Static (Daphnia magna)

Persistence and Degradability   Soluble in water Persistence is unlikely based on information available.

Bioaccumulation/ Accumulation   No information available.

Mobility   . Will likely be mobile in the environment due to its water solubility.

Component	log Pow
n-Butyl alcohol	0.785

13. Disposal considerations

Waste Disposal Methods   Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

Component	RCRA - U Series Wastes	RCRA - P Series Wastes
n-Butyl alcohol - 71-36-3	U031	-

14. Transport information

DOT
    UN-No   UN1120
    Proper Shipping Name   BUTANOLS
    Hazard Class   3
    Packing Group   III
TDG
    UN-No   UN1120
    Proper Shipping Name   BUTANOLS
    Hazard Class   3
    Packing Group   III
IATA
    UN-No   UN1120
    Proper Shipping Name   BUTANOLS
    Hazard Class   3
    Packing Group   III
IMDG/IMO
    UN-No   UN1120
    Proper Shipping Name   BUTANOLS
    Hazard Class   3
    Packing Group   III

15. Regulatory information

All of the components in the product are on the following Inventory lists: X = listed

International Inventories

Component	TSCA	DSL	NDSL	EINECS	ELINCS	NLP	PICCS	ENCS	AICS	IECSC	KECL
n-Butyl alcohol	X	X	-	200-751-6	-		X	X	X	X	X

Legend:
X - Listed
E - Indicates a substance that is the subject of a Section 5(e) Consent order under TSCA.
F - Indicates a substance that is the subject of a Section 5(f) Rule under TSCA.
N - Indicates a polymeric substance containing no free-radical initiator in its inventory name but is considered to cover the designated polymer made with any free-radical initiator regardless of the amount used.
P - Indicates a commenced PMN substance
R - Indicates a substance that is the subject of a Section 6 risk management rule under TSCA.
S - Indicates a substance that is identified in a proposed or final Significant New Use Rule
T - Indicates a substance that is the subject of a Section 4 test rule under TSCA.
XU - Indicates a substance exempt from reporting under the Inventory Update Rule, i.e. Partial Updating of the TSCA Inventory Data Base Production and Site Reports (40 CFR 710(B).
Y1 - Indicates an exempt polymer that has a number-average molecular weight of 1,000 or greater.
Y2 - Indicates an exempt polymer that is a polyester and is made only from reactants included in a specified list of low concern reactants that comprises one of the eligibility criteria for the exemption rule.

<u>**U.S. Federal Regulations**</u>

TSCA 12(b)   Not applicable

SARA 313

Component	CAS-No	Weight %	SARA 313 - Threshold Values %
n-Butyl alcohol	71-36-3	99	1.0

SARA 311/312 Hazard Categories   See section 2 for more information

CWA (Clean Water Act)   Not applicable

Clean Air Act   Not applicable

OSHA Occupational Safety and Health Administration
Not applicable

CERCLA   This material, as supplied, contains one or more substances regulated as a hazardous substance under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302)

Component	Hazardous Substances RQs	CERCLA EHS RQs
n-Butyl alcohol	5000 lb	-

California Proposition 65   This product does not contain any Proposition 65 chemicals

U.S. State Right-to-Know Regulations

Component	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
n-Butyl alcohol	X	X	X	-	X

U.S. Department of Transportation

Reportable Quantity (RQ):   Y
DOT Marine Pollutant   N
DOT Severe Marine Pollutant   N

U.S. Department of Homeland Security
This product does not contain any DHS chemicals.

___

Other International Regulations

Mexico - Grade   Serious risk, Grade 3

16. Other information

Prepared By	Regulatory Affairs Thermo Fisher Scientific Email: EMSDS.RA@thermofisher.com
Creation Date	21-Jan-2009
Revision Date	18-Jan-2018
Print Date	18-Jan-2018
Revision Summary	This document has been updated to comply with the US OSHA HazCom 2012 Standard replacing the current legislation under 29 CFR 1910.1200 to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

Disclaimer

End of SDS

SIGMA-ALDRICH

SAFETY DATA SHEET

Version 5.8
Revision Date 04/13/2018
Print Date 11/10/2018

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1. PRODUCT AND COMPANY IDENTIFICATION

1.1   Product identifiers

Product name   :   **2-Butanol**

Product Number   :   W510254
Brand   :   Aldrich
Index-No.   :   603-127-00-5

CAS-No.   :   78-92-2

1.2   Relevant identified uses of the substance or mixture and uses advised against

Identified uses   :   Laboratory chemicals, Synthesis of substances

1.3   Details of the supplier of the safety data sheet

Company   :   Sigma-Aldrich
                           3050 Spruce Street
                           SAINT LOUIS MO 63103
                           USA

Telephone   :   +1 800-325-5832
Fax   :   +1 800-325-5052

1.4   Emergency telephone number

Emergency Phone #   :   +1-703-527-3887 (CHEMTREC)

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2. HAZARDS IDENTIFICATION

2.1   Classification of the substance or mixture

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)
Flammable liquids (Category 3), H226
Eye irritation (Category 2A), H319
Specific target organ toxicity - single exposure (Category 3), Respiratory system, Central nervous system, H335, H336

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2   GHS Label elements, including precautionary statements

Pictogram

Signal word   Warning

Hazard statement(s)
H226   Flammable liquid and vapour.
H319   Causes serious eye irritation.
H335   May cause respiratory irritation.
H336   May cause drowsiness or dizziness.

Precautionary statement(s)
P210   Keep away from heat/sparks/open flames/hot surfaces. No smoking.
P233   Keep container tightly closed.
P240   Ground/bond container and receiving equipment.
P241   Use explosion-proof electrical/ ventilating/ lighting/ equipment.
P242   Use only non-sparking tools.
P243   Take precautionary measures against static discharge.

P261	Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray.
P264	Wash skin thoroughly after handling.
P271	Use only outdoors or in a well-ventilated area.
P280	Wear protective gloves/ eye protection/ face protection.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.
P304 + P340 + P312	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER/doctor if you feel unwell.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P337 + P313	If eye irritation persists: Get medical advice/ attention.
P370 + P378	In case of fire: Use dry sand, dry chemical or alcohol-resistant foam to extinguish.
P403 + P233	Store in a well-ventilated place. Keep container tightly closed.
P403 + P235	Store in a well-ventilated place. Keep cool.
P405	Store locked up.
P501	Dispose of contents/ container to an approved waste disposal plant.

2.3   Hazards not otherwise classified (HNOC) or not covered by GHS
May form explosive peroxides.

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1   Substances

Synonyms	:	sec-Butyl alcohol
		(±)-2-Butanol

Formula	:	$C_4H_{10}O$
Molecular weight	:	74.12 g/mol
CAS-No.	:	78-92-2
EC-No.	:	201-158-5
Index-No.	:	603-127-00-5

Hazardous components

Component	Classification	Concentration
Butan-2-ol		
	Flam. Liq. 3; Eye Irrit. 2A; STOT SE 3; H226, H319, H335, H336	90 - 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

4. FIRST AID MEASURES

4.1   Description of first aid measures

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed
The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed
No data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture
No data available

5.3 Advice for firefighters
Wear self-contained breathing apparatus for firefighting if necessary.

5.4 Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures
Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.
For personal protection see section 8.

6.2 Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up
Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations (see section 13).

6.4 Reference to other sections
For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling
Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.
Keep away from sources of ignition - No smoking.Take measures to prevent the build up of electrostatic charge.
For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities
Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.
Storage class (TRGS 510): 3: Flammable liquids

7.3 Specific end use(s)
Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

Component	CAS-No.	Value	Control parameters	Basis
Butan-2-ol	78-92-2	TWA	100 ppm	USA. ACGIH Threshold Limit Values (TLV)
	Remarks	Central Nervous System impairment Upper Respiratory Tract irritation		

		TWA	100 ppm	USA. NIOSH Recommended
			305 mg/m3	Exposure Limits
		ST	150 ppm	USA. NIOSH Recommended
			455 mg/m3	Exposure Limits
		TWA	150 ppm	USA. Occupational Exposure Limits
			450 mg/m3	(OSHA) - Table Z-1 Limits for Air
				Contaminants
	The value in mg/m3 is approximate.			
		PEL	100 ppm	California permissible exposure
			305 mg/m3	limits for chemical contaminants
				(Title 8, Article 107)

8.2   Exposure controls

Appropriate engineering controls
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact
Material: Nitrile rubber
Minimum layer thickness: 0.4 mm
Break through time: 480 min
Material tested:Camatril® (KCL 730 / Aldrich Z677442, Size M)

Splash contact
Material: Nature latex/chloroprene
Minimum layer thickness: 0.6 mm
Break through time: 30 min
Material tested:Lapren® (KCL 706 / Aldrich Z677558, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection
Impervious clothing, Flame retardant antistatic protective clothing., The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure
Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

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9. PHYSICAL AND CHEMICAL PROPERTIES

9.1   Information on basic physical and chemical properties

a)   Appearance   Form: liquid

b)   Odour   No data available

c)	Odour Threshold	No data available
d)	pH	No data available
e)	Melting point/freezing point	Melting point/range: -115 °C (-175 °F) - lit.
f)	Initial boiling point and boiling range	98 °C (208 °F) - lit.
g)	Flash point	27 °C (81 °F) - closed cup
h)	Evaporation rate	No data available
i)	Flammability (solid, gas)	No data available
j)	Upper/lower flammability or explosive limits	Upper explosion limit: 9.8 %(V) Lower explosion limit: 1.7 %(V)
k)	Vapour pressure	15.3 hPa (11.5 mmHg) at 20 °C (68 °F) 24.4 hPa (18.3 mmHg) at 25 °C (77 °F)
l)	Vapour density	2.56 - (Air = 1.0)
m)	Relative density	0.808 g/cm3 at 25 °C (77 °F)
n)	Water solubility	soluble
o)	Partition coefficient: n-octanol/water	log Pow: 0.146
p)	Auto-ignition temperature	No data available
q)	Decomposition temperature	No data available
r)	Viscosity	No data available
s)	Explosive properties	No data available
t)	Oxidizing properties	No data available

9.2   Other safety information

Surface tension	23 mN/m at 20 °C (68 °F)
Relative vapour density	2.56 - (Air = 1.0)

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10. STABILITY AND REACTIVITY

10.1   Reactivity
No data available

10.2   Chemical stability
Stable under recommended storage conditions.

10.3   Possibility of hazardous reactions
Vapours may form explosive mixture with air.

10.4   Conditions to avoid
Heat, flames and sparks.

10.5   Incompatible materials
acids, Acid chlorides, Acid anhydrides, Oxidizing agents, Halogens, Peroxides

10.6   Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides
Other decomposition products - No data available
In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1   Information on toxicological effects

Acute toxicity
LD50 Oral - Rat - male and female - 2,193 mg/kg
(OECD Test Guideline 423)

LD50 Dermal - Rat - male and female - > 2,000 mg/kg
(OECD Test Guideline 402)

No data available

Skin corrosion/irritation
Skin - Rabbit
Result: No skin irritation - 4 h
(OECD Test Guideline 404)

Serious eye damage/eye irritation
No data available

Respiratory or skin sensitisation
Maximisation Test - Guinea pig
Result: Does not cause skin sensitisation.
(OECD Test Guideline 406)

Germ cell mutagenicity
Ames test
S. typhimurium
Result: negative

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.

Reproductive toxicity

Reproductive toxicity - Rat - Inhalation
Effects on Fertility: Post-implantation mortality (e.g., dead and/or resorbed implants per total number of implants). Effects on Embryo or Fetus: Fetal death. Specific Developmental Abnormalities: Musculoskeletal system.

Developmental Toxicity - Rat - Inhalation
Effects on Embryo or Fetus: Fetotoxicity (except death, e.g., stunted fetus).

Specific target organ toxicity - single exposure
No data available

Specific target organ toxicity - repeated exposure
No data available

Aspiration hazard
No data available

Additional Information
RTECS: EO1750000

Nausea, Dizziness, Headache, To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

12. ECOLOGICAL INFORMATION

12.1   Toxicity

Toxicity to fish   LC50 - Pimephales promelas (fathead minnow) - 3,670 mg/l - 96 h

static test LC50 - Leuciscus idus melanotus - 3,520 - 3,540 mg/l - 48 h

| Toxicity to daphnia and other aquatic invertebrates | EC50 - Daphnia magna (Water flea) - 4,227 mg/l - 48 h |

12.2 Persistence and degradability
Biodegradability   aerobic - Exposure time 5 d
Result: 86 % - Readily biodegradable.

12.3 Bioaccumulative potential
No data available

12.4 Mobility in soil
No data available

12.5 Results of PBT and vPvB assessment
PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects

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13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

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14. TRANSPORT INFORMATION

DOT (US)
UN number: 1120   Class: 3   Packing group: III
Proper shipping name: Butanols
Reportable Quantity (RQ):
Poison Inhalation Hazard: No

IMDG
UN number: 1120   Class: 3   Packing group: III   EMS-No: F-E, S-D
Proper shipping name: BUTANOLS

IATA
UN number: 1120   Class: 3   Packing group: III
Proper shipping name: Butanols

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15. REGULATORY INFORMATION

SARA 302 Components
No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
The following components are subject to reporting levels established by SARA Title III, Section 313:

	CAS-No.	Revision Date
Butan-2-ol	78-92-2	2007-07-01

SARA 311/312 Hazards
Fire Hazard, Acute Health Hazard

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Butan-2-ol	78-92-2	2007-07-01

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Butan-2-ol	78-92-2	2007-07-01

New Jersey Right To Know Components

	CAS-No.	Revision Date
Butan-2-ol	78-92-2	2007-07-01

California Prop. 65 Components

This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

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16. OTHER INFORMATION

Full text of H-Statements referred to under sections 2 and 3.

Eye Irrit.	Eye irritation
Flam. Liq.	Flammable liquids
H226	Flammable liquid and vapour.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.
H336	May cause drowsiness or dizziness.
STOT SE	Specific target organ toxicity - single exposure

HMIS Rating

Health hazard:	2
Chronic Health Hazard:	
Flammability:	3
Physical Hazard	0

NFPA Rating

Health hazard:	2
Fire Hazard:	3
Reactivity Hazard:	0

Further information

Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 5.8   Revision Date: 04/13/2018   Print Date: 11/10/2018

ThermoFisher SCIENTIFIC

SAFETY DATA SHEET

Creation Date 24-Nov-2010   **Revision Date** 15-Feb-2018   **Revision Number** 4

1. Identification

Product Name   Raney Nickel®, activated catalyst, 50% slurry in water

Cat No. :   AC395920000; AC395921000; AC395925000

Synonyms   Catalyst for hydrogenation.

Recommended Use   Laboratory chemicals.
Uses advised against   Not for food, drug, pesticide or biocidal product use

Details of the supplier of the safety data sheet

Company

Fisher Scientific   Acros Organics
One Reagent Lane   One Reagent Lane
Fair Lawn, NJ 07410   Fair Lawn, NJ 07410
Tel: (201) 796-7100

Emergency Telephone Number
For information **US** call: 001-800-ACROS-01 / **Europe** call: +32 14 57 52 11
Emergency Number **US:**001-201-796-7100 / **Europe:** +32 14 57 52 99
CHEMTREC Tel. No.**US:**001-800-424-9300 / **Europe:**001-703-527-3887

2. Hazard(s) identification

Classification
This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Substances/mixtures which, in contact with water, emit flammable gases	Category 2
Skin Corrosion/irritation	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Skin Sensitization	Category 1
Carcinogenicity	Category 1B
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Respiratory system, Central nervous system (CNS).	
Specific target organ toxicity - (repeated exposure)	Category 1
Target Organs - Skin.	

Label Elements

Signal Word
Danger

Hazard Statements
In contact with water releases flammable gas
Causes skin irritation
Causes eye irritation
May cause an allergic skin reaction
May cause cancer

Page 1 / 8

303

May cause respiratory irritation. May cause drowsiness and dizziness
Causes damage to organs through prolonged or repeated exposure

Precautionary Statements
Prevention
Obtain special instructions before use
Do not handle until all safety precautions have been read and understood
Wear protective gloves/protective clothing/eye protection/face protection
Handle under inert gas. Protect from moisture
Wash face, hands and any exposed skin thoroughly after handling
Contaminated work clothing should not be allowed out of the workplace
Use only outdoors or in a well-ventilated area
Do not breathe dust/fume/gas/mist/vapors/spray
Do not eat, drink or smoke when using this product
Response
IF exposed or concerned: Get medical attention/advice
Inhalation
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Skin
Take off contaminated clothing and wash before reuse
IF ON SKIN: Wash with plenty of soap and water
If skin irritation or rash occurs: Get medical advice/attention
Eyes
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention
Fire
Evacuate area
Use CO2, dry chemical, or foam
Storage
Store locked up
Store in a dry place
Store in a well-ventilated place. Keep container tightly closed
Disposal
Dispose of contents/container to an approved waste disposal plant
Hazards not otherwise classified (HNOC)
Toxic to aquatic life with long lasting effects
WARNING. Cancer - https://www.p65warnings.ca.gov/.

3. Composition/Information on Ingredients

Component	CAS-No	Weight %
Water	7732-18-5	47-53
Nickel	7440-02-0	46-49
Aluminium powder	7429-90-5	1-4

4. First-aid measures

Eye Contact　　　　　　　　　　Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.

Skin Contact	Obtain medical attention. Wash off immediately with plenty of water for at least 15 minutes.
Inhalation	Move to fresh air. If breathing is difficult, give oxygen. Obtain medical attention.
Ingestion	Do not induce vomiting. Obtain medical attention.
Most important symptoms and effects	May cause allergic skin reaction. Symptoms of allergic reaction may include rash, itching, swelling, trouble breathing, tingling of the hands and feet, dizziness, lightheadedness, chest pain, muscle pain or flushing
Notes to Physician	Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media	Water spray. Carbon dioxide (CO_2). Dry chemical. Use water spray to cool unopened containers. Chemical foam.
Unsuitable Extinguishing Media	No information available
Flash Point	No information available
Method -	No information available
Autoignition Temperature	No information available
Explosion Limits	
Upper	No data available
Lower	No data available
Sensitivity to Mechanical Impact	No information available
Sensitivity to Static Discharge	No information available

Specific Hazards Arising from the Chemical
Self-heating; exposure to air may cause substance to self-heat without an energy supply. This material poses an explosion hazard when dry.

Hazardous Combustion Products
Burning produces obnoxious and toxic fumes
Protective Equipment and Precautions for Firefighters
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
3	2	0	W

6. Accidental release measures

Personal Precautions	Ensure adequate ventilation. Use personal protective equipment.
Environmental Precautions	Do not flush into surface water or sanitary sewer system. See Section 12 for additional ecological information.
Methods for Containment and Clean Up	Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Keep in suitable, closed containers for disposal. Remove all sources of ignition. Use spark-proof tools and explosion-proof equipment. Do not flush into surface water or sanitary sewer system.

7. Handling and storage

Handling	Do not breathe vapors or spray mist. Do not get in eyes, on skin, or on clothing. Take precautionary measures against static discharges. Use only in area provided with appropriate exhaust ventilation. Use explosion-proof equipment. Use only non-sparking tools. Minimize dust generation and accumulation. Wear personal protective equipment.
Storage	Keep in a dry, cool and well-ventilated place. Keep container tightly closed. Keep away from heat and sources of ignition. Flammables area. Material can explode if dry. Keep at

temperatures below 40°C. Do not freeze.

8. Exposure controls / personal protection

Exposure Guidelines

Component	ACGIH TLV	OSHA PEL	NIOSH IDLH	Mexico OEL (TWA)
Nickel	TWA: 1.5 mg/m³	(Vacated) TWA: 1 mg/m³ TWA: 1 mg/m³	IDLH: 10 mg/m³ TWA: 0.015 mg/m³	TWA: 1 mg/m³
Aluminium powder	TWA: 1 mg/m³	(Vacated) TWA: 15 mg/m³ (Vacated) TWA: 5 mg/m³ TWA: 15 mg/m³ TWA: 5 mg/m³	TWA: 10 mg/m³ TWA: 5 mg/m³	TWA: 10 mg/m³ TWA: 5 mg/m³

Legend

ACGIH - American Conference of Governmental Industrial Hygienists
OSHA - Occupational Safety and Health Administration
NIOSH IDLH: The National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

Engineering Measures   Use explosion-proof electrical/ventilating/lighting/equipment. Ensure that eyewash stations and safety showers are close to the workstation location.

Personal Protective Equipment

    Eye/face Protection   Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

    Skin and body protection   Wear appropriate protective gloves and clothing to prevent skin exposure.

    Respiratory Protection   Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

    Hygiene Measures   Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Slurry Liquid
Appearance	Dark grey
Odor	Odorless
Odor Threshold	No information available
pH	10-11 1500 g/L aq.sol
Melting Point/Range	No data available
Boiling Point/Range	No information available
Flash Point	No information available
Evaporation Rate	No information available
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	No data available
Lower	No data available
Vapor Pressure	23.5 mbar @ 20 °C
Vapor Density	No information available
Specific Gravity	No information available
Solubility	No information available
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	No information available
Decomposition Temperature	> 100°C
Viscosity	No information available
Molecular Formula	Ni

Page 4 / 8

Molecular Weight   58.69

10. Stability and reactivity

Reactive Hazard   Yes

Stability   Stable. Do not allow evaporation to dryness. This material poses an explosion hazard when dry.

Conditions to Avoid   Heat, flames and sparks. Keep away from open flames, hot surfaces and sources of ignition. Exposure to air. Incompatible products.

Incompatible Materials   Acids, Ammonia, Ammonium nitrate: fertilizers capable of self-sustaining decomposition, Halogens, Fluorine, Organic materials, nitriles

Hazardous Decomposition Products Burning produces obnoxious and toxic fumes

Hazardous Polymerization Hazardous polymerization does not occur.

Hazardous Reactions   None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information
Oral LD50   Based on ATE data, the classification criteria are not met. ATE > 2000 mg/kg.
Dermal LD50   Based on ATE data, the classification criteria are not met. ATE > 2000 mg/kg.
Vapor LC50   Based on ATE data, the classification criteria are not met. ATE > 20 mg/l.
Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Water	-	Not listed	Not listed
Nickel	LD50 > 9000 mg/kg (Rat)	Not listed	Not listed

Toxicologically Synergistic   No information available
Products

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Irritation   Irritating to eyes, respiratory system and skin Vapors may cause drowsiness and dizziness

Sensitization   May cause sensitization by skin contact

Carcinogenicity   The table below indicates whether each agency has listed any ingredient as a carcinogen.

Component	CAS-No	IARC	NTP	ACGIH	OSHA	Mexico
Water	7732-18-5	Not listed	Not listed	Not listed	Not listed	Not listed
Nickel	7440-02-0	Group 2B	Reasonably Anticipated	Not listed	X	Not listed
Aluminium powder	7429-90-5	Not listed	Not listed	Not listed	Not listed	Not listed

Mutagenic Effects   No information available

Reproductive Effects   No information available.

Developmental Effects   No information available.

Teratogenicity   No information available.

