ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DYNAMIC CONTROL OF ALTERNATIVE BIOETHANOL PURIFICATION PROCESSES

M.Sc. THESIS

Damla Gizem ARSLAN

Department of Chemical Engineering

Chemical Engineering Programme

Thesis Advisor: Assoc. Prof. Devrim Barış KAYMAK

DECEMBER 2015

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ALTERNATİF BİYOETANOL SAFLAŞTIRMA PROSESLERİNİN KONTROLÜ

YÜKSEK LİSANS TEZİ

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ARALIK 2015

Damla Gizem ARSLAN, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **506131011**, successfully defended the **thesis** entitled **"Dynamic Control of Alternative Bioethanol Purification Processes",** which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 26 November 2015
Date of Defense : 24 December 2015

To my family,

FOREWORD

To start, I would like to thank to my supervisor Doc. Dr. Devrim Barıs KAYMAK for his suggestions, encouragement, support and guidance in writing my thesis. He was always behind me with his technical and moral advices during my thesis study. I feel myself lucky due to that I met with his and was a part of ITU-family.

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December 2015

Damla Gizem Arslan
(Chemical Engineer)

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ABBREVIATIONS

AD : Azeotropic Distillation
AKI : Anti-Knock Index
ED : Extractive Distillation
C : Column
CAFE : Corporate Average Fuel Economy
CLR : Conventional Separation Sequences with Liquid Recycle
CVR : Conventional Separation Sequences with Vapor Recycle
DMF : Dimethylformamide
EISA : Energy Independence and Security Act
EPA : Environmental Protection Agency
HIAG : Holz Industrie Acetien Geselleschaft
HK : Heavy Key
HHK : Heavy Heavy Key
IL : Ionic Liquid
IMC : Internal Model Control
LK : Light Key
MON : Motor Octane
OD : Ordinary Distillation
PDMS : Polydimethylsiloxane
PDMS-PS IPN : Polydimethylsiloxanepolystyrene Interpenetrating Polymer Network
PG : Polyglycerol
PI : Proportional Integral
PTMSP : Poly(1-trimethylsilyl-1-propyne)
PVA : Poly Vinyl Alcohol
RFA : Renewable Fuels Association
RON : Research Octane
SSVR : Side Stream Vapor Recycle
SVD : Singular Value Decomposition
TC : Temperature Controller
VLE : Vapor–Liquid Equilibrium
VMD : Vacuum Membrane Distillat

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Kc : The controller gain (proportional gain)
τ_I : Integral time

DYNAMIC CONTROL OF ALTERNATIVE BIOETHANOL PURIFICATION PROCESSES

SUMMARY

Bioethanol is an alternative fuel obtained generally by biochemical reaction of biomass. Bioethanol is produced efficiently and economically with cleaning, extraction, treatment, saccharification, fermentation, distillation and dehydration steps of sugarcane, corn, wheat and cellulose, simultaneously.

Ethanol can be used as raw material, additives and solvent, such as cosmetics, sprays, perfumery, paints, medicines, food, varnishes and explosives industries. Therefore, ethanol produced from biomass is regarded as the fuel of the future. Due to the fact that ethanol has important advantages like it is produced from renewable energy sources that are environmentally beneficial; it has the lower greenhouse gas emissions than gasoline. Ethanol has also a higher octane number, wider flammability limits, and higher heats of vaporization than gasoline. Furthermore, it can be used as additive with gasoline and also used directly. On the contrary, the major disadvantages of ethanol are including lower energy density, lower vapor pressure and miscibility with water.

Several alternative processes are applied to produce bioethanol: ordinary distillation, pervaporation, adsorption, pressure-swing distillation, extractive distillation, azeotropic distillation, liquid–liquid extraction, adsorption as well as hybrid methods combining these options.

In this thesis, the simulation and control of bioethanol production processes using extractive distillation method are studied. The thesis consists of two stages. In the first stage, the processes selected are simulated in Aspen Plus using the data in the relevant article. Three bioethanol separation processes formed by Errico et al have been selected. The first one is a four-column configuration which includes the preconcentrator column, the extractive distillation column, the solvent recovery column, and the concentrator column. In first column, fermentation broth is converted into the azeotropic mixture, and also the mixture is sent to the second column to produce pure ethanol using ethylene glycol as a solvent. While this is obtained from the distillate of the second column,the bottom of the column is sent to the next column for solvent recovery. A small amount of fresh solvent is added as make up to prevent any losses of solvent during this recycle. The distillate of the solvent recovery column is separated as water and an azetropic mixture and also the mixture is turned back to the first column in the last column.

The second configuration is called conventional separation sequences with liquid recycle (CLR) and also consists of three columns: preconcentrator, extractive and solvent recovery column. While the same sequences occurs in both preconcentrator and extractive column, changes are made in the solvent recovery column. The

solvent is obtained from the bottom of the solvent recovery column and is turned to the second column (extractive column) not to the first column.

The last configuration is called SSVR, includes two column: preconcentrator column and extractive column. The preconcentrator column is performed same in the other processes. In the extractive column, , pure ethanol is obtained from the distillate, the solvent is recovered at the bottom. The vapor side stream includes a mixture of water and ethanol and also is turned to the preconcentrator column.

Before being sent to Aspen Dynamics, column sizing is applied to the columns of these three structures to determine the diameter and length of the vessel. Then, the procedure for “exporting” is performed.

Three process control structure has been established by examining the control structure in the literature. In the control structures of four column and three column configurations: reflux drum levels for all columns are controlled by manipulating the distillate flow rates in the first configuration. In the CLR and SSVR, the control of the partial condenser is applied. The base levels for all columns except the solvent recovery column are controlled by manipulating the bottoms flow rates. The base level for recovery column is controlled by manipulating the makeup flow rate. The top pressures of both columns are controlled by manipulating the corresponding condenser duties. The entrainer flow rate is ratioted to the azeotropic feed and the ratio is controlled by manipulating the bottoms flow rate of the recovery column. Reflux ratios are held constant in each column at their nominal values during disturbances. The fresh feed to the preconcentrator column is flow control in order to guarantee the constant flowrate. The entrainer feed temperature is controlled by manipulating cooler duty. The reboiler duties of both columns are used to control the temperature in a particular stage of each column.

In the two column process, reflux drum level for extractive column is controlled by manipulating the distillate flow rate. The reflux drum level for preconcentrator column is controlled by manipulating reflux. The base level for preconcentrator column is controlled by manipulating the bottoms flow rates. The base level for second column is controlled by manipulating the makeup flow rate. The top pressures of both columns are controlled by manipulating the corresponding condenser duties. The entrainer flow rate is ratioted to the azeotropic feed and the ratio is controlled by manipulating the bottoms flow rate of the recovery column. Reflux ratio is held constant in extractive column at their nominal values during disturbances. Distillate flow rate of the preconcentrator column is ratioed to the reflux flow rate. The fresh feed to the preconcentrator column is flow control in order to guarantee the constant flowrate. The entrainer feed temperature is controlled by manipulating cooler duty. The reboiler duties of both columns are used to control the temperature in a particular stage of each column. The temperature of the vapor sidestream is controlled by manipulating the bottom of the second column.

After the design of the structures, two type distorbances are given to the processes: ethanol composition disturbances and Fresh feed flow disturbances. Ethanol composition disturbances, from 5 to 6 mol% ethanol and from 5 to 4 mol% ethanol, for 10 hours. Therefore, fresh feed flow disturbances of ±20% are applied for 10 hours. The results are recorded and shown by using MATLAB. Dynamic responses of the all systems are given in the Figures. The designed three control structures are affected from disturbance with small changes and soon stabilize and so the systems give good dynamic behaviours.

ALTERNATİF BİYOETANOL SAFLAŞTIRMA PROSESLERİNİN KONTROLÜ

ÖZET

Biyoetanol, biyokütleden biyokimyasal bir reaksiyonla genel olarak elde edilen alternatif bir yakıttır. Biyoetanol; temizleme, ekstraksiyon, işleme, sakarifikasyon, fermantasyon, damıtma ve dehidrasyon adımları ile üretilir. Etanol hammadde, katkı maddeleri ve çözücü olarak da kullanılabilir. Bu nedenle, biyokütleden elde edilen etanol geleceğin yakıtı olarak kabul edilmektedir. Avantajlarından en önemlisi çevre açısından yararlı olan, yenilenebilir enerji kaynaklarından üretilmesidir, bunun nedeni; benzinden daha düşük sera gazı emisyonlarını açığa çıkarmasıdır. Etanol aynı zamanda yüksek oktan sayısına, geniş yanıcılık sınırlarına ve benzinden daha yüksek buharlaşma ısıları vardır. Buna ek olarak, benzin katkı maddesi olarak kullanılabilir ve hatta doğrudan kullanılabilir.