STOT - single exposure   Respiratory system Central nervous system (CNS)
STOT - repeated exposure Skin

Aspiration hazard   No information available

Symptoms / effects,both acute and delayed	Symptoms of allergic reaction may include rash, itching, swelling, trouble breathing, tingling of the hands and feet, dizziness, lightheadedness, chest pain, muscle pain or flushing
Endocrine Disruptor Information	No information available
Other Adverse Effects	The toxicological properties have not been fully investigated. See actual entry in RTECS for complete information.

12. Ecological information

Ecotoxicity

Do not flush into surface water or sanitary sewer system. Do not allow material to contaminate ground water system. Do not empty into drains. The product contains following substances which are hazardous for the environment. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
Nickel	EC50 = 0.1 mg/L 72h EC50 = 0.18 mg/L 72h	LC50: = 10.4 mg/L, 96h static (Cyprinus carpio) LC50: = 1.3 mg/L, 96h semi-static (Cyprinus carpio) LC50: > 100 mg/L, 96h (Brachydanio rerio)	Not listed	EC50 = 510 µg/L 96h

Persistence and Degradability	Insoluble in water
Bioaccumulation/ Accumulation	No information available.
Mobility	. Is not likely mobile in the environment due its low water solubility.

13. Disposal considerations

Waste Disposal Methods	Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

14. Transport information

DOT
  UN-No   UN1378
  Proper Shipping Name   METAL CATALYST, WETTED
  Hazard Class   4.2
  Packing Group   II
TDG
  UN-No   UN1378
  Proper Shipping Name   METAL CATALYST, WETTED
  Hazard Class   4.2
  Packing Group   II
IATA
  UN-No   1378
  Proper Shipping Name   METAL CATALYST, WETTED
  Hazard Class   4.2
  Packing Group   II
IMDG/IMO
  UN-No   1378
  Proper Shipping Name   METAL CATALYST, WETTED
  Hazard Class   4.2
  Packing Group   II

15. Regulatory information

International Inventories

Component	TSCA	DSL	NDSL	EINECS	ELINCS	NLP	PICCS	ENCS	AICS	IECSC	KECL
Water	X	X	-	231-791-2	-		X	-	X	X	X
Nickel	X	X	-	231-111-4	-		X	-	X	X	X
Aluminium powder	X	X	-	231-072-3	-		X	-	X	X	X

Legend:
X - Listed
E - Indicates a substance that is the subject of a Section 5(e) Consent order under TSCA.
F - Indicates a substance that is the subject of a Section 5(f) Rule under TSCA.
N - Indicates a polymeric substance containing no free-radical initiator in its inventory name but is considered to cover the designated polymer made with any free-radical initiator regardless of the amount used.
P - Indicates a commenced PMN substance
R - Indicates a substance that is the subject of a Section 6 risk management rule under TSCA.
S - Indicates a substance that is identified in a proposed or final Significant New Use Rule
T - Indicates a substance that is the subject of a Section 4 test rule under TSCA.
XU - Indicates a substance exempt from reporting under the Inventory Update Rule, i.e. Partial Updating of the TSCA Inventory Data Base Production and Site Reports (40 CFR 710(B).
Y1 - Indicates an exempt polymer that has a number-average molecular weight of 1,000 or greater.
Y2 - Indicates an exempt polymer that is a polyester and is made only from reactants included in a specified list of low concern reactants that comprises one of the eligibility criteria for the exemption rule.

U.S. Federal Regulations

TSCA 12(b)   Not applicable

SARA 313

Component	CAS-No	Weight %	SARA 313 - Threshold Values %
Nickel	7440-02-0	46-49	0.1
Aluminium powder	7429-90-5	1-4	1.0

SARA 311/312 Hazard Categories See section 2 for more information

CWA (Clean Water Act)

Component	CWA - Hazardous Substances	CWA - Reportable Quantities	CWA - Toxic Pollutants	CWA - Priority Pollutants
Nickel	-	-	X	X

Clean Air Act

Component	HAPS Data	Class 1 Ozone Depletors	Class 2 Ozone Depletors
Nickel	X		-

OSHA Occupational Safety and Health Administration
Not applicable

CERCLA   This material, as supplied, contains one or more substances regulated as a hazardous substance under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302)

Component	Hazardous Substances RQs	CERCLA EHS RQs
Nickel	100 lb	-

California Proposition 65 This product contains the following proposition 65 chemicals

Component	CAS-No	California Prop. 65	Prop 65 NSRL	Category
Nickel	7440-02-0	Carcinogen	-	Carcinogen

U.S. State Right-to-Know Regulations

Component	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
Water	-	-	X	-	-
Nickel	X	X	X	X	X

Aluminium powder	X	X	X	-	X

U.S. Department of Transportation

Reportable Quantity (RQ):   N
DOT Marine Pollutant   N
DOT Severe Marine Pollutant   N

U.S. Department of Homeland Security
This product contains the following DHS chemicals:

Other International Regulations

Mexico - Grade   No information available

16. Other information

Prepared By	Regulatory Affairs Thermo Fisher Scientific Email: EMSDS.RA@thermofisher.com

Creation Date	24-Nov-2010
Revision Date	15-Feb-2018
Print Date	15-Feb-2018
Revision Summary	This document has been updated to comply with the US OSHA HazCom 2012 Standard replacing the current legislation under 29 CFR 1910.1200 to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

Disclaimer

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text

End of SDS

28.5 Ethyl Acetate Product Specifications

Celanese Chemicals

 Celanese

Sales Specification

1 of 1

Ethyl Acetate, Urethane Grade

Specifications		Limits
Ethyl Acetate, wt.%[1]	min.	99.7
Ethanol, wt.%	max.	0.05
Water, wt.%	max.	0.03
Color, Pt-Co Units	max.	10
Acidity, as Acetic Acid, wt.%	max.	0.005
Odor [2]		Nonresidual

References:

1 By Difference – 100.0% minus (acid plus water plus impurities as determined by Gas Chromatography).

2 Product conforms to limit, but test is not routinely performed.

Test methods used for each specification analysis are available. Contact your Customer Service Representative to request copies.

Product Number: HCCG-070 UG Revised: February 1996
Reviewed: April 2004 Supersedes: June 1988

This information is based on our present state of knowledge and is intended to provide general notes on our products and their uses. It should therefore not be construed as guaranteeing specific properties of the products described or their suitability for a particular application. Any existing industrial property rights must be observed. The quality of our products is guaranteed under our General Conditions of Sale.

Celanese Chemicals (North America)
1601 West LBJ Freeway
Dallas, TX 75234
1-972-443-4000

Celanese Chemicals (Europe GmbH)
Frankfurter Straße 111
61476 Kronberg im Taunus
Deutschland / Germany
Tel: ++49 (0) 69 305 16000

SS-070 UG 8/06 9073

28.6   Project Statement

Ethanol to Ethyl Acetate

(Recommended by Bruce M. Vrana, DuPont and UPenn)

Ethyl acetate is used in a variety of applications, including as a solvent, because of its low toxicity. Key applications are nail polish remover, paints, adhesives, cleaning circuit boards, etc. Global sales exceed $4 billion per year and are growing faster than global GDP. Although the ethyl part of the molecule can come from either fermentation or synthetic ethanol (making it at least sometimes green), the acetate part of the molecule comes almost exclusively from synthetic acetic acid, made from methanol and carbon monoxide (decidedly not green, given the energy intensity and acute toxicity of CO).

Greenyug, LLC, a small, privately-held startup company based in Santa Barbara, has developed and is commercializing a new process that uses (fermentation) ethanol as the sole feedstock. Although the process will be much more sustainable than conventional ethyl acetate, coming 100% from renewable resources, Greenyug also claims that it will be cost competitive with or even more economical than petrochemical ethyl acetate, depending on the relative price of oil and ethanol.

Wild claims from startup companies, especially in the biotech arena, are commonplace, and usually do not translate into commercial success. Often, they seem like a ploy to get attention (and money) from venture capital firms or existing players in the industry. As a conventional manufacturer of ethyl acetate, your company has dismissed such claims in the past. However, the fact that in 2018 Greenyug is in the midst of actually building and starting up a commercial scale facility at ADMs corn processing plant in Columbus, NE caught your senior management off guard.

Although the ethanol feedstock comes from a fermentation plant, Greenyug is not doing any biotech. They have patent applications using heterogeneous catalysis to convert ethanol directly to ethyl acetate. Furthermore, their applications indicate they have reactive distillation technology to make ethyl acetate in a simple, low cost process. Reactive

distillation has recently received attention from the AIChE as part of its RAPID process intensification effort. And Greenyug has demonstrated the technology at a pilot plant in Pune, India. Unfortunately for you, all of that makes their claims a bit more credible.

A 9/5/18 local news report of the ribbon-cutting ceremony (last reference, including video) caused your CEO to take immediate action and commission your team to rapidly put together a process design for the Greenyug plant and to estimate their capital and operating cost. The key question is what green premium if any Greenyug will need to get on top of the market price of ethyl acetate to achieve a 15% IRR on their investment. And how does this premium vary with the prices of ethanol and oil? Under what circumstances can they compete economically with you (putting your company and your job at risk)?

Assume that the trade journals are correct and that Greenyug (through its subsidiary Prairie Catalytic LLC) is building a 50 kt plant. Assume that ADM will supply steam and other utilities at market prices. But otherwise, Greenyug (Prairie Catalytic) will be an independent company, responsible for its own investment, maintenance, operations, technical support, etc.

The overall main chemical reaction is: $2C_2H_5OH \rightarrow H_3COOC_2H_5 + 2H_2$

This begs the question of what to do with the hydrogen coproduct. The patent applications indicate that it can be used to hydrogenate liquid coproducts such as butyraldehyde and 2-butanone (MEK). It seems likely that this will be needed to meet the typical purity spec of 99.8% min for ethyl acetate, which Greenyug must meet to sell into all markets. But there will still be an excess of hydrogen. Assume that excess hydrogen can be used on the site complex at a value of $1/lb (2019 dollars). If this is a crucial part of your economics, estimate a fair price to sell hydrogen to ADM as rigorously as possible and include it in your sensitivity analysis. You will also need to decide what to do with the other byproducts after they are separated from the main ethyl acetate product.

Obviously, your company and thus your group cannot have any contact with Greenyug at this time, since they are a potential competitor. Thus, you must base your design only

313

on what can be gleaned from public information, such as the references and any other published information you can find. You may not contact anyone affiliated with Greenyug, including academic partners at UCSB and elsewhere.

You will need to make many assumptions to complete your design, since the data you have is far from complete. State them explicitly in your report, so that management may understand the uncertainty in your design and economic projections in deciding whether Greenyug is a threat. Test your economics to reasonable ranges of your assumptions. If there are any possible show-stoppers (i.e., possible fatal flaws, if one assumption is incorrect that would make the design either technically infeasible or uneconomical), these need to be clearly communicated and understood before your management can decide on an action plan.

The plant design should be as environmentally friendly as possible, at a minimum meeting Federal and state emissions regulations. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Be sure to consider how the plant will be started up in your design.

References

http://www.biofuelsdigest.com/bdigest/2016/06/20/sweet-smell-of-success-greenyug-adm-taking- biobased-chemicals-to-scale/

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U. S. Patent Application US 2013/0197266 A1 (Gadewar et al., assigned to Greenyug)

U. S. Patent Application US 2014/0012037 A1 (Gadewar et al., assigned to Greenyug)

http://newschannelnebraska.com/local-news/prairie-catalytic-ribbon-cutting-ceremony/

28.7   ASPEN Process Simulation

28.7.1   Process Flowsheet

Figure 16: Overall ASPEN Flowsheet

28.7.2 Input File

```
;
;Input Summary created by Aspen Plus Rel. 36.0 at 13:40:38 Sun Apr 14, 2019
;Directory S:\Senior Design\Ethanol to Ethyl Acetate Numbers- Final (18)  Filename
C:\Users\kheuser\AppData\Local\Temp\~apcf7a.txt
;

DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar' SHORT-LENGTH=mm

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES ADSCNVG=NO

MODEL-OPTION

DATABANKS 'APV100 PURE36' / 'APV100 AQUEOUS' / 'APV100 SOLIDS' &
        / 'APV100 INORGANIC' / 'APESV100 AP-EOS' /  &
        'NISTV100 NIST-TRC' / NOASPENPCD

PROP-SOURCES 'APV100 PURE36' / 'APV100 AQUEOUS' /  &
        'APV100 SOLIDS' / 'APV100 INORGANIC' / 'APESV100 AP-EOS' &
        / 'NISTV100 NIST-TRC'

COMPONENTS
    HYDROGEN H2 /
    WATER H2O /
    ETHANOL C2H6O-2 /
    ETHYLACE C4H8O2-3 /
    ACETA-01 C2H4O-1 /
    METHY-01 C4H8O-3 /
    N-BUT-01 C4H8O-1 /
    N-BUT-02 C4H10O-1 /
    2-BUT-01 C4H10O-2

HENRY-COMPS HC-1 HYDROGEN

SOLVE
    RUN-MODE MODE=SIM

CHEMISTRY C-1
    PARAM
```

REAC-COMPS ETHANOL / ACETA-01 / HYDROGEN / ETHYLACE

FLOWSHEET
  BLOCK C-101 IN=5 OUT=6 7
  BLOCK C-100 IN=2 6 OUT=3 5
  BLOCK S-100 IN=7 OUT=8 WATER
  BLOCK SPILT IN=3 OUT=9 4
  BLOCK MIXER IN=9 8 OUT=10
  BLOCK R-100 IN=11 OUT=12
  BLOCK C-102 IN=14 OUT=15 16 17
  BLOCK E-103 IN=12 CH2OIN OUT=13 14 CH2OOUT
  BLOCK E-102 IN=STEAMIN 10 OUT=STEAMOUT 11
  BLOCK P-100 IN=1 OUT=2

PROPERTIES NRTL HENRY-COMPS=HC-1
  PROPERTIES UNIQUAC

PROP-DATA HENRY-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar &
    INVERSE-PRES='1/bar' SHORT-LENGTH=mm
  PROP-LIST HENRY
  BPVAL HYDROGEN ETHANOL -39.88522446 1472.400024 8.548600000 &
    -.0176990000 -60.00000000 50.00000000 0.0
  BPVAL HYDROGEN ETHYLACE 63.32827654 -1951.400024 &
    -8.562000000 0.0 .5000000000 39.80000000 0.0
  BPVAL HYDROGEN N-BUT-02 66.71837454 -1078.300049 &
    -10.60000000 .0186300000 -60.00000000 25.00000000 0.0
  BPVAL HYDROGEN WATER 180.0660745 -6993.510000 -26.31190000 &
    .0150431000 .8500000000 65.85000000 0.0

PROP-DATA NRTL-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar &
    INVERSE-PRES='1/bar' SHORT-LENGTH=mm
  PROP-LIST NRTL
  BPVAL ETHANOL ETHYLACE -1.151200000 524.4238000 .3000000000 &
    0.0 0.0 0.0 40.00000000 78.45000000
  BPVAL ETHYLACE ETHANOL -.2431000000 282.9558000 .3000000000 &
    0.0 0.0 0.0 40.00000000 78.45000000
  BPVAL ETHANOL ACETA-01 12.72680000 -3588.117700 .3000000000 &
    0.0 0.0 0.0 10.00000000 77.70000000
  BPVAL ACETA-01 ETHANOL -1.613500000 69.04160000 .3000000000 &
    0.0 0.0 0.0 10.00000000 77.70000000
  BPVAL ETHANOL METHY-01 -1.560900000 654.5550000 .3000000000 &
    0.0 0.0 0.0 25.00000000 78.30000000

```
BPVAL METHY-01 ETHANOL .7593000000 -132.9897000 .3000000000  &
    0.0 0.0 0.0 25.00000000 78.30000000
BPVAL ETHANOL N-BUT-01 0.0 -94.16330000 .3000000000 0.0  &
    0.0 0.0 72.75000000 78.30000000
BPVAL N-BUT-01 ETHANOL 0.0 288.1581000 .3000000000 0.0 0.0  &
    0.0 72.75000000 78.30000000
BPVAL ETHANOL N-BUT-02 0.0 -85.21880000 .3000000000 0.0  &
    0.0 0.0 70.00000000 110.9500000
BPVAL N-BUT-02 ETHANOL 0.0 128.5015000 .3000000000 0.0 0.0  &
    0.0 70.00000000 110.9500000
BPVAL ETHANOL 2-BUT-01 0.0 -298.1728000 .3000000000 0.0  &
    0.0 0.0 78.90000000 97.50000000
BPVAL 2-BUT-01 ETHANOL 0.0 433.1426000 .3000000000 0.0 0.0  &
    0.0 78.90000000 97.50000000
BPVAL ETHYLACE METHY-01 0.0 173.9450000 .3000000000 0.0  &
    0.0 0.0 76.50000000 79.95000000
BPVAL METHY-01 ETHYLACE 0.0 -105.5695000 .3000000000 0.0  &
    0.0 0.0 76.50000000 79.95000000
BPVAL ETHYLACE N-BUT-02 0.0 206.8239000 .3000000000 0.0  &
    0.0 0.0 77.10000000 117.7000000
BPVAL N-BUT-02 ETHYLACE 0.0 28.48870000 .3000000000 0.0  &
    0.0 0.0 77.10000000 117.7000000
BPVAL ACETA-01 N-BUT-02 0.0 -290.6790000 .3000000000 0.0  &
    0.0 0.0 22.00000000 65.60000000
BPVAL N-BUT-02 ACETA-01 0.0 225.7184000 .3000000000 0.0  &
    0.0 0.0 22.00000000 65.60000000
BPVAL METHY-01 N-BUT-01 0.0 -15.27900000 .3000000000 0.0  &
    0.0 0.0 56.05000000 79.32000000
BPVAL N-BUT-01 METHY-01 0.0 12.84120000 .3000000000 0.0  &
    0.0 0.0 56.05000000 79.32000000
BPVAL METHY-01 N-BUT-02 0.0 -63.57250000 .3000000000 0.0  &
    0.0 0.0 80.70000000 111.2000000
BPVAL N-BUT-02 METHY-01 0.0 241.9607000 .3000000000 0.0  &
    0.0 0.0 80.70000000 111.2000000
BPVAL METHY-01 2-BUT-01 0.0 16.34690000 .3000000000 0.0  &
    0.0 0.0 67.50000000 99.61000000
BPVAL 2-BUT-01 METHY-01 0.0 93.66220000 .3000000000 0.0  &
    0.0 0.0 67.50000000 99.61000000
BPVAL N-BUT-01 N-BUT-02 0.0 147.1343000 .3000000000 0.0  &
    0.0 0.0 77.20000000 114.0000000
BPVAL N-BUT-02 N-BUT-01 0.0 -50.03190000 .3000000000 0.0  &
    0.0 0.0 77.20000000 114.0000000
BPVAL N-BUT-02 2-BUT-01 8.650300000 -2244.355000 .3000000000  &
    0.0 0.0 0.0 40.00000000 69.91000000
```

```
BPVAL 2-BUT-01 N-BUT-02 -5.795400000 1514.080600 .3000000000  &
    0.0 0.0 0.0 40.00000000 69.91000000
BPVAL ETHANOL WATER -.8009000000 246.1800000 .3000000000  &
    0.0 0.0 0.0 24.99000000 100.0000000
BPVAL WATER ETHANOL 3.457800000 -586.0809000 .3000000000  &
    0.0 0.0 0.0 24.99000000 100.0000000
BPVAL ETHYLACE WATER -3.719800000 1286.138300 .2000000000  &
    0.0 0.0 0.0 0.0 70.40000000
BPVAL WATER ETHYLACE 9.463200000 -1705.683000 .2000000000  &
    0.0 0.0 0.0 0.0 70.40000000
BPVAL ACETA-01 WATER 10.91200000 -2709.527300 .3000000000  &
    0.0 0.0 0.0 10.00000000 55.80000000
BPVAL WATER ACETA-01 3.779200000 -977.1515000 .3000000000  &
    0.0 0.0 0.0 10.00000000 55.80000000
BPVAL METHY-01 WATER 0.0 201.3011000 .3000000000 0.0 0.0  &
    0.0 73.30000000 100.0000000
BPVAL WATER METHY-01 0.0 1087.744000 .3000000000 0.0 0.0  &
    0.0 73.30000000 100.0000000
BPVAL N-BUT-01 WATER 0.0 631.1153000 .4700000000 0.0 0.0  &
    0.0 50.00000000 93.10000000
BPVAL WATER N-BUT-01 0.0 969.4386000 .4700000000 0.0 0.0  &
    0.0 50.00000000 93.10000000
BPVAL N-BUT-02 WATER -2.040500000 763.8692000 .3000000000  &
    0.0 0.0 0.0 19.17000000 117.6000000
BPVAL WATER N-BUT-02 13.11020000 -3338.953600 .3000000000  &
    0.0 0.0 0.0 19.17000000 117.6000000
BPVAL 2-BUT-01 WATER 1.063700000 -405.7652000 .3000000000  &
    0.0 0.0 0.0 25.00000000 100.0000000
BPVAL WATER 2-BUT-01 3.512500000 30.67240000 .3000000000  &
    0.0 0.0 0.0 25.00000000 100.0000000
BPVAL ETHYLACE 2-BUT-01 -.6415420000 297.4300000 .1000000000  &
    0.0 0.0 0.0 25.00000000 157.3300000
BPVAL 2-BUT-01 ETHYLACE -.8248780000 380.6190000 .1000000000  &
    0.0 0.0 0.0 25.00000000 157.3300000

PROP-DATA UNIQ-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar' SHORT-LENGTH=mm
  PROP-LIST UNIQ
  BPVAL ETHANOL ETHYLACE .6541000000 -155.2346000 0.0 0.0  &
    40.00000000 78.45000000 0.0
  BPVAL ETHYLACE ETHANOL -.2733000000 -159.1655000 0.0 0.0  &
    40.00000000 78.45000000 0.0
  BPVAL ETHANOL METHY-01 .8809000000 -248.2244000 0.0 0.0  &
```