Tez iki aşamadan oluşmaktadır. İlk aşamada, seçilen üç biyoetanol ayırma prosesi Aspen Plus’ta simüle edilmiştir. Proseslerin ilki ön yoğunlaştıncı kolon, ekstraktif kolon, solvent geri kazanım kolonu ve yoğunlaştırıcı kolonu içeren dört kolonlu bir prosestir. Birinci kolonda, fermentasyon suyundan % 85 etanol ve % 15 su içeren karışım elde edilirken, saf etanol üretmek için etilen glikol ikinci kolona gönderilir. İkinci kolonun distilatından susuz etanol elde edilirken, kolonun dip akımı çözücü geri kazanımı için bir sonraki kolona gönderilir. Solventin küçük bir miktarının, bu geri dönüşüm sırasında kaybını önlemek için telafi olarak makeup eklenir. Solvent geri kazanım kolonundan su ve azetropik karışım elde edilir. Buradaki azeotropik karışım ilk kolona geri gönderilir.

Ikinci proses (CLR), üç kolondan oluşmaktadır: ön yoğunlaştıncı kolon, ekstraktif kolon, solvent geri kazanım kolonu. Dört kolonlu sistemden farkı bir kolon indirgenmesi bunu takiben üçüncü kolonun distilatının birinci kolona gönderilmesidir. Son proses SSVR denilen iki kolonlu prosestir. Burada ön derişiklendirme kolonu aynı çalışırken ekstraktif kolon buhar yan akımına sahiptir ve

bu akımla birinci kolna dönüş yapar. Ektraktif kolonun distilatı saf etanol içerirken; dip akım solvent içerir ve sisteme geri beslenir.

Aspen Dynamics'e gönderilmeden önce gerekli kolon boyutlandırılmaları yapılarak yapılar Aspen Dynamics'e gönderilir. Yeterli literatür araştırması sonucunda proseslere kontrol yapıları kurulmuştur. Yapılara ± %20 besleme akış ve %0.4 ve %0.6 mol besleme kompoziyonu distürbansı uygulanmaktadır ve veriler 10 saat boyunca toplanmaktadır. Elde edilen veriler sonucu MATLAB'te grafikler oluşturularak incelenmiştir. Sistemlerin distürbanslara karşı verdiği cevaplar çok düşük değişimlere sahiptir ve kısa zamanda yatışkın hale ulaşmıştır. Sonuç olarak her üç yapının da dinamik davranışlarının iyi olduğu gözlemlenmiştir.

1. INTRODUCTION

Today, alternative energy resources are remarkably important for different fields such as transport, industrial processes, and heating. The shortage of fossil fuels, the increase in their price and also greenhouse gases, like CO_2, SO_2, NO_x, etc., of fossil fuels which leads to the global warming inrease the interest in the alternative energy resources (Valencia-Marquez, et. al., 2011). For these reasons, several renewable, clean and cheap alternative energy sources are developed. Biofuels, such as bioethanol and biodiesel, are one of these energy sources obtained from biomass and they have two important advantages. The first one is the production from renewable sources, the other one is that it reveals less emissions than fossil fuels (Martínez, et. al., 2011).

Bioethanol is the most promising alternative energy source for transport, industrial processes, and heating. The simple integration with gasoline as a mixture is the most important advantage and in addition to this bioethanol does not need alteration about engines (Kiss and Ignat, 2012).

The production of ethanol is performed from sugar cane, corn, lignocellulosic biomass and integrated lignocellulosic biomass. Anhydrous ethanol is generally used as raw material, solvent or fuel. The most commonly ethanol dehydration processes carried out in order to obtain anhydrous ethanol are: ordinary distillation, azeotropic distillation, extractive distillation, liquid-liquid extraction, adsorption, pressure swing distillation, membrane separation or using some complex hybrid separation methods (Vázquez-Ojeda, et. al., 2012).

Extractive distillation is generally used in the chemical industry. In this processes, entrainer which is the heaviest component is added and it provides no formation of azeotropes by increasing the relative volatility of the key components. When an applicable solvent is used, the process has high product purity and low energy consumption. For bioethanol dehydration process, the use of ethylene glycol as a solvent in the extractive distillation is very popular due to low energy consumption and capital cost (Li and Bai, 2012).

In this thesis, the design and control of extractive distillation processes is investigated to obtain anhydrous ethanol using glycerol. Extractive distillation method is selected for dehydration of bioethanol. Three distillation structures, constituted from the simple to the complex, are designed at steady state. After determining the appropriate control structures, dynamic responses are investigated with feed flow and feed composition disturbances.

2. BIOETHANOL

2.1 What is Ethanol?

Ethanol is one of the most important members of alcohols. It is also known as ethyl alcohol or grain alcohol, and it can be shown as in Figure 2.1:

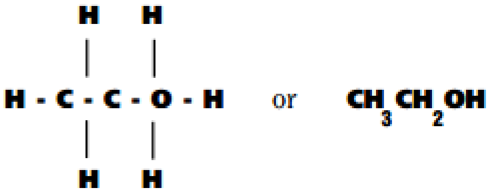


Figure 2.1 The Structure of Ethanol (Bakar, 2008).

Ethanol is colorless, volatile, flammable and also has a characteristic smell. When ethanol is pure, it boils at 78° C (172° F) and freezes at -112° C (-170° F) (Bakar, 2008). It reveals a pale blue flame when burning ethanol and it does not deposit. Moreover, a significant amount of energy is released, and this makes ethanol an ideal fuel.

Ethanol is easily miscible with water and most organic solvents so while making substances such as cosmetics, sprays, perfumery, paints, medicines, food, varnishes and explosives, ethanol is used as solvent and additives. Ethanol is also used in the chemical industry as a raw material in chemical synthesis of esters and ethers (Vázquez-Ojeda, et. al., 2012). In addition, there are three basic ways that ethanol can be used as fuel:

- As a mixture of 10 percent ethanol and 90 percent unleaded gasoline called "E-10 Unleaded",
- As reformulated gasoline component,
- As a mixture of 85 percent ethanol and 15 percent unleaded gasoline called “E-85” (Balat and Balat, 2009).

2.2 History

In the 1800s, ethanol was used as lamp fuel in the United States. During the Civil War the government has put a tax for ethanol. This tax has caused great damages to the ethanol industry. With the abolition of the tax in 1906 the use of ethanol improved well. However, this situation did not take a long time. Because of the competition of big companies, ethanol use was again in the fall (Otulugbu, 2012).

The first far-reaching use of ethanol as fuel occurred in the early 1900s, while Europe had less resources. Henry Ford's Model T automobile and automobiles in early 1920 were designed to run on alcohol fuels in U.S. During World War II, both Germany and U.S. have used ethanol for their armies. After the war, the use of ethanol has declined with the fall in oil prices. The limited use of ethanol continued until the oil crisis of the 1970s (Solomon, et. al, 2007). Since the late 1970s the use of ethanol has increased as a fuel. Ethanol was first used as a gasoline additive due to the oil shortages. In 1973, Petroleum Exporting Countries Organization (OPEC) increased prices and blocked the crude oil shipments to the US so this led to gasoline shortages. OPEC then drew attention to the world's dependence on oil. Thereupon again increased interest in alternative fuels such as ethanol. It is called “gasohol” gasoline containing ethanol. After the end of the oil shortages, the use of ethanol-blended gasoline was continued. "E-10 Unleaded" and "super unleaded" are the names used today (Sorda, et. al., 2010).

2.3 Advantages and Disadvantages

Ethanol is regarded as the fuel of the future due to its many advantages. The most important one is: it is produced from renewable energy sources that are environmentally beneficially. In other words ethanol improves the quality of the environment (Shirsat, et. al., 2013).

Engines using ethanol as fuel have many advantages. For instance, ethanol raises the octane number (Table 2.1) which allows a higher compression ratio and shorter burn time. Therefore, ethanol increases motor efficiency, improves gas mileage, provides better acceleration and also improves starting qualities. Many high-performance racing engines work with pure alcohol. Because when they use ethanol mixtures, valve burning drops. (Balat and Balat, 2009).

Table 2.1 Ethanol's Octane Content Compared to Other Gasoline Components.

	Gasoline	n-Butane	Isobutanol	Benzene	Ethanol
Research Octane (RON)	92	91	105	101	109
Motor Octane (MON)	83	92	90	99	90
Anti-Knock Index (AKI)	87.5	91.5	97.5	100	99.5

Ethanol allows adjustments for gasoline additive. Certain chemicals such as olefins used to produce gasoline causes deposits on port fuel injectors. The solution of this is to add detergent additives to gasoline. Thus, fuel injectors and valves deposition are blocked (Lang, et. al., 2001).

Ethanol is also antiknock agent as well as engine cleansing agent by absorbing moisture and cleaning the fuel system. It keeps the engine clean in new vehicles. It also solves contaminants and residues in older vehicles. These substances dissolved are collected in the fuel filter and can be easily retrieved from this filter.

All alcohols have the water absorption property. When mixed with gasoline, alcohol absorbs water in the fuel system and fuel system does not allow water to collect and freeze. Hence, addition of at least 10 wt % ethanol to fuel eliminates the necessary to antifreeze for cold weather. Participation of ethanol to fuel provides fuel savings and also improves the combustion of the fuel. Thus, the amount of carbon monoxide released into the environment is reduced (Frolkova and Raeva**,** 2009).

Bioethanol blended with gasoline extends crude oil usage, reduces dependence on oil imports and helps lessen the increasing oil prices (Huang, et. al. 2008).

Bioethanol has less energy density than gasoline. In addition to this, bioethanol has corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult), miscibility with water, toxicity to ecosystems, and also it increases in exhaust emissions of acetaldehyde, and increases in vapor pressure (and evaporative emissions) by blending with gasoline. These are the disadvantages of bioethanol (Balat and Balat, 2009).

2.4 Ethanol and the Environment

One of the main reasons of air pollution is the vehicle exhaust. The use of cleaner fuels provide remarkable results and can be used as a solution. Ethanol-blended gasoline which can be used as cleaner fuel is an oxygenated fuel (Tavan and Hosseini, 2013).

Crude oil is composed of hydrocarbons. Petroleum and gasoline also consist of more than 250 hydrocarbon mixtures. Most of them are poisonous even some of them are carcinogens such as benzene. Hydrocarbons filling the gas tank, during working of the vehicle from the vehicle's gas tank and the carburetor and also from the engine exhaust are released. Evaporating hydrocarbons from gasoline called volatile organic compounds and if not checked, 30-50 per cent of the total hydrocarbon emissions of air caused by transportation. Another damage of hydrocarbons on earth is to contribute the form of ozone. However, ethanol does not constitute hydrocarbons while burning since ethanol is an alcohol.

Ozone is formed by the reaction of hydrocarbons and nitrogen oxides in the air in the presence of sunlight. Because of this reaction, photochemical smog consists. The content of photochemical smog are together with a large amount of ozone, acrolein, formaldehyde and various radicals. Therefore, sometimes photochemical smog is called ozone. Photochemical smog is seen as the brown haze and when the accumulation of smog occurs in air this increases the air temperature. The increase of ozone in the atmosphere damages to human respiratory system, plants and crops. This ozone does not increase the ozone in the stratosphere which prevents harmful ultraviolet rays of the sun. According to the studies, the amount of ozone formed by ethanol blends is almost the same as the amount of ozone formed by gasoline.

Aldehyde emissions released by burning ethanol blends are a little greater than those released while burning gasoline alone. However, this amount is extremely small and also according to the Royal Society of Canada the possibility of adverse health effects of the released aldehyde emissions from ethanol blends is far.

Carbon monoxide caused by the lack of complete combustion is a poisonous gas. Carbon monoxide is formed by the combustion of fuel petroleum in the absence of oxygen. Especially, if an excessive amount of fuel-air mixture is sent to the engine and burned, it produced. Therefore, the combustion becomes more complete by adding ethanol containing oxygen, and it decreases the amount of released carbon monoxide. According to the car type and age, and also depending on the emission system and the atmospheric conditions this reduction may reach up to 30 percent.

Nitrogen oxides (NOx) occur due to the combustion at high temperatures and cause the formation of photochemical smog. The addition of ethanol to gasoline likewise reduces nitrogen oxide emissions because ethanol is an oxygenated fuel containing 35% oxygen. In some studies carried out by the Environmental Protection Agency (EPA), it is shown that the use of ethanol slightly increases NOx emissions. However, this is not certain (Balat and Balat, 2009).

Unlike other gases, carbon dioxide is not toxic but it causes the greenhouse effect. All petroleum derivatives exposes carbon dioxide gas and increases the carbon dioxide level in the air. However, renewable fuels such as ethanol-blended fuels do not increase the carbon dioxide levels. Because the carbon dioxide, which releases when ethanol-blended fuel uses, is used to produce ethanol by plants so equilibrium is achieved (Shirsat, et. al., 2013).

2.5 Ethanol in the World

The world fuel ethanol production is indicated in Figure 2.2. Nearly 75 percent of the ethanol produced in the world is used as fuel ethanol. Fuel ethanol is mainly bioethanol obtained from enzymatic processes.

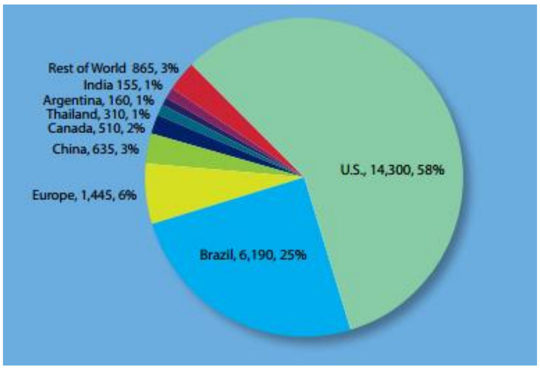


Figure 2.2 2014 Global Fuel Ethanol Production, (Country, million gallons, share of global production) (RFA, 2015).

Bioethanol is only obtained for fuel in the countries. The production of biofuels 2000-2013 and shares 2014-2022 are shown in Figure 2.3.

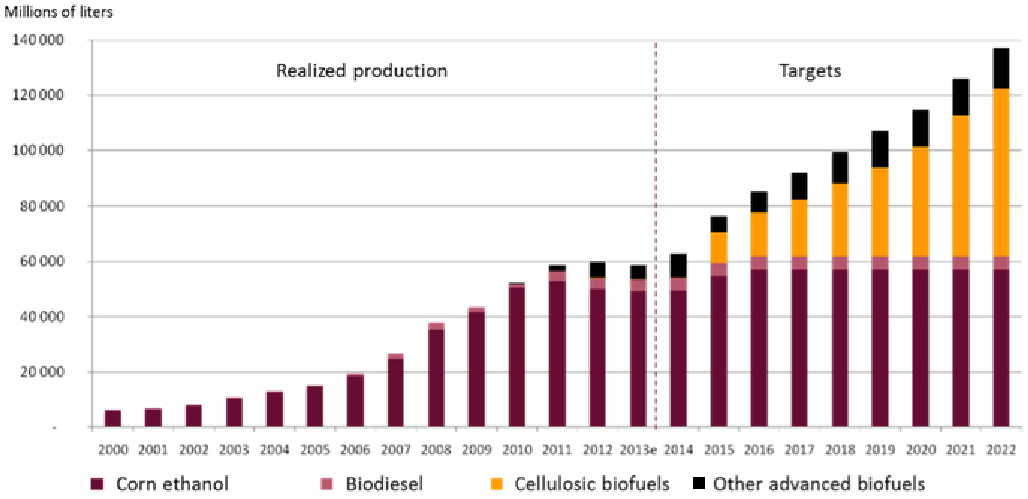


Figure 2.3 Biofuels Production 2000-2013 and Shares 2014-2022.

Especially the U.S., Brazil, Canada, some EU countries, India and China continue to improve ethanol production. In many countries, the governments provide support for biofuels and also America and the European Union provide additional support for the production of ethanol. This support includes tax credits and regulations which consist of the obligatory use of biofuels.