25.00000000 78.30000000 0.0
BPVAL METHY-01 ETHANOL -.8330000000 96.99680000 0.0 0.0 &
    25.00000000 78.30000000 0.0
BPVAL ETHANOL N-BUT-01 0.0 266.7760000 0.0 0.0 50.00000000 &
    80.00000000 0.0
BPVAL N-BUT-01 ETHANOL 0.0 -672.8540000 0.0 0.0 &
    50.00000000 80.00000000 0.0
BPVAL ETHANOL N-BUT-02 0.0 87.26290000 0.0 0.0 70.00000000 &
    110.9500000 0.0
BPVAL N-BUT-02 ETHANOL 0.0 -132.5787000 0.0 0.0 &
    70.00000000 110.9500000 0.0
BPVAL ETHANOL 2-BUT-01 0.0 168.7464000 0.0 0.0 78.90000000 &
    97.50000000 0.0
BPVAL 2-BUT-01 ETHANOL 0.0 -253.8458000 0.0 0.0 &
    78.90000000 97.50000000 0.0
BPVAL ETHYLACE METHY-01 0.0 -116.7700000 0.0 0.0 &
    76.50000000 79.95000000 0.0
BPVAL METHY-01 ETHYLACE 0.0 84.98250000 0.0 0.0 &
    76.50000000 79.95000000 0.0
BPVAL ETHYLACE N-BUT-02 0.0 -101.6525000 0.0 0.0 &
    77.10000000 117.7000000 0.0
BPVAL N-BUT-02 ETHYLACE 0.0 23.94160000 0.0 0.0 &
    77.10000000 117.7000000 0.0
BPVAL ETHYLACE 2-BUT-01 0.0 -26.96800000 0.0 0.0 &
    20.00000000 40.00000000 0.0
BPVAL 2-BUT-01 ETHYLACE 0.0 -40.81700000 0.0 0.0 &
    20.00000000 40.00000000 0.0
BPVAL METHY-01 N-BUT-01 0.0 5.668900000 0.0 0.0 &
    56.05000000 79.32000000 0.0
BPVAL N-BUT-01 METHY-01 0.0 -4.801400000 0.0 0.0 &
    56.05000000 79.32000000 0.0
BPVAL METHY-01 N-BUT-02 0.0 68.80310000 0.0 0.0 &
    80.70000000 111.2000000 0.0
BPVAL N-BUT-02 METHY-01 0.0 -136.1885000 0.0 0.0 &
    80.70000000 111.2000000 0.0
BPVAL METHY-01 2-BUT-01 0.0 18.18400000 0.0 0.0 &
    67.50000000 99.61000000 0.0
BPVAL 2-BUT-01 METHY-01 0.0 -56.68620000 0.0 0.0 &
    67.50000000 99.61000000 0.0
BPVAL N-BUT-01 N-BUT-02 0.0 -48.26360000 0.0 0.0 &
    77.20000000 114.0000000 0.0
BPVAL N-BUT-02 N-BUT-01 0.0 16.71510000 0.0 0.0 &
    77.20000000 114.0000000 0.0
BPVAL N-BUT-02 2-BUT-01 -4.099400000 1017.906100 0.0 0.0 &

```
        40.00000000 69.91000000 0.0
    BPVAL 2-BUT-01 N-BUT-02 2.632300000 -644.8218000 0.0 0.0  &
        40.00000000 69.91000000 0.0
    BPVAL ETHANOL ACETA-01 -7.963400000 2209.547900 0.0 0.0  &
        10.00000000 77.70000000 0.0
    BPVAL ACETA-01 ETHANOL 1.226700000 -113.5067000 0.0 0.0  &
        10.00000000 77.70000000 0.0
    BPVAL N-BUT-02 ACETA-01 0.0 -83.82230000 0.0 0.0  &
        22.00000000 65.60000000 0.0
    BPVAL ACETA-01 N-BUT-02 0.0 95.45970000 0.0 0.0  &
        22.00000000 65.60000000 0.0
    BPVAL ETHANOL WATER 2.004600000 -728.9705000 0.0 0.0  &
        24.99000000 100.0000000 0.0
    BPVAL WATER ETHANOL -2.493600000 756.9477000 0.0 0.0  &
        24.99000000 100.0000000 0.0
    BPVAL ETHYLACE WATER 2.721400000 -1212.889200 0.0 0.0 0.0  &
        70.40000000 0.0
    BPVAL WATER ETHYLACE -2.053200000 531.0333000 0.0 0.0 0.0  &
        70.40000000 0.0
    BPVAL ACETA-01 WATER 12.27620000 -4345.301300 0.0 0.0  &
        10.00000000 55.80000000 0.0
    BPVAL WATER ACETA-01 -4.639600000 1516.808600 0.0 0.0  &
        10.00000000 55.80000000 0.0
    BPVAL METHY-01 WATER 0.0 -311.2552000 0.0 0.0 73.30000000  &
        100.0000000 0.0
    BPVAL WATER METHY-01 0.0 -71.01930000 0.0 0.0 73.30000000  &
        100.0000000 0.0
    BPVAL N-BUT-01 WATER 0.0 -440.7517000 0.0 0.0 50.00000000  &
        93.10000000 0.0
    BPVAL WATER N-BUT-01 0.0 -26.12870000 0.0 0.0 50.00000000  &
        93.10000000 0.0
    BPVAL N-BUT-02 WATER 3.764400000 -1446.611300 0.0 0.0  &
        19.17000000 117.6000000 0.0
    BPVAL WATER N-BUT-02 -4.993400000 1569.050900 0.0 0.0  &
        19.17000000 117.6000000 0.0
    BPVAL 2-BUT-01 WATER -1.236100000 369.1626000 0.0 0.0  &
        25.00000000 100.0000000 0.0
    BPVAL WATER 2-BUT-01 .0482000000 -213.2224000 0.0 0.0  &
        25.00000000 100.0000000 0.0


PROP-SET PS-1 TBUB SUBSTREAM=MIXED


PROP-SET PS-2 KVL SUBSTREAM=MIXED
```

STREAM 1
  SUBSTREAM MIXED TEMP=35. PRES=1.
  MASS-FLOW ETHANOL 54.59 <ktonne/oper-year>

STREAM 2
  SUBSTREAM MIXED TEMP=35. PRES=20.
  MASS-FLOW ETHANOL 54.59 <ktonne/year>

STREAM 6
  SUBSTREAM MIXED TEMP=43. PRES=20. &
    MASS-FLOW=2.87 <ktonne/year>
  MOLE-FRAC HYDROGEN 0.42 / WATER 0.1 / ETHANOL 0.02 / &
    ETHYLACE 0.46

STREAM 16
  SUBSTREAM MIXED TEMP=98. PRES=2.

STREAM CH2OIN
  SUBSTREAM MIXED TEMP=90. <F> PRES=1. MASS-FLOW=46400.
  MOLE-FRAC WATER 1.

STREAM STEAMIN
  SUBSTREAM MIXED PRES=150. <psig> VFRAC=1. MASS-FLOW=320.
  MASS-FRAC WATER 1.

BLOCK MIXER MIXER
  PARAM PRES=4.

BLOCK SPILT FSPLIT
  FRAC 4 0.9

BLOCK S-100 SEP
  PARAM
  FRAC STREAM=WATER SUBSTREAM=MIXED COMPS=HYDROGEN WATER &
    ETHANOL ETHYLACE ACETA-01 METHY-01 N-BUT-01 N-BUT-02 &
    2-BUT-01 FRACS=0. 1. 0. 0. 0. 0. 0. 0. 0.

BLOCK E-102 HEATX
  PARAM T-COLD=150. CALC-TYPE=DESIGN U-OPTION=PHASE &
    F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
  FEEDS HOT=STEAMIN COLD=10
  OUTLETS-HOT STEAMOUT
  OUTLETS-COLD 11
  HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO

COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    TQ-PARAM CURVE=YES

BLOCK E-103 HEATX
    PARAM T-HOT=50. CALC-TYPE=DESIGN PRES-HOT=0. U-OPTION=PHASE &
        F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
    FEEDS HOT=12 COLD=CH2OIN
    OUTLETS-HOT 13 V / 14 L
    OUTLETS-COLD CH2OOUT
    HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    TQ-PARAM CURVE=YES

BLOCK C-100 RADFRAC
    PARAM NSTAGE=5 ALGORITHM=STANDARD INIT-OPTION=STANDARD &
        MAXOL=200 DAMPING=NONE
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    FEEDS 2 1 / 6 5 ON-STAGE
    PRODUCTS 5 5 L / 3 1 V
    P-SPEC 1 20.
    COL-SPECS

BLOCK C-101 RADFRAC
    SUBOBJECTS INTERNALS = CS-1 CS-2
    PARAM NSTAGE=20 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD &
        HYDRAULIC=NO MAXOL=200 TOLOL=0.001 NPHASE=2 DAMPING=NONE
    PARAM2 STATIC-DP=YES
    COL-CONFIG CONDENSER=PARTIAL-V CA-CONFIG=INT-1
    FEEDS 5 12 ON-STAGE
    PRODUCTS 6 1 V / 7 20 L
    P-SPEC 1 20.
    COL-SPECS DP-STAGE=0.1 <psi> MASS-B=51.7655 <ktonne/year> &
        MOLE-RR=1.6
    REAC-STAGES 12 12 ETHYLACE
    BLOCK-OPTION FREE-WATER=NO
    REPORT NOHYDRAULIC
    INTERNALS CS-1 STAGE1=2 STAGE2=11 P-UPDATE=NO
    TRAY-SIZE 1 2 11 SIEVE
    INTERNALS CS-2 STAGE1=12 STAGE2=19 P-UPDATE=NO
    TRAY-SIZE 2 12 19 SIEVE

BLOCK C-102 RADFRAC
    SUBOBJECTS INTERNALS = CS-1 CS-2
    PARAM NSTAGE=20 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD &

```
      HYDRAULIC=NO MAXOL=200 TOLOL=0.001 DAMPING=NONE
    PARAM2 STATIC-DP=YES
    COL-CONFIG CONDENSER=PARTIAL-V-L CA-CONFIG=INT-1
    FEEDS 14 10 ON-STAGE-LIQ
    PRODUCTS 16 1 L / 17 20 L / 15 1 V
    P-SPEC 1 2.
    COL-SPECS MASS-RDV=0.00012958 MASS-D=50. <ktonne/year>  &
      MOLE-RR=10.
    SC-REFLUX
    T-EST 1 98.
    REPORT NOHYDRAULIC
    INTERNALS CS-1 STAGE1=2 STAGE2=9 P-UPDATE=NO
    TRAY-SIZE 1 2 9 SIEVE
    INTERNALS CS-2 STAGE1=10 STAGE2=19 P-UPDATE=NO
    TRAY-SIZE 2 10 19 SIEVE

BLOCK R-100 RPLUG
    PARAM TYPE=ADIABATIC LENGTH=5. DIAM=1.
    REACTIONS RXN-IDS=HYDROGEN

BLOCK P-100 PUMP
    PARAM PRES=20.

DESIGN-SPEC PURITY
    DEFINE PURITY MASS-FRAC STREAM=7 SUBSTREAM=MIXED  &
      COMPONENT=ETHYLACE
    SPEC "PURITY" TO "0.985"
    TOL-SPEC "0.002"
    VARY BLOCK-VAR BLOCK=C-101 VARIABLE=MOLE-RR  &
      SENTENCE=COL-SPECS
    LIMITS "0.5" "2"

DESIGN-SPEC PURITY2
    DEFINE PURITY2 MASS-FRAC STREAM=16 SUBSTREAM=MIXED  &
      COMPONENT=ETHYLACE
    SPEC "PURITY2" TO "0.998"
    TOL-SPEC "0.0001"
    VARY BLOCK-VAR BLOCK=C-102 VARIABLE=MOLE-RR  &
      SENTENCE=COL-SPECS
    LIMITS "1" "100"

EO-CONV-OPTI

SENSITIVITY CONDENSE
```

```
    DEFINE TEMP STREAM-VAR STREAM=16 SUBSTREAM=MIXED  &
       VARIABLE=TEMP UOM="F"
    DEFINE MASSFRAC MASS-FRAC STREAM=16 SUBSTREAM=MIXED  &
       COMPONENT=ETHYLACE
    TABULATE 1 "TEMP"
    TABULATE 2 "MASSFRAC"
    VARY BLOCK-VAR BLOCK=C-102 VARIABLE=MASS-RDV  &
       SENTENCE=COL-SPECS
    RANGE OPT-LIST=RANGE LOWER="0.00005" UPPER="0.0003"  &
       NPOINT="1000"

SENSITIVITY HX1-SENS
    DEFINE AREA BLOCK-VAR BLOCK=E-102 VARIABLE=CALC-AREA  &
       SENTENCE=RESULTS UOM="sqft"
    TABULATE 1 "AREA"
    VARY STREAM-VAR STREAM=STEAMIN SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW UOM="kg/hr"
    RANGE OPT-LIST=RANGE LOWER="320" UPPER="600" INCR="1"

SENSITIVITY HX2-SENS
    DEFINE AREA BLOCK-VAR BLOCK=E-103 VARIABLE=CALC-AREA  &
       SENTENCE=RESULTS UOM="sqft"
    DEFINE TEMP STREAM-VAR STREAM=CH2OOUT SUBSTREAM=MIXED  &
       VARIABLE=TEMP UOM="C"
    TABULATE 2 "AREA"
    TABULATE 1 "TEMP"
    VARY STREAM-VAR STREAM=CH2OIN SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW UOM="kg/hr"
    RANGE OPT-LIST=RANGE LOWER="10000" UPPER="100000" INCR="100"

CONV-OPTIONS
    PARAM TEAR-METHOD=WEGSTEIN TOL=0.01 COMB-METHOD=BROYDEN
    WEGSTEIN MAXIT=9999

TEAR
    TEAR 6 0.0001

STREAM-REPOR MOLEFLOW

PROPERTY-REP PCES NOPARAM-PLUS

REACTIONS ETHYLACE REAC-DIST
    REAC-DATA 1 EQUIL
    REAC-DATA 2 EQUIL
```

```
  REAC-DATA 3 CONV
  K-STOIC 1 A=16.5 B=-9136.4
  K-STOIC 2 A=-4.79 B=4386.
  STOIC 1 ETHANOL -1. / HYDROGEN 1. / ACETA-01 1.
  STOIC 2 ACETA-01 -1. / ETHANOL -1. / HYDROGEN 1. /  &
     ETHYLACE 1.
  STOIC 3 ACETA-01 -2. / HYDROGEN -1. / WATER 1. /  &
     METHY-01 0.5 / N-BUT-01 0.5
  CONV 3 CONV-A=0.2 KEY-CID=ACETA-01

REACTIONS HYDROGEN POWERLAW
  REAC-DATA 1 PHASE=V CBASIS=PARTIALPRES
  REAC-DATA 2 PHASE=V CBASIS=PARTIALPRES
  RATE-CON 1 PRE-EXP=220. ACT-ENERGY=7730.
  RATE-CON 2 PRE-EXP=220. ACT-ENERGY=7730.
  STOIC 1 MIXED METHY-01 -1. / HYDROGEN -1. / 2-BUT-01 1.
  STOIC 2 MIXED HYDROGEN -1. / N-BUT-01 -1. / N-BUT-02 1.
  POWLAW-EXP 1 MIXED METHY-01 1. / MIXED HYDROGEN -0.5
  POWLAW-EXP 2 MIXED HYDROGEN -0.5 / MIXED N-BUT-01 1.

PROP-TABLE PURE-1 PROPS
  IN-UNITS MET PRESSURE=bar TEMPERATURE=F DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar' SHORT-LENGTH=mm
  ANALYSIS ANAL-TYPE=PURE PURE-PROP='PL' PURE-PHASES= L
  MOLE-FLOW ETHYLACE 1
  PROPERTIES NRTL HENRY-COMPS=HC-1 FREE-WATER=STEAM-TA  &
     SOLU-WATER=3 TRUE-COMPS=YES
  VARY TEMP
  RANGE VARVALUE=RANGE LOWER=0 UPPER=300. NPOINT=200
  VARY PRES
  RANGE LIST=1.013250000
  PARAM

PROP-TABLE MIX-1 FLASHCURVE
  IN-UNITS MET PRESSURE=bar TEMPERATURE=F DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar' SHORT-LENGTH=mm
  MOLE-FLOW WATER 0.5 / N-BUT-02 0.25 / 2-BUT-01 0.25
  VARY PRES
  RANGE VARVALUE=LIST LIST=2.25
  VARY TEMP
  RANGE VARVALUE=RANGE LOWER=0 UPPER=250. NPOINT=100
  PARAM
  TABULATE PROPERTIES=PS-1
```

```
PROP-TABLE MIX-2 FLASHCURVE
    IN-UNITS MET PRESSURE=bar TEMPERATURE=F DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar' SHORT-LENGTH=mm
    MOLE-FLOW HYDROGEN 0.66 / WATER 0.005 / ETHYLACE 0.325 /  &
        N-BUT-02 0.0025 / 2-BUT-01 0.0025
    VARY PRES
    RANGE VARVALUE=LIST LIST=2.125
    VARY TEMP
    RANGE VARVALUE=RANGE LOWER=190. UPPER=210. NPOINT=10
    PARAM
    TABULATE PROPERTIES=PS-2

DISABLE
    SENSITIVITY CONDENSE
    DESIGN-SPEC PURITY PURITY2
;
;
;
;
;
```

28.7.3 Block Reports

```
BLOCK: C-100   MODEL: RADFRAC
-------------------------------
 INLETS  - 2     STAGE  1
      6     STAGE  5
 OUTLETS - 3     STAGE  1
      5     STAGE  5
 PROPERTY OPTION SET:  NRTL    RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID:     HC-1


           ***  MASS AND ENERGY BALANCE  ***
                 IN          OUT      RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(KMOL/HR )      291.434      291.434      0.00000
   MASS(KG/HR   )      7671.50      7671.50    -0.699475E-14
   ENTHALPY(CAL/SEC )   -0.290902E+07  -0.290902E+07  0.891480E-07


           ***  CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E        0.00000    KG/HR
 PRODUCT STREAMS CO2E       0.00000    KG/HR
 NET STREAMS CO2E PRODUCTION  0.00000    KG/HR
 UTILITIES CO2E PRODUCTION    0.00000    KG/HR
 TOTAL CO2E PRODUCTION       0.00000    KG/HR


           *********************
           ****  INPUT DATA  ****
           *********************


 ****  INPUT PARAMETERS  ****

 NUMBER OF STAGES                 5
 ALGORITHM OPTION               STANDARD
 ABSORBER OPTION             NO
 INITIALIZATION OPTION          STANDARD
 HYDRAULIC PARAMETER CALCULATIONS        NO
 INSIDE LOOP CONVERGENCE METHOD         BROYDEN
 DESIGN SPECIFICATION METHOD          NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS      200
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS      10
 MAXIMUM NUMBER OF FLASH ITERATIONS       30
 FLASH TOLERANCE            0.000100000
 OUTSIDE LOOP CONVERGENCE TOLERANCE        0.000100000


 ****  COL-SPECS  ****
```

MOLAR VAPOR DIST / TOTAL DIST   1.00000
CONDENSER DUTY (W/O SUBCOOL) CAL/SEC   0.0
REBOILER DUTY   CAL/SEC   0.0

****   PROFILES   ****

P-SPEC   STAGE 1 PRES, BAR   20.0000

            ****
            **** RESULTS ****
            ****

***   COMPONENT SPLIT FRACTIONS   ***

            OUTLET STREAMS
            ----
        3   5
COMPONENT:
HYDROGEN   .99289   .71106E-02
WATER   .87420E-08   1.0000
ETHANOL   .86985E-02   .99130
ETHYLACE   .96532E-06   1.0000
ACETA-01   .37903E-04   .99996
METHY-01   .28853E-06   1.0000
N-BUT-01   .11874E-06   1.0000

***   SUMMARY OF KEY RESULTS   ***

TOP STAGE TEMPERATURE   C   39.5848
BOTTOM STAGE TEMPERATURE   C   87.6679
TOP STAGE LIQUID FLOW   KMOL/HR   136.211
BOTTOM STAGE LIQUID FLOW   KMOL/HR   157.270
TOP STAGE VAPOR FLOW   KMOL/HR   134.164
BOILUP VAPOR FLOW   KMOL/HR   146.605
CONDENSER DUTY (W/O SUBCOOL) CAL/SEC   0.0
REBOILER DUTY   CAL/SEC   0.0

****   MAXIMUM FINAL RELATIVE ERRORS   ****

DEW POINT   0.96802E-06 STAGE= 3
BUBBLE POINT   0.98321E-04 STAGE= 3
COMPONENT MASS BALANCE   0.36697E-05 STAGE= 2 COMP=HYDROGEN
ENERGY BALANCE   0.12380E-04 STAGE= 2

```
****   PROFILES   ****

**NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
     FROM THE STAGE INCLUDING ANY SIDE PRODUCT.


                         ENTHALPY
STAGE TEMPERATURE  PRESSURE       CAL/MOL        HEAT DUTY
    C          BAR       LIQUID     VAPOR     CAL/SEC


 1  39.585     20.000    -65554.    -390.46
 2  45.521     20.000    -65360.    -522.11
 4  73.629     20.000    -64583.    -2187.8
 5  87.668     20.000    -66256.    -4604.2
```

STAGE	FLOW RATE KMOL/HR		FEED RATE KMOL/HR			PRODUCT RATE KMOL/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	136.2	134.2	135.1768				134.1642
2	137.5	135.2					
4	147.6	140.1					
5	157.3	146.6			156.2569	157.2696	

```
 ****  MASS FLOW PROFILES  ****
```

STAGE	FLOW RATE KG/HR		FEED RATE KG/HR			PRODUCT RATE KG/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	6248.	322.3	6227.4697				322.2797
2	6309.	343.2					
4	6791.	567.5					
5	7349.	885.9			1444.0287	7349.2187	

```
          ****   MOLE-X-PROFILE   ****
STAGE   HYDROGEN    WATER      ETHANOL     ETHYLACE    ACETA-01
  1  0.44465E-02  0.56832E-07  0.99552    0.18947E-05  0.31576E-04
  2  0.45774E-02  0.44477E-05  0.99484    0.45640E-04  0.53074E-03
  4  0.53554E-02  0.41867E-02  0.96982    0.74962E-02  0.13128E-01
  5  0.60558E-02  0.52997E-01  0.85226    0.58796E-01  0.29774E-01


          ****   MOLE-X-PROFILE   ****
STAGE   METHY-01    N-BUT-01
  1  0.11439E-08  0.15083E-09
```

```
 2   0.35427E-07  0.58218E-08
 4   0.94668E-05  0.21465E-05
 5   0.91434E-04  0.22887E-04


          ****   MOLE-Y-PROFILE   ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE    ACETA-01
 1   0.99123     0.54309E-09  0.87664E-02  0.66531E-07  0.13229E-05
 2   0.98813     0.57797E-07  0.11834E-01  0.19749E-05  0.33125E-04
 4   0.95420     0.19510E-03  0.40782E-01  0.73172E-03  0.40941E-02
 5   0.91251     0.42156E-02  0.62495E-01  0.75480E-02  0.13220E-01


          ****   MOLE-Y-PROFILE   ****
STAGE    METHY-01    N-BUT-01
 1   0.30925E-10  0.31855E-11
 2   0.11832E-08  0.15512E-09
 4   0.72984E-06  0.14440E-06
 5   0.95323E-05  0.21614E-05


          ****   K-VALUES       ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE    ACETA-01
 1   222.93      0.95560E-02  0.88058E-02  0.35114E-01  0.41897E-01
 2   215.87      0.12995E-01  0.11896E-01  0.43272E-01  0.62413E-01
 4   178.18      0.46601E-01  0.42051E-01  0.97613E-01  0.31186
 5   150.68      0.79544E-01  0.73329E-01  0.12838      0.44401


          ****   K-VALUES       ****
STAGE    METHY-01    N-BUT-01
 1   0.27034E-01  0.21120E-01
 2   0.33398E-01  0.26645E-01
 4   0.77095E-01  0.67273E-01
 5   0.10425      0.94437E-01


          ****   MASS-X-PROFILE   ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE    ACETA-01
 1   0.19540E-03  0.22319E-07  0.99977      0.36391E-05  0.30323E-04
 2   0.20117E-03  0.17469E-05  0.99920      0.87668E-04  0.50974E-03
 4   0.23467E-03  0.16395E-02  0.97118      0.14356E-01  0.12571E-01
 5   0.26124E-03  0.20431E-01  0.84021      0.11086      0.28069E-01


          ****   MASS-X-PROFILE   ****
STAGE    METHY-01    N-BUT-01
 1   0.17981E-08  0.23708E-09
 2   0.55693E-07  0.91521E-08
 4   0.14838E-04  0.33644E-05
```