In the United States, the production and use of biofuels, especially bioethanol produced from corn, started in the early 1980s. The aim of this is widely to refresh the farming sector. Nationally, the Energy Policy Act of 2005 (EPAct 2005) is one of the most important steps. Besides, additional incentives for cellulosic bioethanol are given for both big and small bioethanol producers. In 2007, the US Congress passed and the President signed the Energy Independence and Security Act of 2007 (EISA) to help to improve vehicle fuel economy and decrease dependency on foreign oil sources. As a result of Congress, new fuel and vehicle fuel economy standards (Corporate Average Fuel Economy [CAFE] standards) are accepted as part of the EISA (Balat and Balat, 2009). Today, over 95% of ethanol production comes from corn, with the rest made from wheat, barley, cheese whey, and beverage residues in the United States (Mussatto, et. al., 2010).

Brazil and Sweden also prefer to use ethanol as a fuel significantly. Brazil has the most advanced and combined biofuels program in the world. Its history dates back to the oil crisis of the 1970s when the National Alcohol Fuel Program (ProAlcool) was started. Ethanol is obtained mainly from sugar cane in Brazil. Now, more than 80% of Brazil's current automobile production has flexible-fuel capability, up from 30% in 2004. Brazilian consumers now choose mainly between anhydrous bioethanol/gasoline and a 25% bioethanol/gasoline mixture. Pure ethanol is used in 40 percent of vehicles. The 76 percent gasoline and 24 percent ethanol is used in other vehicles. Furthermore, Brazil is not only producing ethanol for consumption but also is exporting to other countries (Sorda, et. al., 2010).

In Europe, wheat and sugar-beet are used to obtain the major amount of ethanol. In the European Commission's view, the use of biofuels will advance energy supply security, decrease greenhouse gas emissions, and improve rural incomes and employment. For example, France set up an ambitious bio-fuels plan, with goals of 7% by 2010, and 10% by 2015 and also Belgium set a 5.75% target for 2010 (Balat and Balat, 2009). In Sweden, ethanol is used in the chemical industry for decades. Therefore, the use of ethanol as a fuel has expanded rapidly. First decline in crude oil consumption was observed. Later reduction in gasoline and diesel use were observed (Su, et. al., 2015).

India began to use ethanol with 10 percent and 15 percent ethanol additive. In 2003, the Planning Commission of the Government brought out an extensive report on the development of biofuels and bioethanol (Mussatto, et. al., 2010). Although India has a huge population to feed and limited land availability, it carries out to develop bio-ethanol technologies which use biomass feedstock that does not have food or feed value. The most suitable bioethanol technology for India is production from lignocellulosic biomass, such as rice straw, rice husk, wheat straw, sugarcane tops and bagasse (Sukumaran, et al., 2010).

New bioethanol facilities have been operated in Columbia, Central America, Turkey, Pakistan, Peru, Argentina, and Paraguay.

3. BIOETHANOL SEPARATION PROCESSES

3.1 How is Ethanol Obtained?

Ethanol is a product which is mostly a result of fermentation of substances such as sugar cane and corn. Sugar produced in fermentation substitutes for ethanol and carbon dioxide. In other words, fermentation is a series of reactions in the absence of oxygen, which releases energy from organic substances (Gaykawad, et. al., 2012).

For example, ethanol obtainment from the fermentation of corn consists of many steps. First operation applied to corn is chewing the corn. Later operation applied to corn cooking the corn and adding the enzymes accelerating chemical changes alpha amylase and gluco amylase. Because before fermentation, the starch in the corn is necessary to turn into simple sugars. Yeast is then added to the simple sugars obtained. Yeast is a single-celled fungus that causes fermentation. Also yeast feeds on the sugar and when yeast feeds on the sugar it produces alcohol (ethanol) and carbon dioxide (Prasad, et. al., 2007).

There are three basic types of ethanol production from biomass. The first of these ethanol from sugar cane, secondly ethanol from corn, then ethanol from lignocellulosic biomass and ethanol from integrated lignocellulosic biomass (Kiss and Suszwalak, 2011).

3.1.1 Ethanol from sugar cane

Ethanol production from sugarcane contains these steps: cleaning of sugarcane and extraction of sugars; juice treatment, concentration and sterilization; fermentation; distillation and dehydration. A detailed description of these steps is shown in Fig. 3.1.

A dry–cleaning system is used to remove the dirt dragged along with the sugarcane from the fields. Sugar extraction is performed using mills to enhance sugar recovery. Sugarcane juice and bagasse are gained in the mills. Sugarcane juice contains sugar and it is sent to the juice treatment operations; bagasse contains 50% humidity and it is burnt in boilers for generation of steam and electrical energy.

Sugarcane juice contains impurities, such as minerals, salts, acids, dirt and fibre, besides water and sugars. Therefore physical and chemical treatments are used to remove these impurities. While in the physical treatment, screens and hydrocyclones are used to remove fibre and dirt particles; in a subsequent chemical treatment, phosphoric acid is used to raise juice phosphates content and impurities removal (Chen and Chou, 1993).

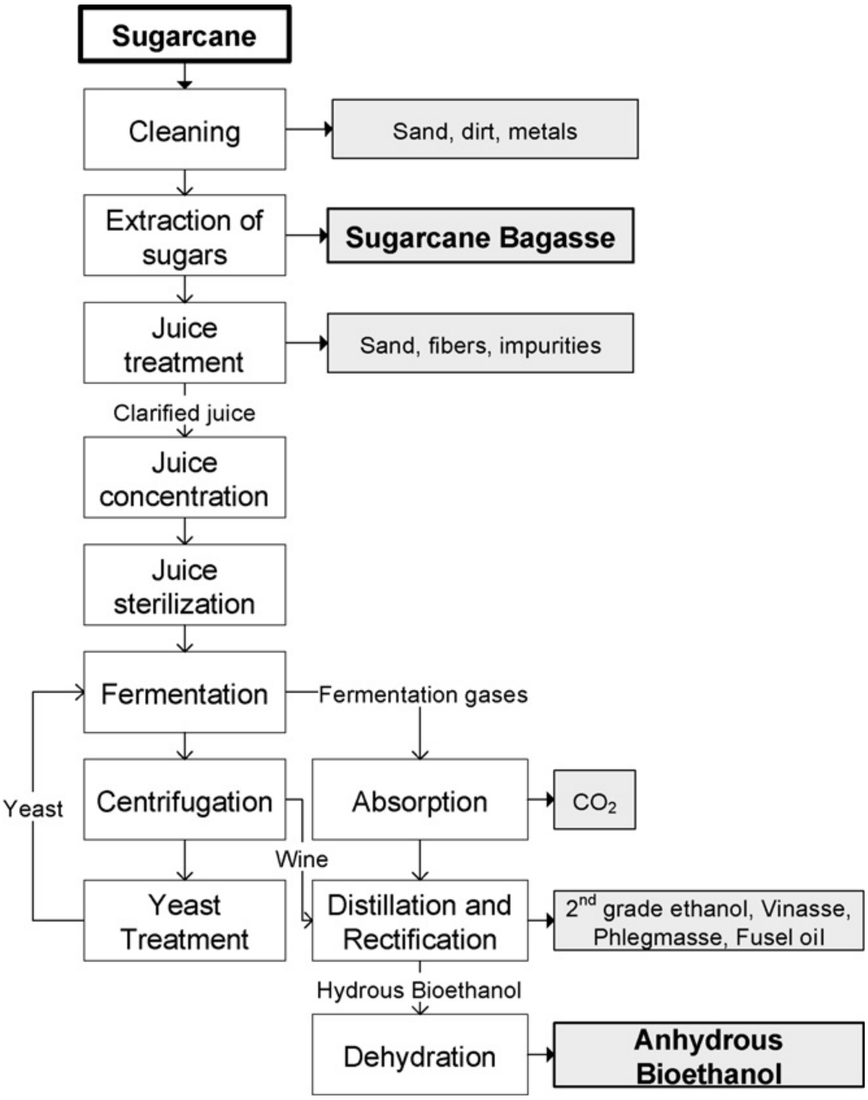


Figure 3.1 Block Flow Diagram of the Conventional Bioethanol Production Process from Sugarcane (Dias, Ensinas, et. al., 2009).

The next operation performs in the settler where two streams (mud and clarified juice) are obtained. Clarified juice must be concentrated before fermentation because it contains about 15 wt.% diluted solids. Then, in the fermentation, sucrose is hydrolyzed into fructose and glucose, then they are converted into ethanol and carbon dioxide. Two streams are obtained, wine and gases, in the fermentation operation. Fermentation gases are sent to an absorber column to obtain evaporated ethanol, and wine is centrifuged to recover yeast cells. Centrifuged wine is added the alcoholic solution from the absorber and then sent to the distillation unit. After the distillation and dehydration process, anhydrous ethanol is obtained (Dias, Ensinas, et. al., 2009).

3.1.2 Ethanol from corn

The conversion of starch in the corn to sugar and then transformation these sugars to ethanol is a complex process. For the implementation of the process and development chemistry, engineering and microbiology are needed.

There are two standard processes for ethanol produced from corn (Figure 3.2). Both of these processes are used for commercial production. These are: wet milling and dry milling. Dry milling factories to build cost less and also the yield of ethanol obtained from this process is higher (2.7 gallons per bushel of corn). However, the crop of co-products is lower. In the wet milling process, high-value co-products are produced such as fiber, germ and gluten by pre-processing before fermentation of ethanol. Therefore this process requires more capital and energy (Huang, et. al., 2008).

The most used microorganism is Saccharomyces cerevisiae because of its ability to hydrolyze cane sucrose into glucose and fructose which are hexoses. Though this microorganism can grow under anaerobic conditions; for the production of substances like fatty acids and sterols, small amounts of oxygen are needed. So aeration is an significant factor for growth and ethanol production by Saccharomyces cerevisiae. Another yeast is Schizosaccharomyces pombe which has advantages about toleration high osmotic pressures (high amounts of salts) and high solids content. In the class of bacteria, the most used microorganism is Zymomonas mobilis, which has a low energy efficiency and also a higher ethanol yield (up to 97% of theoretical maximum). However, its range of fermentable sugar is too limited (glucose, fructose and sucrose) (Sánchez and Cardona, 2007).

Dry Milling

This method is used in many factories in countries. The basic steps of dry milling:

1. Milling: Corn (or other grain or biomass) after cleaning is passed through hammer mills to become a fine powder.

2. Liquefaction: Wherein the starch is liquefied. Firstly, the meal which is unscreened coarse flour is mixed with water and an enzyme (alpha amylase), then it is passed through furnaces. The purpose of the furnaces is to perform the liquefaction. Furnaces used with a high temperature (120º-150º C) stage are utilized. High temperatures reduce levels of bacteria in the mixture. Sulfuric acid or sodium hydroxide is used to keep pH 7.

3. Saccharification: The mixture called mash comes from the furnaces and is cooled. Then gluco amylase enzyme is added for the conversion of sugar i.e., dextrose to starch molecules.

4. Fermentation: Yeast is added to the mixture to convert the obtained sugar to ethanol and carbon dioxide. In the continuous process, the mixture flows through many fermenters until completely fermented then the mixture exits the tank. In the batch system, about 48 hours the mixture remains in a single fermenter (Dias, Modesto, et. al., 2010).

5. Distillation: The fermented mash called beer includes about 10 percent alcohol. The other contents of mash are non-fermentable solids from the corn and the yeast cells. The fermented mash is then sent to the multi-column distillation system with continuous flow. In the distillation system alcohol is removed from the solids and water. While alcohol is taken from the top of the last column, the residue mash called stillage is taken from the bottom of the column and is sent to the co-product processing area.

6. Dehydration: Alcohol obtained from the distillation is sent to the dehydration system to remove the remaining water. After dehydration, alcohol is called anhydrous i.e. without water ethanol, and its alcoholic strength is approximately 200.

7. Denaturing: Ethanol that is used for fuel is then denatured with a small amount (2-5%) of some product, such as gasoline, to make it unfit for human consumption (Naser, 2014).

Wet Milling

This process is more complex. Because the grain needs to be separated into its component. After milling, the corn is heated for 24 to 48 hours in the solution of water and sulfur dioxide. Its purpose is to solve the germ and hull fibers.

The germ is then removed from the kernel, and also corn oil is extracted from the germ. The remaining germ meal which is unscreened coarse flour is added to the hulls and fiber to produce corn gluten feed. The corn gluten comes from the separation of a high-protein portion of the kernel and also is used for animal feed. After the separation of gluten and starch, the same steps, saccharification, fermentation, distillation and dehydration of ethanol, etc., occur. Only starch is fermented in wet milling contrast to the dry milling.

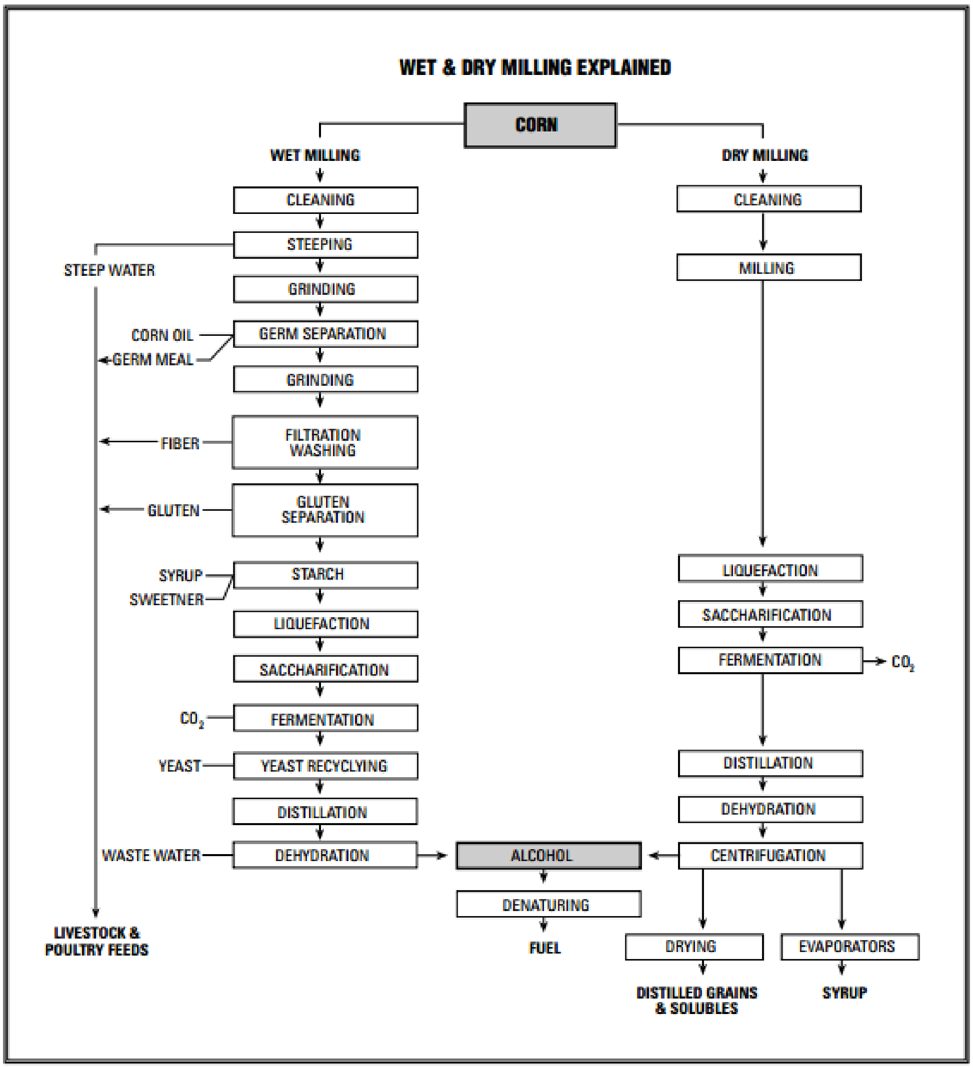


Figure 3.2 Dry Milling and Wet Milling (Huang, et. al., 2008).

3.1.3 Ethanol from lignocellulosic biomass

Lignocellulosic biomass is the most plentiful biopolymer in the Earth. Lignocellulosic biomass sources used in ethanol production are agricultural residues (such as corn stover, crop straws, sugar cane bagasse), herbaceous crops (such as alfalfa, switchgrass), forestry wastes, wood (hardwoods, softwoods), waste paper and other wastes (such as municipal waste) (Gaykawad, et. al., 2012).

Although lignocellulosic or cellulosic biomass to ethanol process has a great development, it has not been commercialized yet due to technical, economic and trade barriers. Ethanol from lignocellulosic biomass is more effective and hopeful than ethanol from corn. Because it reduces the net greenhouse gas emissions like ethanol from corn process (Mussatto, et. al., 2010).

Ethanol from lignocellulosic biomass process is composed of eight main steps as shown Figure 3.3. These are respectively: feedstock handling, pretreatment and conditioning/detoxification, saccharification and co-fermentation, product separation and purification, wastewater treatment, product storage, lignin combustion for production of electricity and steam, and all other utilities (Gaykawad, et. al., 2012).