5   0.14109E-03 0.35316E-04

          ****   MASS-Y-PROFILE   ****
STAGE   HYDROGEN   WATER   ETHANOL   ETHYLACE   ACETA-01
  1   0.83185   0.40730E-08 0.16813   0.24403E-05 0.24262E-04
  2   0.78461   0.41013E-06 0.21475   0.68539E-04 0.57479E-03
  4   0.47486   0.86770E-03 0.46382   0.15915E-01 0.44525E-01
  5   0.30441   0.12568E-01 0.47645   0.11005   0.96375E-01

          ****   MASS-Y-PROFILE   ****
STAGE   METHY-01   N-BUT-01
  1   0.92831E-09 0.95623E-10
  2   0.33605E-07 0.44057E-08
  4   0.12992E-04 0.25705E-05
  5   0.11375E-03 0.25791E-04

BLOCK: C-101   MODEL: RADFRAC

 INLETS - 5   STAGE 12
 OUTLETS - 6   STAGE 1
       7   STAGE 20
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

          *** MASS AND ENERGY BALANCE ***
               IN   OUT   GENERATION   RELATIVE DIFF.
 TOTAL BALANCE
 MOLE(KMOL/HR)   157.270   224.271   67.0001   -0.521458E-05
 MASS(KG/HR)   7349.22   7349.29   -0.937569E-05
 ENTHALPY(CAL/SEC) -0.289446E+07 -0.238788E+07   -0.175017

          *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION 0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

          ****
          **** INPUT DATA ****
          ****

****   INPUT PARAMETERS   ****

```
NUMBER OF STAGES                              20
ALGORITHM OPTION                          NONIDEAL
INITIALIZATION OPTION                     STANDARD
HYDRAULIC PARAMETER CALCULATIONS                NO
INSIDE LOOP CONVERGENCE METHOD              NEWTON
DESIGN SPECIFICATION METHOD              NESTED
MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS        200
MAXIMUM NO. OF INSIDE LOOP ITERATIONS          10
MAXIMUM NUMBER OF FLASH ITERATIONS             30
FLASH TOLERANCE                    0.000100000
OUTSIDE LOOP CONVERGENCE TOLERANCE         0.00100000
```

**** COL-SPECS ****

```
MOLAR VAPOR DIST / TOTAL DIST              1.00000
MOLAR REFLUX RATIO                  1.60000
MASS BOTTOMS RATE        KG/HR      5,905.26
```

**** REAC-STAGES SPECIFICATIONS ****

```
STAGE  TO  STAGE        REACTIONS/CHEMISTRY ID
 12      12             ETHYLACE
```

  ***** REACTION PARAGRAPH ETHYLACE*****

   **** REACTION PARAMETERS ****

```
RXN NO. TYPE      PHASE    CONC.  TEMP APP TO EQUIL   CONVERSION
                  BASIS      C
 1  EQUILIBRIUM  LIQUID    MOLE-GAMMA    0.0000
 2  EQUILIBRIUM  LIQUID    MOLE-GAMMA    0.0000
 3  CONVERSION                        SIMULTANEOUS
```

  ** STOICHIOMETRIC COEFFICIENTS **

RXN NO.	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01
1	1.000	0.000	-1.000	0.000	1.000
2	1.000	0.000	-1.000	1.000	-1.000
3	-1.000	1.000	0.000	0.000	-2.000

RXN NO.	METHY-01	N-BUT-01
1	0.000	0.000
2	0.000	0.000
3	0.5000	0.5000

** COEFFICIENTS OF EQUILIBRIUM CONSTANT EXPRESSION **

RXN NO.	A	B	C	D
1	16.500	-9136.4	0.0000	0.0000
2	-4.7900	4386.0	0.0000	0.0000

** COEFFICIENTS OF CONVERSION EXPRESSION **

RXN NO.	COMPONENT ID	A	B	C	D
3	ACETA-01	0.20000	0.0000	0.0000	0.0000

**** PROFILES ****

P-SPEC   STAGE 1 PRES, BAR   20.0000

```
                   ******************
                   ****  RESULTS  ****
                   ******************
```

*** COMPONENT SPLIT FRACTIONS ***
        OUTLET STREAMS

	6	7
COMPONENT:		
HYDROGEN	1.0000	0.0000
WATER	.89167	.10833
ETHANOL	.97876	.21237E-01
ETHYLACE	.12290	.87710
ACETA-01	.99998	.16777E-04
METHY-01	.27631E-01	.97237
N-BUT-01	.70624E-02	.99294

*** SUMMARY OF KEY RESULTS ***

TOP STAGE TEMPERATURE	C	97.1078
BOTTOM STAGE TEMPERATURE	C	207.194
TOP STAGE LIQUID FLOW	KMOL/HR	250.009
BOTTOM STAGE LIQUID FLOW	KMOL/HR	68.0140
TOP STAGE VAPOR FLOW	KMOL/HR	156.256
BOILUP VAPOR FLOW	KMOL/HR	912.593
MOLAR REFLUX RATIO		1.60000
MOLAR BOILUP RATIO		13.4177
CONDENSER DUTY (W/O SUBCOOL)	CAL/SEC	-673,482.
REBOILER DUTY	CAL/SEC	1,180,090.

```
****   MAXIMUM FINAL RELATIVE ERRORS   ****

 DEW POINT                0.16623E-04  STAGE= 16
 BUBBLE POINT             0.30014E-04  STAGE= 16
 COMPONENT MASS BALANCE      0.18807E-07  STAGE= 20 COMP=WATER
 ENERGY BALANCE           0.62004E-05  STAGE= 20


 ****    PROFILES   ****

 **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
     FROM THE STAGE INCLUDING ANY SIDE PRODUCT.


                 ENTHALPY
STAGE TEMPERATURE  PRESSURE      CAL/MOL        HEAT DUTY
     C        BAR       LIQUID     VAPOR     CAL/SEC

 1   97.108    20.000    -80585.    -9992.5    -.67348+06
 2  163.16     20.007    -79390.    -47466.
11  168.54     20.069    -79891.    -52173.
12  168.70     20.076    -82591.    -52504.
13  185.42     20.083    -84303.    -72606.
18  204.92     20.117    -0.10203E+06 -95253.
19  206.38     20.124    -0.10293E+06 -97158.
20  207.19     20.131    -0.10343E+06 -98239.     .11801+07
```

STAGE	FLOW RATE		FEED RATE			PRODUCT RATE	
	KMOL/HR		KMOL/HR			KMOL/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	250.0	156.3			156.2569		
2	323.5	406.3					
11	331.1	485.6					
12	635.5	487.3		157.2696			
13	716.7	567.4					
18	959.2	856.3					
19	980.6	891.2					
20	68.01	912.6			68.0139		

```
  **** MASS FLOW PROFILES ****
```

STAGE	FLOW RATE		FEED RATE			PRODUCT RATE	
	KG/HR		KG/HR			KG/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	0.1091E+05	1444.			1443.9706		

```
 2 0.1409E+05 0.1236E+05
11 0.1464E+05 0.1579E+05
12 0.3112E+05 0.1608E+05                    7349.2187
13 0.3770E+05 0.2522E+05
18 0.8081E+05 0.6928E+05
19 0.8424E+05 0.7491E+05
20  5905.    0.7833E+05                      5905.2589
```

**** MOLE-X-PROFILE ****

STAGE	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01
1	0.67248E-02	0.59654	0.17830E-02	0.34939	0.44715E-01
2	0.38752E-02	0.61919	0.16334E-02	0.35747	0.16799E-01
11	0.34658E-02	0.61697	0.70556E-03	0.36823	0.53856E-02
12	0.39472E-02	0.54785	0.64856E-03	0.43518	0.57529E-02
13	0.74525E-04	0.50274	0.59933E-03	0.48635	0.22484E-02
18	0.61690E-12	0.51676E-01	0.49462E-04	0.93361	0.12027E-04
19	0.16947E-13	0.28058E-01	0.23652E-04	0.95709	0.37721E-05
20	0.46999E-15	0.14888E-01	0.10950E-04	0.97022	0.11551E-05

**** MOLE-X-PROFILE ****

STAGE	METHY-01	N-BUT-01
1	0.66242E-03	0.18099E-03
2	0.80021E-03	0.23672E-03
11	0.32576E-02	0.19798E-02
12	0.39652E-02	0.26534E-02
13	0.48198E-02	0.31637E-02
18	0.78365E-02	0.68110E-02
19	0.76788E-02	0.71496E-02
20	0.74405E-02	0.74405E-02

**** MOLE-Y-PROFILE ****

STAGE	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01
1	0.85719	0.53338E-01	0.21967E-03	0.59173E-01	0.29968E-01
2	0.33383	0.38762	0.11817E-02	0.23777	0.39043E-01
11	0.27814	0.44216	0.58116E-03	0.26285	0.13259E-01
12	0.27720	0.43625	0.54977E-03	0.26914	0.13268E-01
13	0.44203E-02	0.61173	0.72499E-03	0.37105	0.64423E-02
18	0.24723E-10	0.99366E-01	0.10677E-03	0.88631	0.40410E-04
19	0.66394E-12	0.54484E-01	0.52402E-04	0.93082	0.12856E-04
20	0.18175E-13	0.29039E-01	0.24598E-04	0.95611	0.39671E-05

**** MOLE-Y-PROFILE ****

STAGE	METHY-01	N-BUT-01
1	0.92032E-04	0.23035E-04

2	0.44304E-03	0.12024E-03
11	0.19362E-02	0.10742E-02
12	0.22426E-02	0.13524E-02
13	0.35486E-02	0.20796E-02
18	0.78831E-02	0.62932E-02
19	0.78667E-02	0.67630E-02
20	0.76965E-02	0.71280E-02

**** K-VALUES ****

STAGE	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01
1	127.47	0.89412E-01	0.12320	0.16936	0.67022
2	86.144	0.62601	0.72347	0.66515	2.3242
11	80.252	0.71666	0.82368	0.71382	2.4620
12	70.229	0.79629	0.84767	0.61845	2.3063
13	59.312	1.2168	1.2097	0.76293	2.8652
18	40.075	1.9227	2.1586	0.94933	3.3600
19	39.177	1.9418	2.2156	0.97256	3.4082
20	38.669	1.9505	2.2464	0.98546	3.4345

**** K-VALUES ****

STAGE	METHY-01	N-BUT-01
1	0.13893	0.12728
2	0.55366	0.50792
11	0.59437	0.54260
12	0.56557	0.50968
13	0.73625	0.65732
18	1.0059	0.92397
19	1.0245	0.94592
20	1.0344	0.95799

**** RATES OF GENERATION ****
KMOL/HR

STAGE	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01	METHY-01
1	0.000	0.000	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.000	0.000	0.000
11	0.000	0.000	0.000	0.000	0.000	0.000
12	133.0	1.012	-134.0	65.99	0.2374E-03	0.5061
13	0.000	0.000	0.000	0.000	0.000	0.000
18	0.000	0.000	0.000	0.000	0.000	0.000
19	0.000	0.000	0.000	0.000	0.000	0.000
20	0.000	0.000	0.000	0.000	0.000	0.000

**** RATES OF GENERATION ****
KMOL/HR

```
STAGE    N-BUT-01
 1   0.000
 2   0.000
11   0.000
12  0.5061
13   0.000
18   0.000
19   0.000
20   0.000


         ****   MASS-X-PROFILE   ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE    ACETA-01
 1   0.31052E-03  0.24617    0.18815E-02  0.70513     0.45120E-01
 2   0.17939E-03  0.25615    0.17280E-02  0.72323     0.16994E-01
11   0.15802E-03  0.25140    0.73518E-03  0.73380     0.53662E-02
12   0.16245E-03  0.20150    0.61001E-03  0.78281     0.51742E-02
13   0.28556E-05  0.17215    0.52481E-03  0.81450     0.18827E-02
18   0.14761E-13  0.11050E-01 0.27048E-04 0.97638     0.62887E-05
19   0.39769E-15  0.58843E-02 0.12684E-04 0.98165     0.19345E-05
20   0.10912E-16  0.30891E-02 0.58102E-05 0.98455     0.58608E-06


         ****   MASS-X-PROFILE   ****
STAGE    METHY-01    N-BUT-01
 1   0.10941E-02  0.29893E-03
 2   0.13250E-02  0.39196E-03
11   0.53128E-02  0.32288E-02
12   0.58373E-02  0.39062E-02
13   0.66060E-02  0.43361E-02
18   0.67072E-02  0.58295E-02
19   0.64457E-02  0.60015E-02
20   0.61793E-02  0.61793E-02


         ****   MASS-Y-PROFILE   ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE    ACETA-01
 1   0.18699     0.10398    0.10951E-02  0.56417     0.14286
 2   0.22122E-01  0.22955    0.17897E-02  0.68866     0.56541E-01
11   0.17245E-01  0.24500    0.82346E-03  0.71229     0.17966E-01
12   0.16934E-01  0.23816    0.76750E-03  0.71857     0.17712E-01
13   0.20049E-03  0.24796    0.75149E-03  0.73557     0.63856E-02
18   0.61599E-12  0.22125E-01 0.60792E-04 0.96516     0.22002E-04
19   0.15924E-13  0.11678E-01 0.28722E-04 0.97574     0.67383E-05
20   0.42685E-15  0.60950E-02 0.13203E-04 0.98144     0.20361E-05


         ****   MASS-Y-PROFILE   ****
```

STAGE	METHY-01	N-BUT-01
1	0.71812E-03	0.17974E-03
2	0.10502E-02	0.28500E-03
11	0.42941E-02	0.23824E-02
12	0.49002E-02	0.29551E-02
13	0.57573E-02	0.33739E-02
18	0.70255E-02	0.56086E-02
19	0.67489E-02	0.58019E-02
20	0.64658E-02	0.59881E-02

```
        *****************************
        ***** HYDRAULIC PARAMETERS *****
        *****************************
```

*** DEFINITIONS ***

MARANGONI INDEX = SIGMA - SIGMATO
FLOW PARAM = (ML/MV)*SQRT(RHOV/RHOL)
QR = QV*SQRT(RHOV/(RHOL-RHOV))
F FACTOR = QV*SQRT(RHOV)
 WHERE:
 SIGMA IS THE SURFACE TENSION OF LIQUID FROM THE STAGE
 SIGMATO IS THE SURFACE TENSION OF LIQUID TO THE STAGE
 ML IS THE MASS FLOW OF LIQUID FROM THE STAGE
 MV IS THE MASS FLOW OF VAPOR TO THE STAGE
 RHOL IS THE MASS DENSITY OF LIQUID FROM THE STAGE
 RHOV IS THE MASS DENSITY OF VAPOR TO THE STAGE
 QV IS THE VOLUMETRIC FLOW RATE OF VAPOR TO THE STAGE

TEMPERATURE
C

STAGE	LIQUID FROM	VAPOR TO
1	97.108	163.16
2	163.16	167.74
11	168.54	168.70
12	168.70	185.42
13	185.42	187.86
18	204.92	206.38
19	206.38	207.19
20	207.19	207.19

	MASS FLOW		VOLUME FLOW		MOLECULAR WEIGHT	
	KG/HR		L/MIN			
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO

1	10915.	12359.	221.04	12277.	43.657	30.420
2	14088.	15532.	325.22	14645.	43.548	32.374
11	14638.	16082.	341.91	14863.	44.213	33.000
12	31125.	25220.	733.71	17955.	48.980	44.445
13	37704.	31799.	932.93	20627.	52.610	49.023
18	80811.	74906.	2222.7	29427.	84.247	84.051
19	84235.	78330.	2334.7	30175.	85.901	85.833
20	5905.3	0.0000	164.38	0.0000	86.824	

	DENSITY		VISCOSITY		SURFACE TENSION
	GM/CC		CP		DYNE/CM
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM
1	0.82299	0.16777E-01	0.23147	0.15020E-01	40.582
2	0.72197	0.17676E-01	0.13964	0.15020E-01	30.878
11	0.71353	0.18033E-01	0.13549	0.14994E-01	29.957
12	0.70702	0.23411E-01	0.13170	0.14512E-01	27.312
13	0.67357	0.25694E-01	0.12089	0.14262E-01	23.054
18	0.60597	0.42424E-01	0.89572E-01	0.12409E-01	4.9804
19	0.60133	0.43265E-01	0.87824E-01	0.12322E-01	4.0597
20	0.59873		0.86861E-01		3.5506

	MARANGONI INDEX	FLOW PARAM	QR	REDUCED F-FACTOR
STAGE	DYNE/CM		L/MIN	(GM-L)**.5/MIN
1		0.12610	1771.1	50288.
2	-9.7040	0.14192	2320.1	61572.
11	-.36991	0.14470	2393.3	63116.
12	-.81228	0.22457	3322.6	86873.
13	-4.2576	0.23158	4107.7	0.10455E+06
18	-1.6412	0.28546	8074.1	0.19167E+06
19	-.92074	0.28845	8401.7	0.19848E+06
20	-.50910		0.0000	0.0000

```
        ************************************
        ***** TRAY SIZING CALCULATIONS *****
        ************************************


  *******************
  *** SECTION  1 ***
  *******************
```

STARTING STAGE NUMBER	2
ENDING STAGE NUMBER	11
FLOODING CALCULATION METHOD	GLITSCH6

DESIGN PARAMETERS

PEAK CAPACITY FACTOR   1.00000
SYSTEM FOAMING FACTOR   1.00000
FLOODING FACTOR   0.80000
MINIMUM COLUMN DIAMETER   METER   0.30480
MINIMUM DC AREA/COLUMN AREA   0.100000
HOLE AREA/ACTIVE AREA   0.100000

TRAY SPECIFICATIONS

TRAY TYPE   SIEVE
NUMBER OF PASSES   1
TRAY SPACING   METER   0.60960

     ***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****

STAGE WITH MAXIMUM DIAMETER   11
COLUMN DIAMETER   METER   0.80845
DC AREA/COLUMN AREA   0.100000
DOWNCOMER VELOCITY   M/SEC   0.11101
FLOW PATH LENGTH   METER   0.55544
SIDE DOWNCOMER WIDTH   METER   0.12650
SIDE WEIR LENGTH   METER   0.58743
CENTER DOWNCOMER WIDTH   METER   0.0
CENTER WEIR LENGTH   METER   MISSING
OFF-CENTER DOWNCOMER WIDTH   METER   0.0
OFF-CENTER SHORT WEIR LENGTH   METER   MISSING
OFF-CENTER LONG WEIR LENGTH   METER   MISSING
TRAY CENTER TO OCDC CENTER   METER   0.0

          **** SIZING PROFILES ****

STAGE	DIAMETER	TOTAL AREA	ACTIVE AREA	SIDE DC AREA
	METER	SQM	SQM	SQM
2	0.80845	0.51332	0.41066	0.51332E-01
3	0.80845	0.51332	0.41066	0.51332E-01
4	0.80845	0.51332	0.41066	0.51332E-01
5	0.80845	0.51332	0.41066	0.51332E-01
6	0.80845	0.51332	0.41066	0.51332E-01
7	0.80845	0.51332	0.41066	0.51332E-01
8	0.80845	0.51332	0.41066	0.51332E-01
9	0.80845	0.51332	0.41066	0.51332E-01
10	0.80845	0.51332	0.41066	0.51332E-01

```
   11     0.80845     0.51332     0.41066     0.51332E-01
```

**** ADDITIONAL SIZING PROFILES ****

	FLOODING		DC BACKUP/	
STAGE	FACTOR	PRES. DROP	DC BACKUP	(TSPC+WHT)
		BAR	METER	
2	77.36	0.8987E-02	0.2428	36.76
3	78.87	0.9120E-02	0.2481	37.57
4	78.95	0.9127E-02	0.2485	37.62
5	78.94	0.9125E-02	0.2484	37.62
6	78.94	0.9124E-02	0.2484	37.62
7	78.93	0.9122E-02	0.2484	37.62
8	78.93	0.9121E-02	0.2484	37.62
9	78.93	0.9119E-02	0.2484	37.62
10	78.93	0.9118E-02	0.2484	37.61
11	80.00	0.9255E-02	0.2523	38.20

	HEIGHT	DC REL	TR LIQ REL	FRA APPR TO
STAGE	OVER WEIR	FROTH DENS	FROTH DENS	SYS LIMIT
	METER			
2	0.1380	0.6057	0.1855	46.17
3	0.1410	0.6054	0.1843	47.16
4	0.1412	0.6054	0.1842	47.21
5	0.1412	0.6054	0.1842	47.21
6	0.1412	0.6054	0.1842	47.20
7	0.1412	0.6054	0.1843	47.20
8	0.1412	0.6054	0.1843	47.20
9	0.1412	0.6054	0.1843	47.20
10	0.1412	0.6054	0.1843	47.20
11	0.1438	0.6053	0.1833	47.94

```
   *******************
   *** SECTION  2 ***
   *******************
```

STARTING STAGE NUMBER	12
ENDING STAGE NUMBER	19
FLOODING CALCULATION METHOD	GLITSCH6

DESIGN PARAMETERS

PEAK CAPACITY FACTOR	1.00000
SYSTEM FOAMING FACTOR	1.00000

```
FLOODING FACTOR                        0.80000
MINIMUM COLUMN DIAMETER     METER            0.30480
MINIMUM DC AREA/COLUMN AREA                0.100000
HOLE AREA/ACTIVE AREA                0.100000


TRAY SPECIFICATIONS
-------------------
TRAY TYPE                        SIEVE
NUMBER OF PASSES                    1
TRAY SPACING            METER        0.60960

      ***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****


STAGE WITH MAXIMUM DIAMETER                19
COLUMN DIAMETER          METER        1.83112
DC AREA/COLUMN AREA                0.12541
DOWNCOMER VELOCITY        M/SEC          0.11782
FLOW PATH LENGTH         METER        1.16070
SIDE DOWNCOMER WIDTH        METER          0.33521
SIDE WEIR LENGTH          METER        1.41626
CENTER DOWNCOMER WIDTH      METER            0.0
CENTER WEIR LENGTH         METER        MISSING
OFF-CENTER DOWNCOMER WIDTH     METER          0.0
OFF-CENTER SHORT WEIR LENGTH   METER        MISSING
OFF-CENTER LONG WEIR LENGTH    METER        MISSING
TRAY CENTER TO OCDC CENTER     METER          0.0


          **** SIZING PROFILES ****


  STAGE   DIAMETER    TOTAL AREA  ACTIVE AREA  SIDE DC AREA
        METER     SQM      SQM       SQM
   12    1.8311   2.6334   1.9729   0.33026
   13    1.8311   2.6334   1.9729   0.33026
   14    1.8311   2.6334   1.9729   0.33026
   15    1.8311   2.6334   1.9729   0.33026
   16    1.8311   2.6334   1.9729   0.33026
   17    1.8311   2.6334   1.9729   0.33026
   18    1.8311   2.6334   1.9729   0.33026
   19    1.8311   2.6334   1.9729   0.33026


      **** ADDITIONAL SIZING PROFILES ****


    FLOODING             DC BACKUP/
 STAGE FACTOR    PRES. DROP  DC BACKUP  (TSPC+WHT)
```

```
        BAR      METER
12   28.45   0.5653E-02 0.1968    29.80
13   35.60   0.5764E-02 0.2096    31.73
14   42.59   0.6151E-02 0.2269    34.35
15   52.34   0.6664E-02 0.2574    38.98
16   62.54   0.7179E-02 0.2973    45.02
17   70.86   0.7603E-02 0.3360    50.88
18   76.52   0.7899E-02 0.3655    55.34
19   80.00   0.8085E-02 0.3849    58.28


      HEIGHT    DC REL    TR LIQ REL FRA APPR TO
STAGE OVER WEIR  FROTH DENS  FROTH DENS  SYS LIMIT
     METER
12   0.5255E-01 0.6048    0.4177    13.74
13   0.6754E-01 0.6026    0.3735    17.67
14   0.8424E-01 0.6012    0.3394    21.90
15   0.1100     0.5988    0.3027    28.60
16   0.1412     0.5957    0.2735    36.95
17   0.1725     0.5929    0.2546    45.29
18   0.2015     0.5908    0.2437    52.25
19   0.2405     0.5896    0.2377    57.34
```