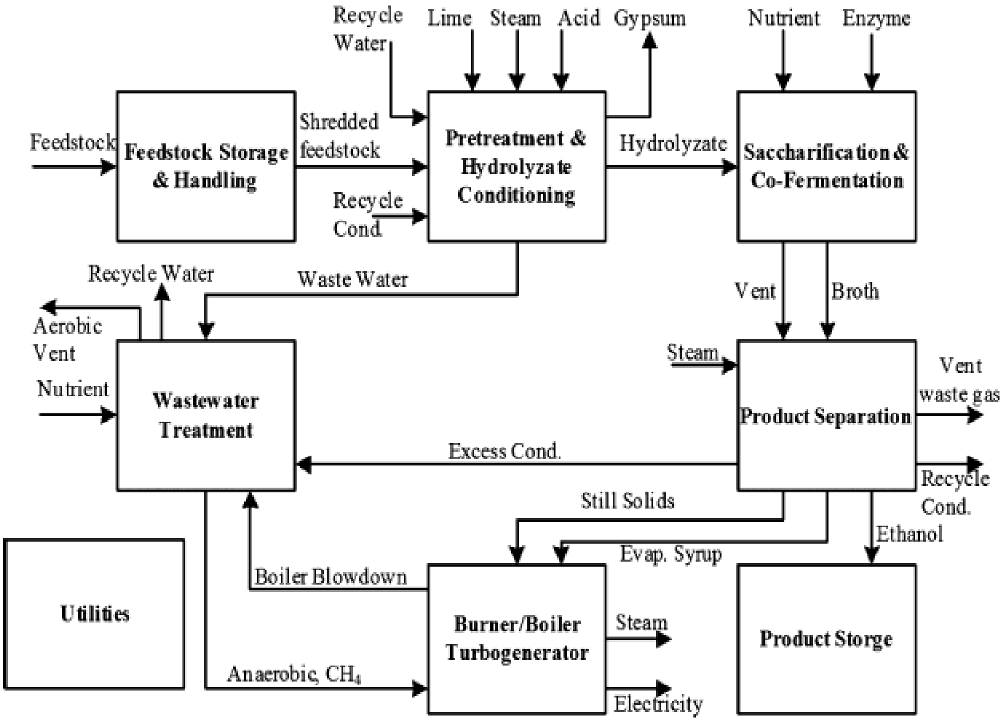


Figure 3.3 Ethanol from Lignocellulosic Biomass Process (Huang, et. al., 2008).

The aims of pretreatment are to increase pore size and decrease cellulose crystallinity. While the hemicellulose layer is hydrolyzed in acid-catalyzed pretreatment, in alkali catalyzed pretreatment a part of the lignin is moved away and hemicellulose is hydrolysed by the use of hemicellulases. Therefore, pretreatment is required to reveal the cellulose fibres to the enzymes or to make the cellulose more reachable to the enzymes. An efficient pretreatment can essentially reduce the enzyme requirements leading to the production costs.

Unlike corn-based ethanol production, lignocellulose-based production is a complicated fermentation in the presence of inhibiting compounds, such as low molecular weight organic acids, furan derivatives, phenolics and inorganic compounds, which are loosened and produceded during pretreatment and/or hydrolysis of the raw material. The hydrolysis is performed in two stages. The first stage is performed in conditions that prioritizes the hemicellulose hydrolysis, and the cellulose converts into glucose in a second stage (Mussatto et. al., 2010).

The classic configuration used for fermenting biomass hydrolyzates includes a sequential process. In this process, the hydrolysis of cellulose and the fermentation are performed in different units. In the alternative modification, the simultaneous saccharification and fermentation, and the hydrolysis and fermentation are performed in a single unit. After the hydrolysis step, sugars can be transformed ethanol by microorganisms. The most used microorganism for fermenting lignocellulosic hydrolyzates is Saccharomyces cerevisiae, which ferments the hexoses but not the pentoses (Sánchez and Cardona, 2007).

Lignocellulosic raw materials include cellulosic hexose sugars (such as glucose and mannose), and hemicellulosic pentoses (especially xylose and arabinose). The pentoses are not fermented to ethanol by the most generally used industrial fermentation microorganism called the yeast Saccharomyces cerevisiae (Mussatto, et. al., 2010).

As a result, the yeast Saccharomyces cerevisiae is developed to obtain ethanol and some microorganisms are also used for this development. Figure 3.4 shows the development of fermentation of ethanol. Ethanol is then separated from water in the purification (Hahn-Hägerdal, et. al., 2006).

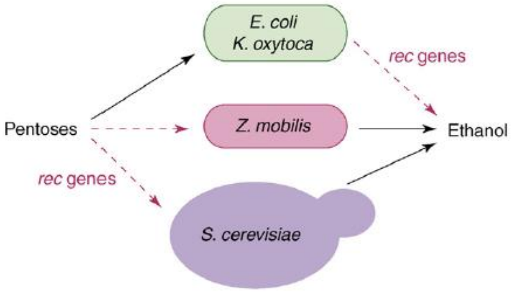


Figure 3.4 The Fermentation of Ethanol (Hahn-Hägerdal, et. al., 2006).

The final ethanol must include less than 0.5 wt % of water for the use as fuel in integration with gasoline, or as oxygenate for gasoline. But ethanol-water mixture composes an azeotrope when a purity of 96 wt % of ethanol is reached, so conventional distillation is not sufficient for purification. Thus, nonconventional methods are necessary to achieve the required ethanol purity (Martínez, et. al., 2011).

3.1.4 Ethanol from integrated lignocellulosic biomass

Forests are an massive source for lignocellulosic biomass. Therefore, an integrated process based on the existing pulp mills have been proposed. The purpose of the process is to produce fuel and chemicals, together with pulp and paper (Figure 3.5).

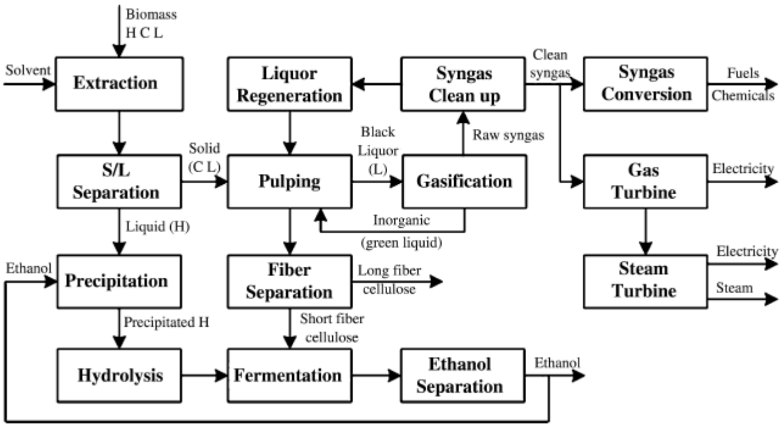


Figure 3.5 Integrated Forest Biorefinery (Huang, et. al., 2008).

This process contains a hemicellulosic sugars pre-extraction before pulping and also the separation of long and short fiber after pulping. While short fiber is converted into ethanol in the bioreactor, the long fiber is used for production of paper and other fiber based materials such as bio-composites in another bioreactor. Furthermore dissolved lignin emerging after pulping can be converted into synthesis gas. The synthesis gas which produced can be used the production of fuel and chemicals and the generation of electricity and steam (Huang, et. al., 2008).

3.2 Recovery of Ethanol and Ethanol Dehydration

Dilute aqueous solutions obtained as a result of fermentation called beer comprises about 5-12 wt % ethanol. A large part of the total energy needs of the process is used to separate ethanol from beer.

Ethanol composes a minimum boiling azeotrope, at 95.6% by weight (97.2% by volume) with water at a temperature of 78.15 °C. It is a prevalent problem for the dehydration of ethanol and even it is impossible to separate ethanol–water in a single conventional distillation column.

Generally, when the mixture comprises 10–85 wt% ethanol, distillation is impressive, but when the mixture comprises more than 85 wt% ethanol, distillation becomes costly. This is because the ethanol concentration in the feed stream is near the azeotropic point (95.6%) and this point requires high reflux ratios and additional equipments, particularly when anhydrous ethanol is needed. Lately, the separation of diluted ethanol-water mixture is generally composed of two major steps: Firstly about 92.4 wt% ethanol is received from a diluted aqueous solution by ordinary distillation, Then ethanol obtained is more dehydrated to obtain anhydrous ethanol by using one of the methods such as ordinary distillation, azeotropic distillation, extractive distillation, liquid-liquid extraction, adsorption, pressure swing distillation, membrane separation or using some complex hybrid separation methods (Kiss and Suszwalak, 2011).

3.2.1 Ordinary distillation

Ordinary distillation (OD) is a generally used for separation of two or more components in a mixture and this process is based on relative volatilities of these components or the difference in their boiling temperatures (Bravo-Bravo, et. al., 2010). The ethanol–water azeotrope can be separated for production of anhydrous ethanol using an ordinary distillation column by only reducing the operation pressure to a vacuum condition like 0.11 atm, but this is an expensive method. For this reason, an ordinary distillation column, also called beer column or pre-concentrator column, is usually used to concentrate dilute ethanol to 92.4 wt%, as pointed out above in biorefineries (Dias, Modesto, et. al., 2010).

3.2.2 Azeotropic distillation (AD)

In azeotropic distillation process A third volatile component which is a lighter component, called entrainer, is used to separate two azeotropic components. The entrainer composes a ternary azeotrope with the two components and thus changes their relative volatilities and lastly changes their separation factor (activity coefficients) in the distillation system. Two components to be split are mainly close boiling components or an azeotropic mixture. Therefore, azeotropic distillation can be used to separate close boiling mixtures or azeotropes (Luyben, 2012).

The azeotropic distillation system generally contains two distillation columns for dehydration of 92.4 wt% ethanol mixture obtained from the ordinary distillation column:

-A dehydration column (azeotropic column) to obtain more concentration in the presence of entrainer.

-An entrainer recovery column (stripping column) to separate entrainer from the product stream (Sun, et. al., 2011).

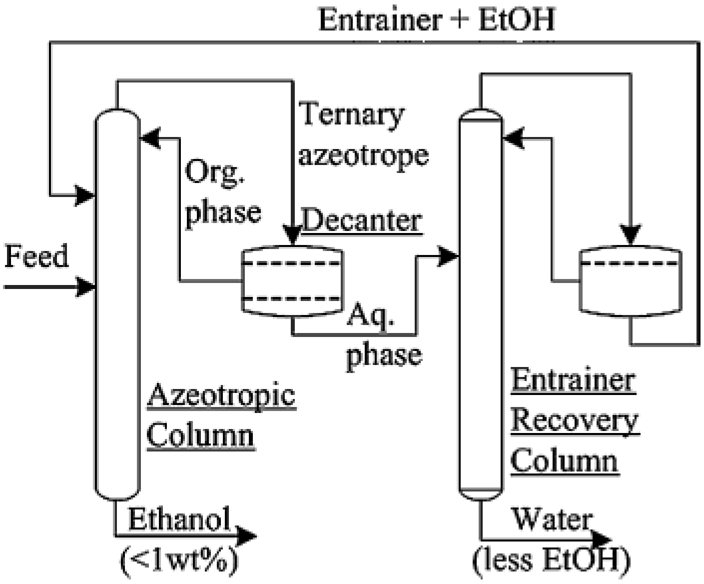


Figure 3.6 Azeotropic Distillation (Huang, et. al., 2008).

In the dehydration column, ethanol (>99 wt%) is taken from the bottoms, whereas water , solvent, and small amounts of ethanol are taken from the top. The top stream is sent a separator, called decanter, and is split into ethanol-entrainer (organic phase) and water-entrainer (aqueous phase) streams. The ethanol-entrainer mixture is refluxed back into the first column, while the water-entrainer mixture is processed in the entrainer recovery column. The process flowsheet is shown in Figure 3.6 (Kiss and Suszwalak, 2011).

The entrainers generally used are benzene, toluene and cyclohexane to separate binary ethanol–water azeotropes by heterogeneous azeotropic distillation. A mixed solvent, for example a mixture of benzene and n-octane can also be used (Shirsat, et. al., 2013). Benzene is an usual entrainer in heterogeneous azeotropic distillation for ethanol dehydration. Despite its carcinogenic impact, benzene has been replaced other solvents for many years. At present, cyclohexane is one of the most used entrainers for separation of ethanol. However, cyclohexane is flammable. Other separation agents are dichloroethane, isobutyl alcohol, butyl acetate, propyl acetate, diethyl ether, diisopropyl ether, cyclohexane, 2,2,4-trimethylpentane, toluene, n-pentane, cyclopentane, methylcyclopentane, n-hexane, 2-methylpentane, hex-1-ene, 2,2-dimethylpentane, and 2,2,3-trimethylbutane (Frolkova and Raeva, 2009).

Azeotropic distillation system including two-columns has many disadvantages. High energy requirement, great capital cost, carcinogenic effect (for benzene) and flammability (for cyclohexane) are these disadvantages. Therefore, azeotropic distillation method is less used in the ethanol production.

3.2.3 Extractive distillation (ED)

Extractive distillation is a notable method to separate binary homogeneous azeotropes. This method is generally studied and is used in the industry (Modla, 2013).

Extractive distillation used to separate two components is a vapor–liquid separation process and also contains the addition of a third component to increase the relative volatility of these components. In the process, a selective high boiling solvent is applied to change the activity coefficients and so increase the separation factor (Huang, et. al., 2008).

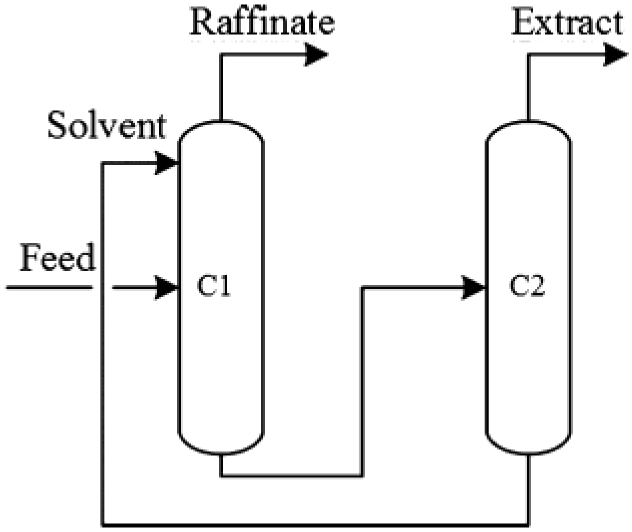


Figure 3.7 Extractive Distillation (Huang, et. al., 2008).

This method needs the least energy with a suitable high boiling solvent called separating agent since the solvent nearly does not evaporate and also is generally used to separate close boiling point or azeotropic mixtures in chemical industry (Frolkova and Raeva, 2009). The third component can be liquid solvent, ionic liquid, dissolved salt, a mixture of volatile liquid solvent and dissolved salt, or hyperbranched polymer. This raises five categories about extractive distillation.

- Extractive distillation with liquid solvent

In extractive distillation process, the ordinary liquid solvents having commonly high boiling points are used as extractants (extractive agents). The classic extractive distillation for ethanol dehydration is depicted in Figure 3.7. Appropriate amount of high-boiling non-ideal solvent is sent in the top part over the feed. One of the most widely used extractive solvents for ethanol dehydration is ethylene glycol to obtain anhydrous ethanol from the fermentation broth (Chávez-Islas, et. al., 2010).

- Extractive distillation with dissolved salt

A dissolved salt can be used as a separating agent for some mixtures such as ethanol–water system in extractive distillation systems. The salt dissolved into the liquid increases significantly the relative volatility of the further volatile component of the mixture so this component is separated from mixture. This is because the called “salt effect”. Figure 3.8 shows flow diagram of this process. The most generally used dissolved salts are potassium acetate, sodium acetate and calcium chloride for dehydration of ethanol in extractive distillation.

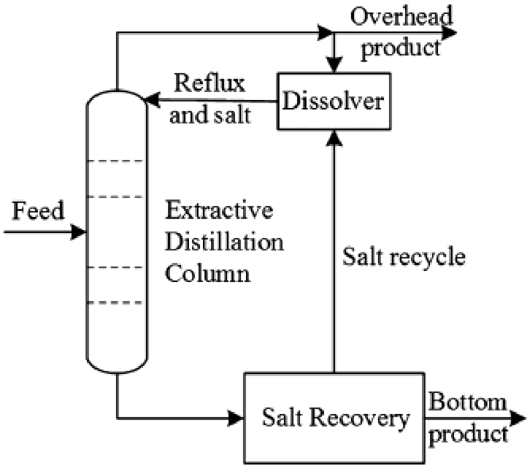


Figure 3.8 Typical Simplified Flow Diagram of the Extractive Distillation with Dissolved Salt (Huang, et. al., 2008).