BLOCK: C-102   MODEL: RADFRAC

 INLETS - 14   STAGE 10
 OUTLETS - 15   STAGE 1
         16   STAGE 1
         17   STAGE 20
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

              *** MASS AND ENERGY BALANCE ***
                 IN   OUT   RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(KMOL/HR)   65.9665   65.9665   0.00000
    MASS(KG/HR)   5784.83   5784.83   -0.199470E-08
    ENTHALPY(CAL/SEC)   -0.206704E+07 -0.207431E+07   0.350385E-02

              *** CO2 EQUIVALENT SUMMARY ***
  FEED STREAMS CO2E   0.00000   KG/HR
  PRODUCT STREAMS CO2E   0.00000   KG/HR
  NET STREAMS CO2E PRODUCTION 0.00000   KG/HR
  UTILITIES CO2E PRODUCTION   0.00000   KG/HR
  TOTAL CO2E PRODUCTION   0.00000   KG/HR

```
                ***********************
                ****  INPUT DATA  ****
                ***********************


****  INPUT PARAMETERS  ****


 NUMBER OF STAGES                        20
 ALGORITHM OPTION                        NONIDEAL
 ABSORBER OPTION                         NO
 INITIALIZATION OPTION                   STANDARD
 HYDRAULIC PARAMETER CALCULATIONS             NO
 INSIDE LOOP CONVERGENCE METHOD               BROYDEN
 DESIGN SPECIFICATION METHOD             NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS       200
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS        10
 MAXIMUM NUMBER OF FLASH ITERATIONS           30
 FLASH TOLERANCE                    0.000100000
 OUTSIDE LOOP CONVERGENCE TOLERANCE           0.00100000


****  COL-SPECS  ****


 MOLAR REFLUX RATIO                      10.0000
 MASS VAPOR DIST / TOTAL DIST            0.00012958
 MASS DISTILLATE RATE       KG/HR        5,703.86


****   PROFILES  ****


 P-SPEC      STAGE  1  PRES, BAR         2.00000

 TEMP-EST     STAGE  1  TEMP, C          98.0000


                ******************
                ****  RESULTS  ****
                ******************


***   COMPONENT SPLIT FRACTIONS  ***


           OUTLET STREAMS
           --------------
        15        16        17
COMPONENT:
HYDROGEN   .54790    .45210    0.0000
WATER    .29235E-03  .99971    .62161E-07
ETHANOL   .24163E-03  .99976    .35165E-06
```

```
ETHYLACE  .11049E-03  .99789     .19989E-02
ACETA-01  .89315E-03  .99911     .90125E-11
N-BUT-02  .46122E-08  .19912E-03  .99980
2-BUT-01  .73642E-05  .13784     .86215
```

*** SUMMARY OF KEY RESULTS ***

```
TOP STAGE TEMPERATURE       C              38.9962
BOTTOM STAGE TEMPERATURE    C              128.444
TOP STAGE LIQUID FLOW       KMOL/HR         648.985
BOTTOM STAGE LIQUID FLOW    KMOL/HR           1.06801
TOP STAGE VAPOR FLOW        KMOL/HR          0.060399
BOILUP VAPOR FLOW           KMOL/HR         841.130
MOLAR REFLUX RATIO                          10.0000
MOLAR BOILUP RATIO                          787.569
CONDENSER DUTY (W/O SUBCOOL)  CAL/SEC     -1,995,670.
REBOILER DUTY          CAL/SEC        1,988,610.
```

**** MAXIMUM FINAL RELATIVE ERRORS ****

```
DEW POINT              0.22234E-02  STAGE= 1
BUBBLE POINT           0.30890E-01  STAGE= 1
COMPONENT MASS BALANCE      0.47654E-06  STAGE= 10 COMP=HYDROGEN
ENERGY BALANCE             0.14746E-02  STAGE= 1
```

**** PROFILES ****

NOTE REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
FROM THE STAGE INCLUDING ANY SIDE PRODUCT.

```
                   ENTHALPY
STAGE TEMPERATURE  PRESSURE      CAL/MOL        HEAT DUTY
    C        BAR      LIQUID    VAPOR     CAL/SEC

 1  38.996    2.0000   -0.11389E+06 -12474.    -.19957+07
 2  99.350    2.0000   -0.11119E+06 -0.10380E+06
 9  99.526    2.0000   -0.11082E+06 -0.10365E+06
10  99.579    2.0000   -0.11065E+06 -0.10354E+06
11  99.653    2.0000   -0.11042E+06 -0.10339E+06
12  99.754    2.0000   -0.11009E+06 -0.10315E+06
19  115.94    2.0000   -85119.    -87355.
20  128.44    2.0000   -77388.    -76616.    .19886+07
```

```
STAGE   FLOW RATE          FEED RATE        PRODUCT RATE
```

	KMOL/HR		KMOL/HR		KMOL/HR		
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	713.8	0.6040E-01				64.8381	.60399-01
2	896.9	713.9					
9	895.5	960.9					
10	981.8	960.4		65.9665			
11	980.8	980.7					
12	979.3	979.8					
19	842.2	879.2					
20	1.068	841.1			1.0680		

**** MASS FLOW PROFILES ****

STAGE	FLOW RATE		FEED RATE		PRODUCT RATE		
	KG/HR		KG/HR		KG/HR		
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	0.6279E+05	0.7391				5703.1167	0.7391
2	0.7897E+05	0.6279E+05					
9	0.7873E+05	0.8453E+05					
10	0.8626E+05	0.8444E+05		5784.8293			
11	0.8609E+05	0.8618E+05					
12	0.8583E+05	0.8600E+05					
19	0.6599E+05	0.7214E+05					
20	80.97	0.6591E+05			80.9735		

**** MOLE-X-PROFILE ****

STAGE	HYDROGEN	WATER	ETHANOL	ETHYLACE	ACETA-01
1	0.67720E-03	0.10709E-09	0.17525E-02	0.99650	0.13044E-05
2	0.87267E-06	0.45009E-10	0.75312E-03	0.99773	0.25590E-06
9	0.11806E-06	0.50492E-11	0.86651E-04	0.98701	0.21119E-07
10	0.11835E-06	0.50217E-11	0.86475E-04	0.98235	0.21150E-07
11	0.13889E-09	0.21163E-11	0.37775E-04	0.97590	0.41546E-08
12	0.16361E-12	0.89321E-12	0.16622E-04	0.96649	0.81674E-09
19	0.54759E-33	0.16321E-14	0.87355E-07	0.30246	0.62324E-14
20	0.56576E-36	0.40423E-15	0.37422E-07	0.12118	0.71432E-15

**** MOLE-X-PROFILE ****

STAGE	N-BUT-02	2-BUT-01
1	0.15518E-05	0.10686E-02
2	0.32888E-05	0.15127E-02
9	0.45062E-03	0.12454E-01
10	0.93258E-03	0.16633E-01
11	0.94714E-03	0.23120E-01
12	0.10070E-02	0.32482E-01

```
19  0.28231      0.41523
20  0.47303      0.40579


          ****  MOLE-Y-PROFILE   ****
STAGE   HYDROGEN    WATER     ETHANOL    ETHYLACE   ACETA-01
 1  0.88104      0.33618E-10 0.45470E-03 0.11844     0.12518E-05
 2  0.75169E-03  0.10708E-09 0.17524E-02 0.99642     0.13044E-05
 9  0.10118E-03  0.12013E-10 0.20029E-03 0.99072     0.10777E-06
10  0.10124E-03  0.11940E-10 0.19914E-03 0.98759     0.10783E-06
11  0.11848E-06  0.50272E-11 0.86569E-04 0.98329     0.21173E-07
12  0.13904E-09  0.21186E-11 0.37817E-04 0.97683     0.41591E-08
19  0.51060E-30  0.49832E-14 0.18454E-06 0.56697     0.43640E-13
20  0.54828E-33  0.16337E-14 0.87418E-07 0.30269     0.62394E-14


          ****  MOLE-Y-PROFILE   ****
STAGE    N-BUT-02   2-BUT-01
 1  0.38586E-07 0.61290E-04
 2  0.15517E-05 0.10686E-02
 9  0.20582E-03 0.87731E-02
10  0.42027E-03 0.11684E-01
11  0.41847E-03 0.16209E-01
12  0.43253E-03 0.22702E-01
19  0.10299      0.33004
20  0.28207      0.41524


          ****  K-VALUES      ****
STAGE   HYDROGEN    WATER      ETHANOL    ETHYLACE   ACETA-01
 1  1347.0    0.31361     0.25859     0.11859     0.96443
 2  861.32    2.3791      2.3269      0.99869     5.0973
 9  857.09    2.3792      2.3117      1.0038      5.1032
10  855.46    2.3777      2.3031      1.0053      5.0985
11  853.16    2.3756      2.2920      1.0076      5.0967
12  849.93    2.3721      2.2756      1.0107      5.0927
19  932.90    3.0532      2.1119      1.8743      7.0038
20  969.74    4.0415      2.3344      2.4973      8.7357


          ****  K-VALUES      ****
STAGE    N-BUT-02   2-BUT-01
 1  0.24490E-01 0.56818E-01
 2  0.47184      0.70641
 9  0.45687      0.70446
10  0.45080      0.70248
11  0.44201      0.70111
12  0.42975      0.69892
```

```
19   0.36465      0.79500
20   0.59615      1.0233


             ****  MASS-X-PROFILE   ****
STAGE   HYDROGEN    WATER      ETHANOL    ETHYLACE    ACETA-01
 1   0.15520E-04  0.21933E-10  0.91789E-03  0.99816    0.65328E-06
 2   0.19979E-07  0.92087E-11  0.39403E-03  0.99833    0.12803E-06
 9   0.27069E-08  0.10346E-11  0.45403E-04  0.98908    0.10582E-07
10   0.27156E-08  0.10297E-11  0.45344E-04  0.98513    0.10605E-07
11   0.31900E-11  0.43439E-12  0.19828E-04  0.97966    0.20853E-08
12   0.37634E-14  0.18361E-12  0.87376E-05  0.97167    0.41056E-09
19   0.14089E-34  0.37526E-15  0.51362E-07  0.34012    0.35041E-14
20   0.15043E-37  0.96052E-16  0.22739E-07  0.14082    0.41505E-15


             ****  MASS-X-PROFILE   ****
STAGE    N-BUT-02    2-BUT-01
 1   0.13077E-05  0.90054E-03
 2   0.27685E-05  0.12734E-02
 9   0.37989E-03  0.10499E-01
10   0.78680E-03  0.14033E-01
11   0.79989E-03  0.19525E-01
12   0.85173E-03  0.27473E-01
19   0.26707      0.39281
20   0.46246      0.39672


             ****  MASS-Y-PROFILE   ****
STAGE   HYDROGEN    WATER      ETHANOL    ETHYLACE    ACETA-01
 1   0.14514      0.49492E-10  0.17118E-02  0.85278     0.45062E-05
 2   0.17229E-04  0.21933E-10  0.91790E-03  0.99816     0.65333E-06
 9   0.23188E-05  0.24603E-11  0.10490E-03  0.99233     0.53973E-07
10   0.23212E-05  0.24465E-11  0.10435E-03  0.98969     0.54030E-07
11   0.27181E-08  0.10307E-11  0.45387E-04  0.98593     0.10615E-07
12   0.31930E-11  0.43480E-12  0.19847E-04  0.98044     0.20873E-08
19   0.12545E-31  0.10941E-14  0.10361E-06  0.60881     0.23430E-13
20   0.14106E-34  0.37561E-15  0.51398E-07  0.34036     0.35079E-14


             ****  MASS-Y-PROFILE   ****
STAGE    N-BUT-02    2-BUT-01
 1   0.23372E-06  0.37124E-03
 2   0.13077E-05  0.90054E-03
 9   0.17343E-03  0.73927E-02
10   0.35432E-03  0.98507E-02
11   0.35300E-03  0.13673E-01
12   0.36523E-03  0.19170E-01
```

```
19   0.93040E-01   0.29815
20   0.26683       0.39281
```

```
        *****************************
        ***** HYDRAULIC PARAMETERS *****
        *****************************
```

  *** DEFINITIONS ***

  MARANGONI INDEX = SIGMA - SIGMATO
  FLOW PARAM = (ML/MV)*SQRT(RHOV/RHOL)
  QR = QV*SQRT(RHOV/(RHOL-RHOV))
  F FACTOR = QV*SQRT(RHOV)
   WHERE:
   SIGMA IS THE SURFACE TENSION OF LIQUID FROM THE STAGE
   SIGMATO IS THE SURFACE TENSION OF LIQUID TO THE STAGE
   ML IS THE MASS FLOW OF LIQUID FROM THE STAGE
   MV IS THE MASS FLOW OF VAPOR TO THE STAGE
   RHOL IS THE MASS DENSITY OF LIQUID FROM THE STAGE
   RHOV IS THE MASS DENSITY OF VAPOR TO THE STAGE
   QV IS THE VOLUMETRIC FLOW RATE OF VAPOR TO THE STAGE

	TEMPERATURE C	
STAGE	LIQUID FROM	VAPOR TO
1	38.996	99.350
2	99.350	99.398
9	99.526	99.579
10	99.579	99.653
11	99.653	99.754
12	99.754	99.904
19	115.94	128.44
20	128.44	128.44

	MASS FLOW KG/HR		VOLUME FLOW L/MIN		MOLECULAR WEIGHT	
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO
1	62787.	62788.	1190.6	0.18425E+06	87.959	87.953
2	78974.	84678.	1648.3	0.24826E+06	88.053	88.042
9	78734.	84438.	1645.4	0.24802E+06	87.922	87.920
10	86258.	86177.	1803.6	0.25332E+06	87.857	87.870
11	86085.	86004.	1801.3	0.25314E+06	87.768	87.781
12	85826.	85745.	1797.8	0.25286E+06	87.637	87.650
19	65988.	65907.	1511.9	0.23404E+06	78.352	78.356

20 80.974   0.0000   1.9276   0.0000   75.817

| | DENSITY | | VISCOSITY | | SURFACE TENSION |
| | GM/CC | | CP | | DYNE/CM |
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM
1	0.87896	0.56797E-02	0.36857	0.95485E-02	21.157
2	0.79855	0.56848E-02	0.20556	0.95467E-02	14.045
9	0.79750	0.56741E-02	0.20661	0.95473E-02	14.035
10	0.79708	0.56698E-02	0.20712	0.95475E-02	14.034
11	0.79650	0.56625E-02	0.20778	0.95481E-02	14.031
12	0.79566	0.56518E-02	0.20876	0.95492E-02	14.028
19	0.72742	0.46934E-02	0.26276	0.99306E-02	13.829
20	0.70013		0.24725		13.470

| | MARANGONI INDEX | FLOW PARAM | QR | REDUCED F-FACTOR |
STAGE	DYNE/CM		L/MIN	(GM-L)**.5/MIN
1		0.80385E-01	14859.	0.43910E+06
2	-7.1120	0.78690E-01	21021.	0.59192E+06
9	-.65137E-03	0.78652E-01	20995.	0.59080E+06
10	-.36636	0.84419E-01	21441.	0.60319E+06
11	-.29892E-02	0.84395E-01	21420.	0.60237E+06
12	-.34278E-02	0.84360E-01	21387.	0.60113E+06
19	-.15010	0.80423E-01	18860.	0.50704E+06
20	-.35861		0.0000	0.0000

```
        **********************************
        ***** TRAY SIZING CALCULATIONS *****
        **********************************
   ********************
   *** SECTION  1 ***
   ********************
```

STARTING STAGE NUMBER   2
ENDING STAGE NUMBER   9
FLOODING CALCULATION METHOD   GLITSCH6

DESIGN PARAMETERS

PEAK CAPACITY FACTOR   1.00000
SYSTEM FOAMING FACTOR   1.00000
FLOODING FACTOR   0.80000
MINIMUM COLUMN DIAMETER   METER   0.30480
MINIMUM DC AREA/COLUMN AREA   0.100000
HOLE AREA/ACTIVE AREA   0.100000

TRAY SPECIFICATIONS

TRAY TYPE   SIEVE
NUMBER OF PASSES   1
TRAY SPACING   METER   0.60960

        ***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****

STAGE WITH MAXIMUM DIAMETER   3
COLUMN DIAMETER   METER   2.44142
DC AREA/COLUMN AREA   0.100000
DOWNCOMER VELOCITY   M/SEC   0.058705
FLOW PATH LENGTH   METER   1.67738
SIDE DOWNCOMER WIDTH   METER   0.38202
SIDE WEIR LENGTH   METER   1.77397
CENTER DOWNCOMER WIDTH   METER   0.0
CENTER WEIR LENGTH   METER   MISSING
OFF-CENTER DOWNCOMER WIDTH   METER   0.0
OFF-CENTER SHORT WEIR LENGTH   METER   MISSING
OFF-CENTER LONG WEIR LENGTH   METER   MISSING
TRAY CENTER TO OCDC CENTER   METER   0.0

        **** SIZING PROFILES ****

  STAGE   DIAMETER   TOTAL AREA ACTIVE AREA SIDE DC AREA
        METER   SQM   SQM   SQM
    2   2.4414   4.6814   3.7451   0.46814
    3   2.4414   4.6814   3.7451   0.46814
    4   2.4414   4.6814   3.7451   0.46814
    5   2.4414   4.6814   3.7451   0.46814
    6   2.4414   4.6814   3.7451   0.46814
    7   2.4414   4.6814   3.7451   0.46814
    8   2.4414   4.6814   3.7451   0.46814
    9   2.4414   4.6814   3.7451   0.46814

        **** ADDITIONAL SIZING PROFILES ****

    FLOODING   DC BACKUP/
  STAGE FACTOR   PRES. DROP DC BACKUP (TSPC+WHT)
          BAR   METER
  2   79.98   0.9405E-02 0.2866   43.40
  3   80.00   0.9408E-02 0.2867   43.42
  4   80.00   0.9406E-02 0.2867   43.42
  5   79.99   0.9404E-02 0.2867   43.41

```
6   79.97   0.9400E-02 0.2866    43.40
7   79.95   0.9395E-02 0.2865    43.39
8   79.92   0.9388E-02 0.2864    43.36
9   79.87   0.9377E-02 0.2862    43.33


       HEIGHT     DC REL     TR LIQ REL  FRA APPR TO
STAGE OVER WEIR  FROTH DENS  FROTH DENS  SYS LIMIT
     METER
 2   0.1509   0.6075   0.1810   54.65
 3   0.1510   0.6075   0.1809   54.67
 4   0.1510   0.6075   0.1810   54.66
 5   0.1509   0.6075   0.1810   54.66
 6   0.1509   0.6075   0.1810   54.64
 7   0.1508   0.6075   0.1810   54.63
 8   0.1507   0.6075   0.1811   54.60
 9   0.1506   0.6075   0.1811   54.57


******************
*** SECTION  2 ***
******************


STARTING STAGE NUMBER                      10
ENDING STAGE NUMBER                        19
FLOODING CALCULATION METHOD            GLITSCH6


DESIGN PARAMETERS
-----------------
PEAK CAPACITY FACTOR                 1.00000
SYSTEM FOAMING FACTOR                  1.00000
FLOODING FACTOR                 0.80000
MINIMUM COLUMN DIAMETER     METER          0.30480
MINIMUM DC AREA/COLUMN AREA              0.100000
HOLE AREA/ACTIVE AREA              0.100000


TRAY SPECIFICATIONS
-------------------
TRAY TYPE                      SIEVE
NUMBER OF PASSES                    1
TRAY SPACING         METER         0.60960


       ***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****


STAGE WITH MAXIMUM DIAMETER                10
COLUMN DIAMETER         METER         2.48218
```

```
DC AREA/COLUMN AREA                       0.100000
DOWNCOMER VELOCITY        M/SEC           0.062120
FLOW PATH LENGTH         METER          1.70538
SIDE DOWNCOMER WIDTH        METER          0.38840
SIDE WEIR LENGTH          METER          1.80358
CENTER DOWNCOMER WIDTH      METER             0.0
CENTER WEIR LENGTH          METER          MISSING
OFF-CENTER DOWNCOMER WIDTH     METER          0.0
OFF-CENTER SHORT WEIR LENGTH   METER          MISSING
OFF-CENTER LONG WEIR LENGTH    METER          MISSING
TRAY CENTER TO OCDC CENTER    METER          0.0
```

**** SIZING PROFILES ****

STAGE	DIAMETER	TOTAL AREA	ACTIVE AREA	SIDE DC AREA
	METER	SQM	SQM	SQM
10	2.4822	4.8390	3.8712	0.48390
11	2.4822	4.8390	3.8712	0.48390
12	2.4822	4.8390	3.8712	0.48390
13	2.4822	4.8390	3.8712	0.48390
14	2.4822	4.8390	3.8712	0.48390
15	2.4822	4.8390	3.8712	0.48390
16	2.4822	4.8390	3.8712	0.48390
17	2.4822	4.8390	3.8712	0.48390
18	2.4822	4.8390	3.8712	0.48390
19	2.4822	4.8390	3.8712	0.48390

**** ADDITIONAL SIZING PROFILES ****

	FLOODING		DC BACKUP/	
STAGE	FACTOR	PRES. DROP	DC BACKUP	(TSPC+WHT)
		BAR	METER	
10	80.00	0.9321E-02	0.2945	44.59
11	79.92	0.9302E-02	0.2941	44.54
12	79.79	0.9274E-02	0.2936	44.45
13	79.59	0.9232E-02	0.2927	44.32
14	79.28	0.9167E-02	0.2914	44.12
15	78.77	0.9064E-02	0.2892	43.80
16	77.84	0.8883E-02	0.2853	43.20
17	75.89	0.8526E-02	0.2772	41.98
18	72.16	0.7859E-02	0.2623	39.73
19	69.70	0.7264E-02	0.2529	38.29

```
HEIGHT    DC REL     TR LIQ REL  FRA APPR TO
```

```
STAGE OVER WEIR   FROTH DENS  FROTH DENS  SYS LIMIT
     METER
 10   0.1591     0.6075      0.1821      53.93
 11   0.1588     0.6075      0.1823      53.86
 12   0.1584     0.6075      0.1824      53.77
 13   0.1578     0.6075      0.1827      53.62
 14   0.1569     0.6075      0.1831      53.40
 15   0.1553     0.6074      0.1838      53.02
 16   0.1526     0.6074      0.1851      52.35
 17   0.1468     0.6072      0.1878      50.95
 18   0.1358     0.6069      0.1939      48.25
 19   0.1275     0.6062      0.1997      46.36
```

BLOCK: E-102   MODEL: HEATX

 HOT SIDE:

 INLET STREAM: STEAMIN
 OUTLET STREAM: STEAMOUT
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1
 COLD SIDE:

 INLET STREAM: 10
 OUTLET STREAM: 11
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

            *** MASS AND ENERGY BALANCE ***
                   IN   OUT   RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(KMOL/HR)   98.1805   98.1805   0.00000
   MASS(KG/HR   )   6239.25   6239.25   0.00000
   ENTHALPY(CAL/SEC)   -0.221674E+07 -0.221674E+07   0.00000

            *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION 0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

            *** INPUT DATA ***

356

FLASH SPECS FOR HOT SIDE:
TWO   PHASE   FLASH
MAXIMUM NO. ITERATIONS   30
CONVERGENCE TOLERANCE   0.000100000

FLASH SPECS FOR COLD SIDE:
TWO   PHASE   FLASH
MAXIMUM NO. ITERATIONS   30
CONVERGENCE TOLERANCE   0.000100000

FLOW DIRECTION AND SPECIFICATION:
 COUNTERCURRENT   HEAT EXCHANGER
 SPECIFIED COLD OUTLET TEMP
 SPECIFIED VALUE   C   150.0000
 LMTD CORRECTION FACTOR   1.00000

PRESSURE SPECIFICATION:
 HOT SIDE PRESSURE DROP   BAR   0.0000
 COLD SIDE PRESSURE DROP   BAR   0.0000

HEAT TRANSFER COEFFICIENT SPECIFICATION:
 HOT LIQUID   COLD LIQUID   CAL/SEC-SQCM-K   0.0203
 HOT 2-PHASE COLD LIQUID   CAL/SEC-SQCM-K   0.0203
 HOT VAPOR   COLD LIQUID   CAL/SEC-SQCM-K   0.0203
 HOT LIQUID   COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
 HOT 2-PHASE COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
 HOT VAPOR   COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
 HOT LIQUID   COLD VAPOR   CAL/SEC-SQCM-K   0.0203
 HOT 2-PHASE COLD VAPOR   CAL/SEC-SQCM-K   0.0203
 HOT VAPOR   COLD VAPOR   CAL/SEC-SQCM-K   0.0203

            *** OVERALL RESULTS ***

STREAMS:

          | |
STEAMIN ----->| HOT |-----> STEAMOUT
T= 1.8558D+02 | | T= 1.1828D+02
P= 1.1355D+01 | | P= 1.1355D+01
V= 1.0000D+00 | | V= 0.0000D+00
          | |
11   <-----| COLD |<----- 10
T= 1.5000D+02 | | T= 1.1671D+02
P= 4.0000D+00 | | P= 4.0000D+00

```
V= 1.0000D+00 |                    |   V= 8.1811D-01
         ------------------------------------
DUTY AND AREA:
  CALCULATED HEAT DUTY      CAL/SEC        49626.5247
  CALCULATED (REQUIRED) AREA   SQM           5.6507
  ACTUAL EXCHANGER AREA      SQM            5.6507
  PER CENT OVER-DESIGN                 0.0000


HEAT TRANSFER COEFFICIENT:
  AVERAGE COEFFICIENT (DIRTY)  CAL/SEC-SQCM-K      0.0203
  UA (DIRTY)          CAL/SEC-K      1147.1987


LOG-MEAN TEMPERATURE DIFFERENCE:
  LMTD CORRECTION FACTOR              1.0000
  LMTD (CORRECTED)      C         43.2589
  NUMBER OF SHELLS IN SERIES           1


PRESSURE DROP:
  HOTSIDE, TOTAL        BAR         0.0000
  COLDSIDE, TOTAL       BAR         0.0000

           ***  ZONE RESULTS  ***

TEMPERATURE LEAVING EACH ZONE:


               HOT
    ----------------------------------------------------------
    |        |        |         |
HOT IN |    COND   |    COND   |   LIQ   | HOT OUT
------> |        |        |       |----->
185.6 |      185.6|      185.6|         | 118.3
    |        |        |       |
COLDOUT |    VAP   |    BOIL   |   BOIL   | COLDIN
<------ |        |        |       |<------
150.0 |      118.5|      117.2|         | 116.7
    |        |        |       |
    ----------------------------------------------------------
           COLD


ZONE HEAT TRANSFER AND AREA:

ZONE    HEAT DUTY    AREA    LMTD    AVERAGE U    UA
      CAL/SEC    SQM    C    CAL/SEC-SQCM-K CAL/SEC-K
  1   20325.372    2.0152   49.6805   0.0203      409.1218
```

```
    2    21983.247      1.5989    67.7227   0.0203      324.6069
    3     7317.906      2.0366    17.6988   0.0203      413.4701
```

HEATX COLD-TQCU E-102   TQCURV INLET

 PRESSURE PROFILE: CONSTANT2
 PRESSURE DROP: 0.0   BAR
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

```
------------------------------------------------------
! DUTY    ! PRES    ! TEMP    ! VFRAC   !
!       !       !       !       !
!       !       !       !       !
!       !       !       !       !
! CAL/SEC  ! BAR    ! C    !      !
!       !       !       !       !
!===========!===========!===========!===========!
!   0.0  !  4.0000 ! 150.0000 !  1.0000 !
! 2363.1678 !  4.0000 ! 146.4223 !  1.0000 !
! 4726.3357 !  4.0000 ! 142.8228 !  1.0000 !
! 7089.5035 !  4.0000 ! 139.2009 !  1.0000 !
! 9452.6714 !  4.0000 ! 135.5563 !  1.0000 !
!-----------+-----------+-----------+-----------!
! 1.1816+04 !  4.0000 ! 131.8886 !  1.0000 !
! 1.4179+04 !  4.0000 ! 128.1971 !  1.0000 !
! 1.6542+04 !  4.0000 ! 124.4816 !  1.0000 !
! 1.8905+04 !  4.0000 ! 120.7414 !  1.0000 !
! 2.0325+04 !  4.0000 ! 118.4819 ! DEW>1.0000 !
!-----------+-----------+-----------+-----------!
! 2.1269+04 !  4.0000 ! 118.4351 !  0.9941 !
! 2.3632+04 !  4.0000 ! 118.3153 !  0.9792 !
! 2.5995+04 !  4.0000 ! 118.1918 !  0.9644 !
! 2.8358+04 !  4.0000 ! 118.0644 !  0.9497 !
! 3.0721+04 !  4.0000 ! 117.9329 !  0.9349 !
!-----------+-----------+-----------+-----------!
! 3.3084+04 !  4.0000 ! 117.7971 !  0.9202 !
! 3.5448+04 !  4.0000 ! 117.6568 !  0.9055 !
! 3.7811+04 !  4.0000 ! 117.5118 !  0.8909 !
! 4.0174+04 !  4.0000 ! 117.3620 !  0.8762 !
! 4.2309+04 !  4.0000 ! 117.2222 !  0.8631 !
!-----------+-----------+-----------+-----------!
! 4.2537+04 !  4.0000 ! 117.2070 !  0.8616 !
! 4.4900+04 !  4.0000 ! 117.0466 !  0.8471 !
```

```
! 4.7263+04 !   4.0000 ! 116.8805 !   0.8326 !
! 4.9627+04 !   4.0000 ! 116.7085 !   0.8181 !
-----------------------------------------------------

HEATX HOT-TQCUR E-102   TQCURV INLET
--------------------------------------
  PRESSURE PROFILE:    CONSTANT2
  PRESSURE DROP:       0.0      BAR
  PROPERTY OPTION SET:  NRTL    RENON (NRTL) / IDEAL GAS
  HENRY-COMPS ID:       HC-1
-----------------------------------------------------
! DUTY    ! PRES    ! TEMP    ! VFRAC   !
!        !        !        !        !
!        !        !        !        !
!        !        !        !        !
! CAL/SEC  ! BAR     ! C      !        !
!        !        !        !        !
!===========!===========!===========!===========!
!   0.0   ! 11.3554 ! 185.5767 !   1.0000 !
! 2363.1678 !  11.3554 ! 185.5767 !   0.9441 !
! 4726.3357 !  11.3554 ! 185.5767 !   0.8883 !
! 7089.5035 !  11.3554 ! 185.5767 !   0.8324 !
! 9452.6714 !  11.3554 ! 185.5767 !   0.7766 !
!-----------+-----------+-----------+-----------!
! 1.1816+04 !  11.3554 ! 185.5767 !   0.7207 !
! 1.4179+04 !  11.3554 ! 185.5767 !   0.6649 !
! 1.6542+04 !  11.3554 ! 185.5767 !   0.6090 !
! 1.8905+04 !  11.3554 ! 185.5767 !   0.5532 !
! 2.0325+04 !  11.3554 ! 185.5767 !   0.5196 !
!-----------+-----------+-----------+-----------!
! 2.1269+04 !  11.3554 ! 185.5767 !   0.4973 !
! 2.3632+04 !  11.3554 ! 185.5767 !   0.4414 !
! 2.5995+04 !  11.3554 ! 185.5767 !   0.3856 !
! 2.8358+04 !  11.3554 ! 185.5767 !   0.3297 !
! 3.0721+04 !  11.3554 ! 185.5767 !   0.2739 !
!-----------+-----------+-----------+-----------!
! 3.3084+04 !  11.3554 ! 185.5767 !   0.2180 !
! 3.5448+04 !  11.3554 ! 185.5767 !   0.1622 !
! 3.7811+04 !  11.3554 ! 185.5767 !   0.1063 !
! 4.0174+04 !  11.3554 ! 185.5767 ! 5.0457-02 !
! 4.2309+04 !  11.3554 ! 185.5767 ! BUB>0.0   !
!-----------+-----------+-----------+-----------!
! 4.2537+04 !  11.3554 ! 183.6517 !   0.0   !
! 4.4900+04 !  11.3554 ! 163.0686 !   0.0   !
! 4.7263+04 !  11.3554 ! 141.2711 !   0.0   !
```

! 4.9627+04 ! 11.3554 ! 118.2789 !   0.0   !

BLOCK: E-103   MODEL: HEATX

 HOT SIDE:

 INLET STREAM: 12
 OUTLET VAPOR   STREAM: 13
 OUTLET LIQUID   STREAM: 14
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1
 COLD SIDE:

 INLET STREAM: CH2OIN
 OUTLET STREAM: CH2OOUT
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1
             *** MASS AND ENERGY BALANCE ***
                 IN   OUT   RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(KMOL/HR)   2655.00   2655.00   0.00000
   MASS(KG/HR   )   52319.5   52319.5   0.00000
   ENTHALPY(CAL/SEC)   -0.506343E+08 -0.506343E+08   0.397291E-14

          *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION   0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

            *** INPUT DATA ***

 FLASH SPECS FOR HOT SIDE:
 TWO   PHASE   FLASH
 MAXIMUM NO. ITERATIONS   30
 CONVERGENCE TOLERANCE   0.000100000

 FLASH SPECS FOR COLD SIDE:
 TWO   PHASE   FLASH
 MAXIMUM NO. ITERATIONS   30
 CONVERGENCE TOLERANCE   0.000100000

 FLOW DIRECTION AND SPECIFICATION:

COUNTERCURRENT   HEAT EXCHANGER
SPECIFIED HOT OUTLET TEMP
SPECIFIED VALUE   C   50.0000
LMTD CORRECTION FACTOR   1.00000

PRESSURE SPECIFICATION:
  HOT SIDE PRESSURE DROP   BAR   0.0000
  COLD SIDE PRESSURE DROP   BAR   0.0000

HEAT TRANSFER COEFFICIENT SPECIFICATION:
  HOT LIQUID   COLD LIQUID   CAL/SEC-SQCM-K   0.0203
  HOT 2-PHASE   COLD LIQUID   CAL/SEC-SQCM-K   0.0203
  HOT VAPOR   COLD LIQUID   CAL/SEC-SQCM-K   0.0203
  HOT LIQUID   COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
  HOT 2-PHASE   COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
  HOT VAPOR   COLD 2-PHASE   CAL/SEC-SQCM-K   0.0203
  HOT LIQUID   COLD VAPOR   CAL/SEC-SQCM-K   0.0203
  HOT 2-PHASE   COLD VAPOR   CAL/SEC-SQCM-K   0.0203
  HOT VAPOR   COLD VAPOR   CAL/SEC-SQCM-K   0.0203

          *** OVERALL RESULTS ***

STREAMS:

          | |
12   ----->| HOT |-----> 13
          | |-----> 14
T= 1.5650D+02 | | T= 5.0000D+01
P= 4.0000D+00 | | P= 4.0000D+00
V= 1.0000D+00 | | V= 1.6925D-01
          | |
CH2OOUT <-----| COLD |<----- CH2OIN
T= 4.8873D+01 | | T= 3.2222D+01
P= 1.0000D+00 | | P= 1.0000D+00
V= 0.0000D+00 | | V= 0.0000D+00

DUTY AND AREA:
  CALCULATED HEAT DUTY   CAL/SEC   214424.7275
  CALCULATED (REQUIRED) AREA   SQM   25.4508
  ACTUAL EXCHANGER AREA   SQM   25.4508
  PER CENT OVER-DESIGN   0.0000

HEAT TRANSFER COEFFICIENT:

AVERAGE COEFFICIENT (DIRTY)   CAL/SEC-SQCM-K   0.0203
UA (DIRTY)   CAL/SEC-K   5167.0025

LOG-MEAN TEMPERATURE DIFFERENCE:
  LMTD CORRECTION FACTOR   1.0000
  LMTD (CORRECTED)   C   41.4989
  NUMBER OF SHELLS IN SERIES   1

PRESSURE DROP:
  HOTSIDE, TOTAL   BAR   0.0000
  COLDSIDE, TOTAL   BAR   0.0000

                  *** ZONE RESULTS ***

TEMPERATURE LEAVING EACH ZONE:

                        HOT

         | | |
        HOT IN | VAP | COND | HOT OUT
        ------> | | |------>
         156.5 | 119.4| | 50.0
         | | |
        COLDOUT | LIQ | LIQ | COLDIN
        <------ | | |<------
         48.9 | 47.0| | 32.2
         | | |

                        COLD

  ZONE HEAT TRANSFER AND AREA:

  ZONE   HEAT DUTY   AREA   LMTD   AVERAGE U   UA
          CAL/SEC   SQM   C   CAL/SEC-SQCM-K CAL/SEC-K
   1   24066.509   1.3346   88.8220   0.0203   270.9522
   2   190358.218   24.1162   38.8800   0.0203   4896.0503

HEATX COLD-TQCU E-103   TQCURV INLET

  PRESSURE PROFILE: CONSTANT2
  PRESSURE DROP: 0.0   BAR
  PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
  HENRY-COMPS ID: HC-1

```
------------------------------------------------------
! DUTY     ! PRES    ! TEMP    ! VFRAC    !
!      !       !       !       !
!      !       !       !       !
!      !       !       !       !
! CAL/SEC  ! BAR    ! C     !       !
!      !       !       !       !
!==========!==========!==========!==========!
!   0.0  !  1.0000 !  48.8731 !   0.0  !
! 1.0211+04 !   1.0000 !  48.0871 !   0.0  !
! 2.0421+04 !   1.0000 !  47.3003 !   0.0  !
! 2.4067+04 !   1.0000 !  47.0193 !   0.0  !
! 3.0632+04 !   1.0000 !  46.5129 !   0.0  !
!-----------+-----------+-----------+-----------!
! 4.0843+04 !   1.0000 !  45.7247 !   0.0  !
! 5.1054+04 !   1.0000 !  44.9358 !   0.0  !
! 6.1264+04 !   1.0000 !  44.1463 !   0.0  !
! 7.1475+04 !   1.0000 !  43.3560 !   0.0  !
! 8.1686+04 !   1.0000 !  42.5650 !   0.0  !
!-----------+-----------+-----------+-----------!
! 9.1896+04 !   1.0000 !  41.7734 !   0.0  !
! 1.0211+05 !   1.0000 !  40.9811 !   0.0  !
! 1.1232+05 !   1.0000 !  40.1881 !   0.0  !
! 1.2253+05 !   1.0000 !  39.3945 !   0.0  !
! 1.3274+05 !   1.0000 !  38.6001 !   0.0  !
!-----------+-----------+-----------+-----------!
! 1.4295+05 !   1.0000 !  37.8051 !   0.0  !
! 1.5316+05 !   1.0000 !  37.0095 !   0.0  !
! 1.6337+05 !   1.0000 !  36.2132 !   0.0  !
! 1.7358+05 !   1.0000 !  35.4163 !   0.0  !
! 1.8379+05 !   1.0000 !  34.6187 !   0.0  !
!-----------+-----------+-----------+-----------!
! 1.9400+05 !   1.0000 !  33.8205 !   0.0  !
! 2.0421+05 !   1.0000 !  33.0217 !   0.0  !
! 2.1442+05 !   1.0000 !  32.2222 !   0.0  !
------------------------------------------------------
```

HEATX HOT-TQCUR E-103   TQCURV INLET

 PRESSURE PROFILE: CONSTANT2
 PRESSURE DROP: 0.0   BAR
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

```
------------------------------------------------------
! DUTY    ! PRES    ! TEMP    ! VFRAC    !
!         !         !         !          !
!         !         !         !          !
!         !         !         !          !
! CAL/SEC ! BAR     ! C       !          !
!         !         !         !          !
!==========!==========!==========!==========!
!   0.0   !  4.0000 ! 156.5000 !   1.0000 !
! 1.0211+04 !  4.0000 ! 141.0356 !   1.0000 !
! 2.0421+04 !  4.0000 ! 125.1474 !   1.0000 !
! 2.4067+04 !  4.0000 ! 119.3658 ! DEW>1.0000 !
! 3.0632+04 !  4.0000 ! 119.0382 !   0.9585 !
!-----------+-----------+-----------+-----------!
! 4.0843+04 !  4.0000 ! 118.4714 !   0.8942 !
! 5.1054+04 !  4.0000 ! 117.8202 !   0.8305 !
! 6.1264+04 !  4.0000 ! 117.0643 !   0.7675 !
! 7.1475+04 !  4.0000 ! 116.1772 !   0.7054 !
! 8.1686+04 !  4.0000 ! 115.1242 !   0.6444 !
!-----------+-----------+-----------+-----------!
! 9.1896+04 !  4.0000 ! 113.8596 !   0.5849 !
! 1.0211+05 !  4.0000 ! 112.3232 !   0.5271 !
! 1.1232+05 !  4.0000 ! 110.4365 !   0.4717 !
! 1.2253+05 !  4.0000 ! 108.0990 !   0.4192 !
! 1.3274+05 !  4.0000 ! 105.1884 !   0.3705 !
!-----------+-----------+-----------+-----------!
! 1.4295+05 !  4.0000 ! 101.5670 !   0.3264 !
! 1.5316+05 !  4.0000 !  97.0985 !   0.2876 !
! 1.6337+05 !  4.0000 !  91.6743 !   0.2547 !
! 1.7358+05 !  4.0000 !  85.2373 !   0.2278 !
! 1.8379+05 !  4.0000 !  77.7906 !   0.2065 !
!-----------+-----------+-----------+-----------!
! 1.9400+05 !  4.0000 !  69.3844 !   0.1901 !
! 2.0421+05 !  4.0000 !  60.0939 !   0.1780 !
! 2.1442+05 !  4.0000 !  50.0000 !   0.1692 !
------------------------------------------------------
```

BLOCK: MIXER   MODEL: MIXER

 INLET STREAMS: 9   8
 OUTLET STREAM: 10
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

```
             ***  MASS AND ENERGY BALANCE  ***
                 IN        OUT      RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(KMOL/HR )      80.4178      80.4178      0.00000
    MASS(KG/HR  )      5919.25      5919.25      0.00000
    ENTHALPY(CAL/SEC )   -0.193822E+07  -0.193822E+07   0.00000


             ***  CO2 EQUIVALENT SUMMARY ***
  FEED STREAMS CO2E        0.00000    KG/HR
  PRODUCT STREAMS CO2E        0.00000    KG/HR
  NET STREAMS CO2E PRODUCTION  0.00000    KG/HR
  UTILITIES CO2E PRODUCTION    0.00000    KG/HR
  TOTAL CO2E PRODUCTION        0.00000    KG/HR


             ***  INPUT DATA  ***
  TWO    PHASE    FLASH
  MAXIMUM NO. ITERATIONS                30
  CONVERGENCE TOLERANCE                 0.000100000
  OUTLET PRESSURE   BAR              4.00000


BLOCK:  P-100    MODEL: PUMP
---------------------------
 INLET STREAM:        1
 OUTLET STREAM:       2
 PROPERTY OPTION SET:   NRTL      RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID:      HC-1


             ***  MASS AND ENERGY BALANCE  ***
                 IN        OUT      RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(KMOL/HR )      135.177      135.177      0.00000
    MASS(KG/HR  )      6227.47      6227.47      0.00000
    ENTHALPY(CAL/SEC )   -0.247786E+07  -0.247527E+07  -0.104471E-02


             ***  CO2 EQUIVALENT SUMMARY ***
  FEED STREAMS CO2E        0.00000    KG/HR
  PRODUCT STREAMS CO2E        0.00000    KG/HR
  NET STREAMS CO2E PRODUCTION  0.00000    KG/HR
  UTILITIES CO2E PRODUCTION    0.00000    KG/HR
  TOTAL CO2E PRODUCTION        0.00000    KG/HR


             ***  INPUT DATA  ***
  OUTLET PRESSURE  BAR                20.0000
  DRIVER EFFICIENCY                   1.00000
```

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS   30
TOLERANCE   0.000100000

            *** RESULTS ***
 VOLUMETRIC FLOW RATE L/MIN   131.906
 PRESSURE CHANGE BAR   19.0000
 NPSH AVAILABLE   M-KGF/KG   11.1668
 FLUID POWER KW   4.17701
 BRAKE POWER KW   10.8382
 ELECTRICITY KW   10.8382
 PUMP EFFICIENCY USED   0.38540
 NET WORK REQUIRED KW   10.8382
 HEAD DEVELOPED M-KGF/KG   246.227

BLOCK: R-100   MODEL: RPLUG

 INLET STREAM: 11
 OUTLET STREAM: 12
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

           *** MASS AND ENERGY BALANCE ***
             IN   OUT   GENERATION   RELATIVE DIFF.
 TOTAL BALANCE
 MOLE(KMOL/HR)   80.4178   79.4057   -1.01212   0.00000
 MASS(KG/HR)   5919.25   5919.47   -0.385903E-04
 ENTHALPY(CAL/SEC) -0.188859E+07 -0.188859E+07   0.00000

           *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION   0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

            *** INPUT DATA ***

 REACTOR TYPE:
  ADIABATIC
  VAPOR FLUID PHASE

367

REACTOR TUBE LENGTH   METER   5.0000
REACTOR DIAMETER   METER   1.0000
REACTOR RISE   METER   0.0000
NUMBER OF REACTOR TUBES   1
REACTOR VOLUME   L   3927.0
PRESSURE DROP OPTION: SPECIFIED
HOLDUP OPTION: NO-SLIP
ERROR TOLERANCE   0.10000E-03
INTEGRATION METHOD   GEAR
CORRECTOR METHOD   NEWTON
INITIAL STEP SIZE FACTOR   0.10000E-01
CORRECTOR TOLERANCE FACTOR   0.10000
MAXIMUM NUMBER OF STEPS   1000

 REACTION PARAGRAPH   ID: HYDROGEN   TYPE: POWERLAW
 GLOBAL BASES:
 KBASIS   MOLE-GAMMA
 CBASIS   MOLARITY
 SBASIS   GLOBAL

 STOICHIOMETRY:

 REACTION NUMBER: 1
  SUBSTREAM: MIXED
   HYDROGEN -1.0000   METHY-01 -1.0000   2-BUT-01   1.0000

 REACTION NUMBER: 2
  SUBSTREAM: MIXED
   HYDROGEN -1.0000   N-BUT-01 -1.0000   N-BUT-02   1.0000

 REAC-DATA ENTRIES:

  REACTION NO   TYPE   PHASE   DELT   BASIS
                    C

    1   KINETIC   V   0.0000   PARTIALPRES
    2   KINETIC   V   0.0000   PARTIALPRES

 RATE PARAMETERS:

  REACTION NO PREEXP. FACTOR ACT. ENERGY TEMP. EXPONENT REF. TEMP
                    CAL/MOL   C

```
      1      220.00     7730.0     0.0000
      2      220.00     7730.0     0.0000
```

POWERLAW EXPONENTS:

REACTION NUMBER: 1
 SUBSTREAM: MIXED
   HYDROGEN -0.50000   METHY-01   1.0000

REACTION NUMBER: 2
 SUBSTREAM: MIXED
   HYDROGEN -0.50000   N-BUT-01   1.0000

            *** RESULTS ***

REACTOR DUTY   CAL/SEC   0.0000
RESIDENCE TIME   HR   0.55377E-02
REACTOR MINIMUM TEMPERATURE C   150.00
REACTOR MAXIMUM TEMPERATURE C   156.50

     *** RESULTS PROFILE (PROCESS STREAM) ***

LENGTH	PRESSURE	TEMPERATURE	VAPOR FRAC	RES-TIME
METER	BAR	C		HR
0.0000	4.0000	150.00	1.0000	0.0000
0.50000	4.0000	156.50	1.0000	0.55378E-03
1.0000	4.0000	156.50	1.0000	0.11075E-02
1.5000	4.0000	156.50	1.0000	0.16613E-02
2.0000	4.0000	156.50	1.0000	0.22151E-02
2.5000	4.0000	156.50	1.0000	0.27688E-02
3.0000	4.0000	156.50	1.0000	0.33226E-02
3.5000	4.0000	156.50	1.0000	0.38764E-02
4.0000	4.0000	156.50	1.0000	0.44301E-02
4.5000	4.0000	156.50	1.0000	0.49839E-02
5.0000	4.0000	156.50	1.0000	0.55377E-02

LENGTH	DUTY	LIQUID HOLDUP
METER	CAL/SEC	
0.0000	0.0000	0.0000
0.50000	0.0000	0.0000
1.0000	0.0000	0.0000
1.5000	0.0000	0.0000
2.0000	0.0000	0.0000

2.5000	0.0000	0.0000
3.0000	0.0000	0.0000
3.5000	0.0000	0.0000
4.0000	0.0000	0.0000
4.5000	0.0000	0.0000
5.0000	0.0000	0.0000

*** TOTAL MOLE FRACTION PROFILE (PROCESS STREAM) ***

LENGTH METER	HYDROGEN	WATER	ETHANOL	ETHYLACE
0.0000	0.16537	0.90605E-10	0.14718E-02	0.82057
0.50000	0.15469	0.91760E-10	0.14906E-02	0.83103
1.0000	0.15469	0.91760E-10	0.14906E-02	0.83103
1.5000	0.15469	0.91760E-10	0.14906E-02	0.83103
2.0000	0.15469	0.91760E-10	0.14906E-02	0.83103
2.5000	0.15469	0.91760E-10	0.14906E-02	0.83103
3.0000	0.15469	0.91760E-10	0.14906E-02	0.83103
3.5000	0.15469	0.91760E-10	0.14906E-02	0.83103
4.0000	0.15469	0.91760E-10	0.14906E-02	0.83103
4.5000	0.15469	0.91760E-10	0.14906E-02	0.83103
5.0000	0.15469	0.91760E-10	0.14906E-02	0.83103

LENGTH METER	ACETA-01	METHY-01	N-BUT-01	N-BUT-02
0.0000	0.11976E-05	0.62929E-02	0.62929E-02	0.0000
0.50000	0.12129E-05	0.0000	0.0000	0.63930E-02
1.0000	0.12129E-05	0.0000	0.0000	0.63930E-02
1.5000	0.12129E-05	0.0000	0.0000	0.63930E-02
2.0000	0.12129E-05	0.0000	0.0000	0.63930E-02
2.5000	0.12129E-05	0.0000	0.0000	0.63930E-02
3.0000	0.12129E-05	0.0000	0.0000	0.63930E-02
3.5000	0.12129E-05	0.0000	0.0000	0.63930E-02
4.0000	0.12129E-05	0.0000	0.0000	0.63930E-02
4.5000	0.12129E-05	0.0000	0.0000	0.63930E-02
5.0000	0.12129E-05	0.0000	0.0000	0.63930E-02

LENGTH METER	2-BUT-01
0.0000	0.0000
0.50000	0.63930E-02

1.0000	0.63930E-02
1.5000	0.63930E-02
2.0000	0.63930E-02
2.5000	0.63930E-02
3.0000	0.63930E-02
3.5000	0.63930E-02
4.0000	0.63930E-02
4.5000	0.63930E-02
5.0000	0.63930E-02

*** TOTAL MASS FRACTION PROFILE (PROCESS STREAM) ***

LENGTH METER	HYDROGEN	WATER	ETHANOL	ETHYLACE
0.0000	0.45291E-02	0.22176E-10	0.92117E-03	0.98222
0.50000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
1.0000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
1.5000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
2.0000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
2.5000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
3.0000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
3.5000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
4.0000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
4.5000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218
5.0000	0.41832E-02	0.22175E-10	0.92114E-03	0.98218

LENGTH METER	ACETA-01	METHY-01	N-BUT-01	N-BUT-02
0.0000	0.71679E-06	0.61647E-02	0.61647E-02	0.0000
0.50000	0.71676E-06	0.0000	0.0000	0.63567E-02
1.0000	0.71676E-06	0.0000	0.0000	0.63567E-02
1.5000	0.71676E-06	0.0000	0.0000	0.63567E-02
2.0000	0.71676E-06	0.0000	0.0000	0.63567E-02
2.5000	0.71676E-06	0.0000	0.0000	0.63567E-02
3.0000	0.71676E-06	0.0000	0.0000	0.63567E-02
3.5000	0.71676E-06	0.0000	0.0000	0.63567E-02
4.0000	0.71676E-06	0.0000	0.0000	0.63567E-02
4.5000	0.71676E-06	0.0000	0.0000	0.63567E-02
5.0000	0.71676E-06	0.0000	0.0000	0.63567E-02

LENGTH METER	2-BUT-01

```
0.0000      0.0000
0.50000     0.63566E-02
1.0000     0.63566E-02
1.5000     0.63566E-02
2.0000     0.63566E-02
2.5000     0.63566E-02
3.0000     0.63566E-02
3.5000     0.63566E-02
4.0000     0.63566E-02
4.5000     0.63566E-02
5.0000     0.63566E-02
```

BLOCK: S-100   MODEL: SEP

 INLET STREAM: 7
 OUTLET STREAMS: 8   WATER
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

              *** MASS AND ENERGY BALANCE ***
                  IN   OUT   RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(KMOL/HR)   68.0140   68.0140   0.417881E-15
   MASS(KG/HR   )   5905.26   5905.26   0.154014E-15
   ENTHALPY(CAL/SEC)   -0.195414E+07 -0.195490E+07   0.388402E-03

              *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION 0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

              *** INPUT DATA ***

 FLASH SPECS FOR STREAM 8
 TWO   PHASE TP FLASH
 PRESSURE DROP   BAR   0.0
 MAXIMUM NO. ITERATIONS   30
 CONVERGENCE TOLERANCE   0.000100000

 FLASH SPECS FOR STREAM WATER
 TWO   PHASE TP FLASH

PRESSURE DROP   BAR   0.0
MAXIMUM NO. ITERATIONS   30
CONVERGENCE TOLERANCE   0.000100000

FRACTION OF FEED
 SUBSTREAM= MIXED
  STREAM= WATER   CPT= HYDROGEN FRACTION=   0.0
            WATER   1.00000
            ETHANOL   0.0
            ETHYLACE   0.0
            ACETA-01   0.0
            METHY-01   0.0
            N-BUT-01   0.0
            N-BUT-02   0.0
            2-BUT-01   0.0

            *** RESULTS ***

 HEAT DUTY   CAL/SEC   -759.29

COMPONENT = WATER
 STREAM   SUBSTREAM   SPLIT FRACTION
 WATER   MIXED   1.00000

COMPONENT = ETHANOL
 STREAM   SUBSTREAM   SPLIT FRACTION
 8   MIXED   1.00000

COMPONENT = ETHYLACE
 STREAM   SUBSTREAM   SPLIT FRACTION
 8   MIXED   1.00000

COMPONENT = ACETA-01
 STREAM   SUBSTREAM   SPLIT FRACTION
 8   MIXED   1.00000

COMPONENT = METHY-01
 STREAM   SUBSTREAM   SPLIT FRACTION
 8   MIXED   1.00000

COMPONENT = N-BUT-01
 STREAM   SUBSTREAM   SPLIT FRACTION
 8   MIXED   1.00000

BLOCK: SPILT   MODEL: FSPLIT

 INLET STREAM: 3
 OUTLET STREAMS: 9   4
 PROPERTY OPTION SET: NRTL   RENON (NRTL) / IDEAL GAS
 HENRY-COMPS ID: HC-1

            *** MASS AND ENERGY BALANCE ***
                IN   OUT   RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(KMOL/HR)   134.164   134.164   0.00000
   MASS(KG/HR)   322.280   322.280   -0.176379E-15
   ENTHALPY(CAL/SEC)   -14551.7   -14551.7   0.00000

            *** CO2 EQUIVALENT SUMMARY ***
 FEED STREAMS CO2E   0.00000   KG/HR
 PRODUCT STREAMS CO2E   0.00000   KG/HR
 NET STREAMS CO2E PRODUCTION 0.00000   KG/HR
 UTILITIES CO2E PRODUCTION   0.00000   KG/HR
 TOTAL CO2E PRODUCTION   0.00000   KG/HR

            *** INPUT DATA ***

 FRACTION OF FLOW   STRM=4   FRAC=   0.90000

            *** RESULTS ***

 STREAM= 9   SPLIT=   0.100000 KEY= 0 STREAM-ORDER= 2
      4   0.90000   0   1

28.7.4 Stream Results

```
1 10 11 12 13
-------------
STREAM ID          1        10       11       12       13
FROM :            ----     MIXER    E-102    R-100    E-103
TO  :            P-100     E-102    R-100    E-103     ----

SUBSTREAM: MIXED
PHASE:           LIQUID    MIXED    VAPOR    VAPOR    VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN         0.0     13.2988  13.2988  12.2835  12.1864
 WATER            0.0    7.2863-09 7.2863-09 7.2863-09 3.4097-10
 ETHANOL        135.1769   0.1184   0.1184   0.1184  4.7010-03
 ETHYLACE         0.0     65.9884  65.9884  65.9884   1.2408
 ACETA-01         0.0    9.6312-05 9.6312-05 9.6312-05 1.1662-05
 METHY-01         0.0      0.5061   0.5061   0.0      0.0
 N-BUT-01         0.0      0.5061   0.5061   0.0      0.0
 N-BUT-02         0.0      0.0      0.0      0.5076  2.3435-03
 2-BUT-01         0.0      0.0      0.0      0.5076  4.9668-03
TOTAL FLOW:
 KMOL/HR        135.1769  80.4178  80.4178  79.4057  13.4392
 KG/HR        6227.4698 5919.2451 5919.2451 5919.4735 134.6441
 L/MIN         131.9056 8913.3630 1.1789+04 1.1819+04 1504.5009
STATE VARIABLES:
 TEMP  C         35.0000 116.7085 150.0000 156.5000  50.0000
 PRES  BAR        1.0000   4.0000   4.0000   4.0000   4.0000
 VFRAC            0.0      0.8181   1.0000   1.0000   1.0000
 LFRAC            1.0000   0.1819   0.0      0.0      0.0
 SFRAC            0.0      0.0      0.0      0.0      0.0
ENTHALPY:
 CAL/MOL       -6.5990+04 -8.6767+04 -8.4545+04 -8.5623+04 -9637.9867
 CAL/GM       -1432.4121 -1178.7974 -1148.6153 -1148.5710 -961.9915
 CAL/SEC      -2.4779+06 -1.9382+06 -1.8886+06 -1.8886+06 -3.5980+04
ENTROPY:
 CAL/MOL-K       -81.8300 -75.5924 -70.0031 -70.8108 -10.0783
 CAL/GM-K         -1.7762  -1.0270  -0.9510  -0.9499  -1.0059
DENSITY:
 MOL/CC         1.7080-02 1.5037-04 1.1369-04 1.1197-04 1.4888-04
 GM/CC           0.7869 1.1068-02 8.3686-03 8.3474-03 1.4916-03
AVG MW          46.0690  73.6062  73.6062  74.5472  10.0188


14 15 16 17 2
-------------
STREAM ID         14       15       16       17        2
FROM :          E-103    C-102    C-102    C-102    P-100
```

TO :   C-102   ----   ----   ----   C-100

SUBSTREAM: MIXED
PHASE: LIQUID   VAPOR   LIQUID   LIQUID   LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN   9.7122-02 5.3214-02 4.3909-02   0.0   0.0
 WATER   6.9453-09 2.0305-12 6.9433-09 4.3172-16   0.0
 ETHANOL   0.1137 2.7463-05   0.1136 3.9967-08 135.1769
 ETHYLACE   64.7477 7.1538-03 64.6111   0.1294   0.0
 ACETA-01   8.4649-05 7.5604-08 8.4574-05 7.6290-16   0.0
 METHY-01   0.0   0.0   0.0   0.0   0.0
 N-BUT-01   0.0   0.0   0.0   0.0   0.0
 N-BUT-02   0.5053 2.3306-09 1.0062-04   0.5052   0.0
 2-BUT-01   0.5027 3.7018-06 6.9289-02   0.4334   0.0
TOTAL FLOW:
 KMOL/HR   65.9665 6.0399-02 64.8381   1.0680 135.1769
 KG/HR   5784.8294   0.7391 5703.1167 80.9736 6227.4698
 L/MIN   111.6711 13.0626 108.1413   1.9276 132.3632
STATE VARIABLES:
 TEMP C   50.0000 38.9962 38.9962 128.4443 37.3071
 PRES BAR   4.0000   2.0000   2.0000   2.0000 20.0000
 VFRAC   0.0   1.0000   0.0   0.0   0.0
 LFRAC   1.0000   0.0   1.0000   1.0000   1.0000
 SFRAC   0.0   0.0   0.0   0.0   0.0
ENTHALPY:
 CAL/MOL   -1.1280+05 -1.2474+04 -1.1389+05 -7.7388+04 -6.5921+04
 CAL/GM   -1286.3539 -1019.3547 -1294.7479 -1020.7144 -1430.9157
 CAL/SEC   -2.0670+06 -209.2818 -2.0511+06 -2.2959+04 -2.4753+06
ENTROPY:
 CAL/MOL-K   -114.0496 -11.2755 -115.6130 -109.9721 -81.6091
 CAL/GM-K   -1.3005 -0.9214 -1.3144 -1.4505 -1.7715
DENSITY:
 MOL/CC   9.8454-03 7.7063-05 9.9928-03 9.2344-03 1.7021-02
 GM/CC   0.8634 9.4303-04   0.8790   0.7001   0.7841
AVG MW   87.6934 12.2372 87.9593 75.8174 46.0690

3 4 5 6 7

STREAM ID   3   4   5   6   7
FROM :   C-100   SPILT   C-100   C-101   C-101
TO :   SPILT   ----   C-101   C-100   S-100

CONV. MAX. REL. ERR: 0.0   0.0   0.0   -7.3607-05   0.0

SUBSTREAM: MIXED
PHASE: VAPOR   VAPOR   LIQUID   VAPOR   LIQUID
COMPONENTS: KMOL/HR

HYDROGEN	132.9879	119.6891	0.9524	133.9403	3.1966-14
WATER	7.2863-08	6.5577-08	8.3348	8.3348	1.0126
ETHANOL	1.1761	1.0585	134.0351	3.4324-02	7.4477-04
ETHYLACE	8.9261-06	8.0335-06	9.2468	9.2468	65.9884
ACETA-01	1.7749-04	1.5974-04	4.6826	4.6827	7.8563-05
METHY-01	4.1491-09	3.7342-09	1.4380-02	1.4380-02	0.5061
N-BUT-01	4.2738-10	3.8465-10	3.5994-03	3.5994-03	0.5061
N-BUT-02	0.0	0.0	0.0	0.0	0.0
2-BUT-01	0.0	0.0	0.0	0.0	0.0

TOTAL FLOW:

KMOL/HR	134.1642	120.7478	157.2696	156.2569	68.0140
KG/HR	322.2797	290.0517	7349.2188	1444.0287	5905.2590
L/MIN	2907.0937	2616.3843	168.0849	4008.7315	164.3826

STATE VARIABLES:

TEMP C	39.5848	39.5848	87.6679	97.1078	207.1942
PRES BAR	20.0000	20.0000	20.0000	20.0000	20.1310
VFRAC	1.0000	1.0000	0.0	1.0000	0.0
LFRAC	0.0	0.0	1.0000	0.0	1.0000
SFRAC	0.0	0.0	0.0	0.0	0.0

ENTHALPY:

CAL/MOL	-390.4614	-390.4614	-6.6256+04	-9992.9776	-1.0343+05
CAL/GM	-162.5481	-162.5481	-1417.8475	-1081.3303	-1191.2964
CAL/SEC	-1.4552+04	-1.3096+04	-2.8945+06	-4.3374+05	-1.9541+06

ENTROPY:

CAL/MOL-K	-5.9618	-5.9618	-74.1117	-9.8692	-91.9422
CAL/GM-K	-2.4819	-2.4819	-1.5860	-1.0679	-1.0589

DENSITY:

MOL/CC	7.6918-04	7.6918-04	1.5594-02	6.4965-04	6.8959-03
GM/CC	1.8477-03	1.8477-03	0.7287	6.0037-03	0.5987
AVG MW	2.4021	2.4021	46.7301	9.2414	86.8242

8 9 CH2OIN CH2OOUT STEAMIN

STREAM ID   8   9   CH2OIN   CH2OOUT   STEAMIN
FROM :   S-100   SPILT   ----   E-103   ----
TO :   MIXER   MIXER   E-103   ----   E-102

SUBSTREAM: MIXED
PHASE: LIQUID   VAPOR   LIQUID   LIQUID   VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN   0.0   13.2988   0.0   0.0   0.0

```
WATER           0.0    7.2863-09 2575.5914 2575.5914   17.7627
ETHANOL       7.4477-04   0.1176    0.0      0.0      0.0
ETHYLACE       65.9884 8.9261-07   0.0      0.0      0.0
ACETA-01      7.8563-05 1.7749-05   0.0      0.0      0.0
METHY-01       0.5061 4.1491-10    0.0      0.0      0.0
N-BUT-01       0.5061 4.2738-11    0.0      0.0      0.0
N-BUT-02        0.0      0.0      0.0      0.0      0.0
2-BUT-01        0.0      0.0      0.0      0.0      0.0
TOTAL FLOW:
 KMOL/HR       67.0014   13.4164 2575.5914 2575.5914   17.7627
 KG/HR        5887.0171   32.2280 4.6400+04 4.6400+04  320.0000
 L/MIN         164.0166  290.7094 783.5485 796.7406 994.3450
STATE VARIABLES:
 TEMP  C       207.1942  39.5848  32.2222  48.8731  185.5767
 PRES  BAR      20.1310  20.0000   1.0000   1.0000   11.3554
 VFRAC          0.0      1.0000    0.0      0.0      1.0000
 LFRAC          1.0000    0.0      1.0000   1.0000    0.0
 SFRAC          0.0      0.0      0.0      0.0      0.0
ENTHALPY:
 CAL/MOL      -1.0406+05 -390.4614 -6.8134+04 -6.7834+04 -5.6449+04
 CAL/GM       -1184.3608 -162.5481 -3781.9979 -3765.3615 -3133.3975
 CAL/SEC      -1.9368+06 -1455.1655 -4.8746+07 -4.8531+07 -2.7852+05
ENTROPY:
 CAL/MOL-K     -93.1030   -5.9618  -38.5412  -37.5895  -11.9045
 CAL/GM-K       -1.0596   -2.4819   -2.1394   -2.0865   -0.6608
DENSITY:
 MOL/CC       6.8084-03 7.6918-04 5.4785-02 5.3878-02 2.9773-04
 GM/CC          0.5982 1.8477-03   0.9870    0.9706 5.3637-03
AVG MW         87.8641    2.4021   18.0153   18.0153   18.0153

STEAMOUT WATER
--------------
STREAM ID          STEAMOUT   WATER
FROM :             E-102    S-100
TO  :              ----     ----

SUBSTREAM: MIXED
PHASE:          LIQUID   LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN        0.0      0.0
 WATER          17.7627   1.0126
 ETHANOL         0.0      0.0
 ETHYLACE        0.0      0.0
 ACETA-01        0.0      0.0
```

```
METHY-01         0.0      0.0
N-BUT-01         0.0      0.0
N-BUT-02         0.0      0.0
2-BUT-01         0.0      0.0
TOTAL FLOW:
 KMOL/HR         17.7627    1.0126
 KG/HR          320.0000   18.2419
 L/MIN            5.9348    0.3832
STATE VARIABLES:
 TEMP  C        118.2789  207.1942
 PRES  BAR       11.3554   20.1310
 VFRAC            0.0      0.0
 LFRAC            1.0000    1.0000
 SFRAC            0.0      0.0
ENTHALPY:
 CAL/MOL         -6.6507+04 -6.4484+04
 CAL/GM          -3691.6959 -3579.4042
 CAL/SEC         -3.2815+05 -1.8138+04
ENTROPY:
 CAL/MOL-K        -33.9158  -29.5373
 CAL/GM-K          -1.8826   -1.6396
DENSITY:
 MOL/CC          4.9883-02 4.4037-02
 GM/CC            0.8987    0.7933
AVG MW           18.0153   18.0153


1
-
STREAM ID        1
FROM :          ----
TO  :           P-100


SUBSTREAM: MIXED
PHASE:          LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN         0.0
 WATER           0.0
 ETHANOL        135.1769
 ETHYLACE         0.0
 ACETA-01         0.0
 METHY-01         0.0
 N-BUT-01         0.0
 N-BUT-02         0.0
 2-BUT-01         0.0
```

TOTAL FLOW:
 KMOL/HR   135.1769
 KG/HR   6227.4698
 L/MIN   131.9056
STATE VARIABLES:
 TEMP   C   35.0000
 PRES   BAR   1.0000
 VFRAC   0.0
 LFRAC   1.0000
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -6.5990+04
 CAL/GM   -1432.4121
 CAL/SEC   -2.4779+06
ENTROPY:
 CAL/MOL-K   -81.8300
 CAL/GM-K   -1.7762
DENSITY:
 MOL/CC   1.7080-02
 GM/CC   0.7869
AVG MW   46.0690

2
-
STREAM ID   2
FROM :   P-100
TO   :   C-100

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   0.0
 ETHANOL   135.1769
 ETHYLACE   0.0
 ACETA-01   0.0
 METHY-01   0.0
 N-BUT-01   0.0
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   135.1769
 KG/HR   6227.4698
 L/MIN   132.3632

STATE VARIABLES:
 TEMP   C   37.3071
 PRES   BAR   20.0000
 VFRAC   0.0
 LFRAC   1.0000
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -6.5921+04
 CAL/GM   -1430.9157
 CAL/SEC   -2.4753+06
ENTROPY:
 CAL/MOL-K   -81.6091
 CAL/GM-K   -1.7715
DENSITY:
 MOL/CC   1.7021-02
 GM/CC   0.7841
AVG MW   46.0690

3
-
STREAM ID   3
FROM :   C-100
TO   :   SPILT

SUBSTREAM: MIXED
PHASE: VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN   132.9879
 WATER   7.2863-08
 ETHANOL   1.1761
 ETHYLACE   8.9261-06
 ACETA-01   1.7749-04
 METHY-01   4.1491-09
 N-BUT-01   4.2738-10
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   134.1642
 KG/HR   322.2797
 L/MIN   2907.0937
STATE VARIABLES:
 TEMP   C   39.5848
 PRES   BAR   20.0000
 VFRAC   1.0000

382

```
  LFRAC          0.0
  SFRAC          0.0
ENTHALPY:
  CAL/MOL      -390.4614
  CAL/GM       -162.5481
  CAL/SEC      -1.4552+04
ENTROPY:
  CAL/MOL-K     -5.9618
  CAL/GM-K      -2.4819
DENSITY:
  MOL/CC       7.6918-04
  GM/CC        1.8477-03
AVG MW          2.4021


4
-
STREAM ID         4
FROM :         SPILT
TO   :          ----

SUBSTREAM: MIXED
PHASE:          VAPOR
COMPONENTS: KMOL/HR
  HYDROGEN      119.6891
  WATER        6.5577-08
  ETHANOL        1.0585
  ETHYLACE      8.0335-06
  ACETA-01      1.5974-04
  METHY-01      3.7342-09
  N-BUT-01      3.8465-10
  N-BUT-02       0.0
  2-BUT-01       0.0
TOTAL FLOW:
  KMOL/HR       120.7478
  KG/HR         290.0517
  L/MIN        2616.3843
STATE VARIABLES:
  TEMP  C        39.5848
  PRES  BAR      20.0000
  VFRAC         1.0000
  LFRAC          0.0
  SFRAC          0.0
ENTHALPY:
  CAL/MOL      -390.4614
```

```
  CAL/GM        -162.5481
  CAL/SEC       -1.3096+04
ENTROPY:
  CAL/MOL-K       -5.9618
  CAL/GM-K        -2.4819
DENSITY:
  MOL/CC         7.6918-04
  GM/CC          1.8477-03
AVG MW            2.4021
```

5

-

```
STREAM ID          5
FROM :          C-100
TO   :          C-101
```

```
SUBSTREAM: MIXED
PHASE:          LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN        0.9524
 WATER           8.3348
 ETHANOL       134.0351
 ETHYLACE        9.2468
 ACETA-01        4.6826
 METHY-01        1.4380-02
 N-BUT-01        3.5994-03
 N-BUT-02        0.0
 2-BUT-01        0.0
TOTAL FLOW:
 KMOL/HR       157.2696
 KG/HR        7349.2188
 L/MIN         168.0849
STATE VARIABLES:
 TEMP  C        87.6679
 PRES  BAR      20.0000
 VFRAC          0.0
 LFRAC          1.0000
 SFRAC          0.0
ENTHALPY:
 CAL/MOL       -6.6256+04
 CAL/GM       -1417.8475
 CAL/SEC       -2.8945+06
ENTROPY:
 CAL/MOL-K      -74.1117
```

```
  CAL/GM-K        -1.5860
DENSITY:
  MOL/CC      1.5594-02
  GM/CC        0.7287
AVG MW        46.7301


6
-
STREAM ID        6
FROM :          C-101
TO   :          C-100


CONV. MAX. REL. ERR: -7.3607-05
SUBSTREAM: MIXED
PHASE:          VAPOR
COMPONENTS: KMOL/HR
  HYDROGEN      133.9403
  WATER          8.3348
  ETHANOL      3.4324-02
  ETHYLACE       9.2468
  ACETA-01       4.6827
  METHY-01     1.4380-02
  N-BUT-01     3.5994-03
  N-BUT-02       0.0
  2-BUT-01       0.0
TOTAL FLOW:
  KMOL/HR      156.2569
  KG/HR       1444.0287
  L/MIN       4008.7315
STATE VARIABLES:
  TEMP   C      97.1078
  PRES   BAR     20.0000
  VFRAC         1.0000
  LFRAC         0.0
  SFRAC         0.0
ENTHALPY:
  CAL/MOL      -9992.9776
  CAL/GM       -1081.3303
  CAL/SEC      -4.3374+05
ENTROPY:
  CAL/MOL-K      -9.8692
  CAL/GM-K       -1.0679
DENSITY:
```

```
  MOL/CC        6.4965-04
  GM/CC         6.0037-03
AVG MW           9.2414


7
-
STREAM ID         7
FROM :           C-101
TO   :           S-100

SUBSTREAM: MIXED
PHASE:            LIQUID
COMPONENTS: KMOL/HR
  HYDROGEN      3.1966-14
  WATER         1.0126
  ETHANOL       7.4477-04
  ETHYLACE      65.9884
  ACETA-01      7.8563-05
  METHY-01      0.5061
  N-BUT-01      0.5061
  N-BUT-02      0.0
  2-BUT-01      0.0
TOTAL FLOW:
  KMOL/HR       68.0140
  KG/HR         5905.2590
  L/MIN         164.3826
STATE VARIABLES:
  TEMP  C       207.1942
  PRES  BAR      20.1310
  VFRAC         0.0
  LFRAC         1.0000
  SFRAC         0.0
ENTHALPY:
  CAL/MOL       -1.0343+05
  CAL/GM        -1191.2964
  CAL/SEC       -1.9541+06
ENTROPY:
  CAL/MOL-K     -91.9422
  CAL/GM-K      -1.0589
DENSITY:
  MOL/CC        6.8959-03
  GM/CC         0.5987
AVG MW          86.8242
```

8
-
STREAM ID   8
FROM :   S-100
TO   :   MIXER

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   0.0
 ETHANOL   7.4477-04
 ETHYLACE   65.9884
 ACETA-01   7.8563-05
 METHY-01   0.5061
 N-BUT-01   0.5061
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   67.0014
 KG/HR   5887.0171
 L/MIN   164.0166
STATE VARIABLES:
 TEMP C   207.1942
 PRES BAR   20.1310
 VFRAC   0.0
 LFRAC   1.0000
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -1.0406+05
 CAL/GM   -1184.3608
 CAL/SEC   -1.9368+06
ENTROPY:
 CAL/MOL-K   -93.1030
 CAL/GM-K   -1.0596
DENSITY:
 MOL/CC   6.8084-03
 GM/CC   0.5982
AVG MW   87.8641

9
-
STREAM ID   9
FROM :   SPILT

TO   :   MIXER

SUBSTREAM: MIXED
PHASE: VAPOR
COMPONENTS: KMOL/HR
  HYDROGEN   13.2988
  WATER   7.2863-09
  ETHANOL   0.1176
  ETHYLACE   8.9261-07
  ACETA-01   1.7749-05
  METHY-01   4.1491-10
  N-BUT-01   4.2738-11
  N-BUT-02   0.0
  2-BUT-01   0.0
TOTAL FLOW:
  KMOL/HR   13.4164
  KG/HR   32.2280
  L/MIN   290.7094
STATE VARIABLES:
  TEMP C   39.5848
  PRES BAR   20.0000
  VFRAC   1.0000
  LFRAC   0.0
  SFRAC   0.0
ENTHALPY:
  CAL/MOL   -390.4614
  CAL/GM   -162.5481
  CAL/SEC   -1455.1655
ENTROPY:
  CAL/MOL-K   -5.9618
  CAL/GM-K   -2.4819
DENSITY:
  MOL/CC   7.6918-04
  GM/CC   1.8477-03
AVG MW   2.4021

10
--
STREAM ID   10
FROM :   MIXER
TO   :   E-102

SUBSTREAM: MIXED
PHASE: MIXED

COMPONENTS: KMOL/HR
 HYDROGEN   13.2988
 WATER   7.2863-09
 ETHANOL   0.1184
 ETHYLACE   65.9884
 ACETA-01   9.6312-05
 METHY-01   0.5061
 N-BUT-01   0.5061
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   80.4178
 KG/HR   5919.2451
 L/MIN   8913.3630
STATE VARIABLES:
 TEMP   C   116.7085
 PRES   BAR   4.0000
 VFRAC   0.8181
 LFRAC   0.1819
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -8.6767+04
 CAL/GM   -1178.7974
 CAL/SEC   -1.9382+06
ENTROPY:
 CAL/MOL-K   -75.5924
 CAL/GM-K   -1.0270
DENSITY:
 MOL/CC   1.5037-04
 GM/CC   1.1068-02
AVG MW   73.6062

11
--
STREAM ID   11
FROM :   E-102
TO   :   R-100

SUBSTREAM: MIXED
PHASE: VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN   13.2988
 WATER   7.2863-09
 ETHANOL   0.1184

```
ETHYLACE        65.9884
ACETA-01        9.6312-05
METHY-01         0.5061
N-BUT-01         0.5061
N-BUT-02         0.0
2-BUT-01         0.0
TOTAL FLOW:
KMOL/HR         80.4178
KG/HR          5919.2451
L/MIN          1.1789+04
STATE VARIABLES:
TEMP   C        150.0000
PRES   BAR        4.0000
VFRAC            1.0000
LFRAC           0.0
SFRAC           0.0
ENTHALPY:
CAL/MOL        -8.4545+04
CAL/GM         -1148.6153
CAL/SEC        -1.8886+06
ENTROPY:
CAL/MOL-K       -70.0031
CAL/GM-K         -0.9510
DENSITY:
MOL/CC          1.1369-04
GM/CC           8.3686-03
AVG MW          73.6062


12
--
STREAM ID          12
FROM :          R-100
TO   :       E-103


SUBSTREAM: MIXED
PHASE:          VAPOR
COMPONENTS: KMOL/HR
HYDROGEN         12.2835
WATER          7.2863-09
ETHANOL          0.1184
ETHYLACE        65.9884
ACETA-01        9.6312-05
METHY-01         0.0
N-BUT-01         0.0
```

```
  N-BUT-02         0.5076
  2-BUT-01         0.5076
TOTAL FLOW:
  KMOL/HR          79.4057
  KG/HR          5919.4735
  L/MIN          1.1819+04
STATE VARIABLES:
  TEMP  C          156.5000
  PRES  BAR          4.0000
  VFRAC              1.0000
  LFRAC              0.0
  SFRAC              0.0
ENTHALPY:
  CAL/MOL         -8.5623+04
  CAL/GM          -1148.5710
  CAL/SEC         -1.8886+06
ENTROPY:
  CAL/MOL-K        -70.8108
  CAL/GM-K          -0.9499
DENSITY:
  MOL/CC          1.1197-04
  GM/CC           8.3474-03
AVG MW            74.5472


13
--
STREAM ID          13
FROM :        E-103
TO   :        ----

SUBSTREAM: MIXED
PHASE:        VAPOR
COMPONENTS: KMOL/HR
  HYDROGEN         12.1864
  WATER          3.4097-10
  ETHANOL        4.7010-03
  ETHYLACE         1.2408
  ACETA-01       1.1662-05
  METHY-01         0.0
  N-BUT-01         0.0
  N-BUT-02       2.3435-03
  2-BUT-01       4.9668-03
TOTAL FLOW:
  KMOL/HR          13.4392
```

```
  KG/HR        134.6441
  L/MIN       1504.5009
STATE VARIABLES:
  TEMP  C      50.0000
  PRES  BAR     4.0000
  VFRAC         1.0000
  LFRAC         0.0
  SFRAC         0.0
ENTHALPY:
  CAL/MOL      -9637.9867
  CAL/GM        -961.9915
  CAL/SEC      -3.5980+04
ENTROPY:
  CAL/MOL-K     -10.0783
  CAL/GM-K       -1.0059
DENSITY:
  MOL/CC        1.4888-04
  GM/CC         1.4916-03
AVG MW          10.0188


14
--
STREAM ID        14
FROM :         E-103
TO   :         C-102

SUBSTREAM: MIXED
PHASE:          LIQUID
COMPONENTS: KMOL/HR
  HYDROGEN      9.7122-02
  WATER         6.9453-09
  ETHANOL       0.1137
  ETHYLACE     64.7477
  ACETA-01      8.4649-05
  METHY-01      0.0
  N-BUT-01      0.0
  N-BUT-02      0.5053
  2-BUT-01      0.5027
TOTAL FLOW:
  KMOL/HR      65.9665
  KG/HR       5784.8294
  L/MIN        111.6711
STATE VARIABLES:
  TEMP  C      50.0000
```

PRES   BAR   4.0000
VFRAC   0.0
LFRAC   1.0000
SFRAC   0.0
ENTHALPY:
 CAL/MOL   -1.1280+05
 CAL/GM   -1286.3539
 CAL/SEC   -2.0670+06
ENTROPY:
 CAL/MOL-K   -114.0496
 CAL/GM-K   -1.3005
DENSITY:
 MOL/CC   9.8454-03
 GM/CC   0.8634
AVG MW   87.6934

15
--
STREAM ID   15
FROM :   C-102
TO   :   ----

SUBSTREAM: MIXED
PHASE: VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN   5.3214-02
 WATER   2.0305-12
 ETHANOL   2.7463-05
 ETHYLACE   7.1538-03
 ACETA-01   7.5604-08
 METHY-01   0.0
 N-BUT-01   0.0
 N-BUT-02   2.3306-09
 2-BUT-01   3.7018-06
TOTAL FLOW:
 KMOL/HR   6.0399-02
 KG/HR   0.7391
 L/MIN   13.0626
STATE VARIABLES:
 TEMP C   38.9962
 PRES   BAR   2.0000
 VFRAC   1.0000
 LFRAC   0.0
 SFRAC   0.0

ENTHALPY:
  CAL/MOL   -1.2474+04
  CAL/GM   -1019.3547
  CAL/SEC   -209.2818
ENTROPY:
  CAL/MOL-K   -11.2755
  CAL/GM-K   -0.9214
DENSITY:
  MOL/CC   7.7063-05
  GM/CC   9.4303-04
AVG MW   12.2372

16
--
STREAM ID   16
FROM :   C-102
TO   :   ----

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
  HYDROGEN   4.3909-02
  WATER   6.9433-09
  ETHANOL   0.1136
  ETHYLACE   64.6111
  ACETA-01   8.4574-05
  METHY-01   0.0
  N-BUT-01   0.0
  N-BUT-02   1.0062-04
  2-BUT-01   6.9289-02
TOTAL FLOW:
  KMOL/HR   64.8381
  KG/HR   5703.1167
  L/MIN   108.1413
STATE VARIABLES:
  TEMP   C   38.9962
  PRES   BAR   2.0000
  VFRAC   0.0
  LFRAC   1.0000
  SFRAC   0.0
ENTHALPY:
  CAL/MOL   -1.1389+05
  CAL/GM   -1294.7479
  CAL/SEC   -2.0511+06

ENTROPY:
  CAL/MOL-K   -115.6130
  CAL/GM-K   -1.3144
DENSITY:
  MOL/CC   9.9928-03
  GM/CC   0.8790
AVG MW   87.9593

17
--
STREAM ID   17
FROM :   C-102
TO :   ----

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
  HYDROGEN   0.0
  WATER   4.3172-16
  ETHANOL   3.9967-08
  ETHYLACE   0.1294
  ACETA-01   7.6290-16
  METHY-01   0.0
  N-BUT-01   0.0
  N-BUT-02   0.5052
  2-BUT-01   0.4334
TOTAL FLOW:
  KMOL/HR   1.0680
  KG/HR   80.9736
  L/MIN   1.9276
STATE VARIABLES:
  TEMP   C   128.4443
  PRES   BAR   2.0000
  VFRAC   0.0
  LFRAC   1.0000
  SFRAC   0.0
ENTHALPY:
  CAL/MOL   -7.7388+04
  CAL/GM   -1020.7144
  CAL/SEC   -2.2959+04
ENTROPY:
  CAL/MOL-K   -109.9721
  CAL/GM-K   -1.4505
DENSITY:

```
   MOL/CC         9.2344-03
   GM/CC          0.7001
  AVG MW          75.8174

CH2OIN

------
STREAM ID         CH2OIN
FROM :            ----
TO   :            E-103

SUBSTREAM: MIXED
PHASE:            LIQUID
COMPONENTS: KMOL/HR
  HYDROGEN           0.0
  WATER          2575.5914
  ETHANOL            0.0
  ETHYLACE           0.0
  ACETA-01           0.0
  METHY-01           0.0
  N-BUT-01           0.0
  N-BUT-02           0.0
  2-BUT-01           0.0
TOTAL FLOW:
  KMOL/HR        2575.5914
  KG/HR          4.6400+04
  L/MIN          783.5485
STATE VARIABLES:
  TEMP  C        32.2222
  PRES  BAR        1.0000
  VFRAC           0.0
  LFRAC           1.0000
  SFRAC           0.0
ENTHALPY:
  CAL/MOL        -6.8134+04
  CAL/GM         -3781.9979
  CAL/SEC        -4.8746+07
ENTROPY:
  CAL/MOL-K       -38.5412
  CAL/GM-K        -2.1394
DENSITY:
  MOL/CC         5.4785-02
  GM/CC          0.9870
 AVG MW          18.0153
```

CH2OOUT

STREAM ID   CH2OOUT
FROM :   E-103
TO :   ----

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   2575.5914
 ETHANOL   0.0
 ETHYLACE   0.0
 ACETA-01   0.0
 METHY-01   0.0
 N-BUT-01   0.0
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   2575.5914
 KG/HR   4.6400+04
 L/MIN   796.7406
STATE VARIABLES:
 TEMP   C   48.8731
 PRES   BAR   1.0000
 VFRAC   0.0
 LFRAC   1.0000
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -6.7834+04
 CAL/GM   -3765.3615
 CAL/SEC   -4.8531+07
ENTROPY:
 CAL/MOL-K   -37.5895
 CAL/GM-K   -2.0865
DENSITY:
 MOL/CC   5.3878-02
 GM/CC   0.9706
AVG MW   18.0153

STEAMIN

STREAM ID   STEAMIN
FROM :   ----

TO   :   E-102

SUBSTREAM: MIXED
PHASE: VAPOR
COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   17.7627
 ETHANOL   0.0
 ETHYLACE   0.0
 ACETA-01   0.0
 METHY-01   0.0
 N-BUT-01   0.0
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   17.7627
 KG/HR   320.0000
 L/MIN   994.3450
STATE VARIABLES:
 TEMP C   185.5767
 PRES BAR   11.3554
 VFRAC   1.0000
 LFRAC   0.0
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -5.6449+04
 CAL/GM   -3133.3975
 CAL/SEC   -2.7852+05
ENTROPY:
 CAL/MOL-K   -11.9045
 CAL/GM-K   -0.6608
DENSITY:
 MOL/CC   2.9773-04
 GM/CC   5.3637-03
AVG MW   18.0153

STEAMOUT

STREAM ID   STEAMOUT
FROM :   E-102
TO   :   ----

SUBSTREAM: MIXED
PHASE: LIQUID

COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   17.7627
 ETHANOL   0.0
 ETHYLACE   0.0
 ACETA-01   0.0
 METHY-01   0.0
 N-BUT-01   0.0
 N-BUT-02   0.0
 2-BUT-01   0.0
TOTAL FLOW:
 KMOL/HR   17.7627
 KG/HR   320.0000
 L/MIN   5.9348
STATE VARIABLES:
 TEMP   C   118.2789
 PRES   BAR   11.3554
 VFRAC   0.0
 LFRAC   1.0000
 SFRAC   0.0
ENTHALPY:
 CAL/MOL   -6.6507+04
 CAL/GM   -3691.6959
 CAL/SEC   -3.2815+05
ENTROPY:
 CAL/MOL-K   -33.9158
 CAL/GM-K   -1.8826
DENSITY:
 MOL/CC   4.9883-02
 GM/CC   0.8987
AVG MW   18.0153

WATER

STREAM ID   WATER
FROM :   S-100
TO   :   ----

SUBSTREAM: MIXED
PHASE: LIQUID
COMPONENTS: KMOL/HR
 HYDROGEN   0.0
 WATER   1.0126
 ETHANOL   0.0

```
ETHYLACE        0.0
ACETA-01        0.0
METHY-01         0.0
N-BUT-01        0.0
N-BUT-02        0.0
2-BUT-01        0.0
TOTAL FLOW:
 KMOL/HR        1.0126
 KG/HR         18.2419
 L/MIN          0.3832
STATE VARIABLES:
 TEMP   C      207.1942
 PRES   BAR     20.1310
 VFRAC          0.0
 LFRAC          1.0000
 SFRAC          0.0
ENTHALPY:
 CAL/MOL        -6.4484+04
 CAL/GM         -3579.4042
 CAL/SEC        -1.8138+04
ENTROPY:
 CAL/MOL-K      -29.5373
 CAL/GM-K       -1.6396
DENSITY:
 MOL/CC         4.4037-02
 GM/CC          0.7933
AVG MW         18.0153
```