In addition, a mixture of two or more salts can also be used in extractive distillation. For instance, a mixture contains 70 percent potassium acetate and 30 percent sodium acetate was used in the HIAG (Holz Industrie Acetien Geselleschaft) extractive distillation process. This process produces more than 99.8 wt% ethanol and also has less capital and operating costs (energy consumption) when compared to conventional azeotropic distillation with benzene or extractive distillation with ethylene glycol (Huang, et. al., 2008).

- Extractive distillation with the mixture of liquid extractant and dissolved salt

The mixture containing both liquid extractant and dissolved salt can be used as separating agent in extractive distillation for ethanol dehydration like the liquid extractant or dissolved salt, and the same process flowsheet can be used. The mixture involving liquid extractant and dissolved salt usually needs merely a little amount of salt.

- Extractive distillation with ionic liquid

Extractive distillation with ionic liquids (IL) as separating agent is a new and promising method to separate ethanol from mixture. Ionic liquids have beneficial properties for instance low viscosity, thermal stability, good solubility and lower corrosiveness than ordinary high melting salts (Pacheco-Basulto, et. al., 2012). Great separation ability and easy operation are the advantages of this method when compared to extractive distillation with the mixture of liquid solvent and solid salt. Ionic liquid can greatly increase the relative volatility of ethanol over water. This is the similar salt effect to the solid salt.

Ionic liquids (IL) are usually a mixture of organic cation and an inorganic anion (Chávez-Islas, et. al., 2010). Ionic liquids which can be applicable commercially for separation in the extractive distillation are 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]+[BF4]−), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]+[BF4]−) and 1-butyl-3-methylimidazolium chloride ([BMIM]+[Cl]−) (Huang, et. al., 2008).

- Extractive distillation with hyperbranched polymers

Hyperbranched polymers are new separation methods such as ionic liquids and also used in extractive distillation to separate ethanol from aqueous mixtures.

Hyperbranched polymers are highly branched macromolecules with a large number of functional groups. To obtain hyperbranched polymers, one-step reactions which are economical agents for large-scale industrial applications can be used. Because of their significant selectivity and capacity, low viscosity and thermal stability contrary to linear polymers, hyperbranched polymers are proposed as entrainers in extractive distillation for separation of azeotropic mixtures.

Hyperbranched polyesters and hyperbranched polyesteramides can be used to separate the ethanol–water azeotrope commercially. Hyperbranched polyglycerol (PG) is the most tested hyperbranched polymer for separation of ethanol–water mixture. The effect of hyperbranched polyglycerol on the relative volatility of ethanol to water was found the same as the conventional entrainer 1,2-ethanediol. Furthermore, during hyperbranched polyglycerol process, the overall heat duty can be saved up to 19% compared to the conventional extractive distillation process.

3.2.4 Liquid–liquid extraction-fermentation hybrid (extractive fermentation)

Liquid–liquid extraction is a hopeful method due to low energy requirement for the recovery of anhydrous ethanol from the aqueous fermentation broth.

Liquid–liquid extraction is commonly integrated with fermentation to constitute extractive-fermentation process. In this process extraction separates ethanol and other inhibitor compounds, so inhibitors is removed and also the ethanol yield increases.

The selection of a high efficient solvent for extracting ethanol from mixture is very substantial. The criteria of solvent selection are:

- non toxic to microorganism,
- high distribution coefficient,
- high selectivity about product,
- low solubility in the aqueous phase,
- density different from that of the broth to ensure phase separation by gravity,
- low viscosity, large interfacial tension and low tendency to emulsify in the broth,
- high stability,
- low-priced.

Some feasible biocompatible solvents used to extract ethanol from beer contain oleyl alcohol, n-dodecanol, isoamyl acetate and isooctyl alcohol, nonanoic acid, etc.

Oleyl alcohol was used as extractant in concurrently extraction to remove ethanol product inhibition with the thermophilic and anaerobic bacterium Clostridium thermohydrosulfuricum as illustrated in Figure 3.9, in the continuous fermentation of ethanol by certain investigators. It was observed that the ethanol yield of the fermentation with extraction is more two times the ethanol yield of fermentations without extraction.

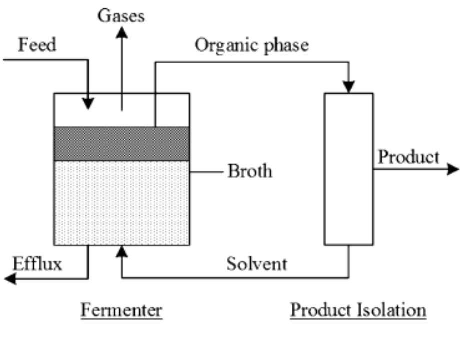


Figure 3.9 Continuous Fermentation with in situ Extraction (Huang, et. al., 2008).

Oleyl alcohol was also used in a simultaneous saccharification and extractive fermentation process. In this process, firstly cellulose hydrolyzate was fermented to ethanol, and the ethanol product was separated by extraction with oleyl alcohol.

Compared to batch simultaneous saccharification and fermentation process without extraction, this process increased ethanol yield of 65% and also reduced the amount of water needed. Hence, the total cost of the ethanol production reduced.

In some studies, n-dodecanol was used as extractant to separate the product, and the fermented broth raffinate was recycled for ethanol production. It reduced the consumption of fresh water of 78%.

Several organic solvents such as isoamyl acetate, iso-octyl alcohol, n-butyl acetate, dibutyl ether and dibutyl oxalate was used as extractants in the liquid–liquid extraction of ethanol from aqueous mixtures. It was found that isoamyl acetate and iso-octyl alcohol were efficient for production of ethanol.

Valeric acid, oleic acid and nonanoic acid, they are fatty acids, was also used as solvents to extract ethanol from fermentation broth in recent times. It was found that nonanoic acid extraction decreases thermal energy of 38% contrary to the conventional distillation process (Huang, et. al., 2008).

3.2.5 Adsorption

There are two types of adsorption for the separation of ethanol-water : the first one is the liquid-phase adsorption of water from the fermentation broth and the other one is the vapor-phase adsorption of water from the process stream out of distillation column.

- Vapor-phase adsorption of water

The most used adsorbents for vapor-phase adsorption of water from ethanol-water mixtures constitute two groups;

-inorganic adsorbents such as molecular sieves, lithium chloride, silica gel, and activated alümina,

-bio-based adsorbents such as corn grits.

- **Inorganic adsorbents.**

Zeolite molecular sieve (type 3A and 4A) are commonly used in separation of ethanol–water mixtures (Kiss, Suszwalak, 2011). 3A zeolite molecular sieves have a nominal pore size of 3 Angstroms (0.30 nm) and also can be used in dehydration of polar liquids such as ethanol. In this process, while ethanol is preserved because of its molecular diameter of almost 0.44 nm, water enters the pores of the molecular sieve adsorbent with an approximate molecular diameter of 0.28 nm (Huang, et. al., 2008).

The use of enormous amount of liquid for the regeneration level of the molecular sieve is the disadvantage of this process.

The implementation of this process in the vapor phase excludes the wetting of the molecular sieves in adsorption and their drying in desorption and so energy consumption is reduced (Frolkova and Raeva, 2009).

- **Bio-based adsorbents**

Bio-based adsorbents contain cornmeal, cracked corn, starch, corn cobs, wheat straw, bagasse, cellulose, hemicellulose, wood chips, other grains, etc. Bio-based adsorbents can be categorized into two groups. These are starch-based (e.g., cornmeal, corn crite), and lignocellulosic adsorbents (e.g., rice straw, bagasse).

- Liquid-phase adsorption of water

Lately, the mixture of starch-based and cellulosic materials have been used for liquid-phase adsorption of water. The mixture contains white corn grits, α-amylase-modified yellow corn grits, polysaccharide-based synthesized adsorbent, and slightly gelled polysaccharide-based synthesized adsorbent.

The starch-based adsorbents adsorb water by producing hydrogen bonds between the hydroxyl groups on the surface of the adsorbent and the water molecules.

- Advantages and disadvantages of adsorbents

Zeolite molecular sieves are very selective, but water is very strongly adsorbed. Therefore, high temperatures and/or low pressures are needed to reproduce zeolite molecular sieves.

Bio-based adsorbents have lower separation capacity than molecular sieves. However, they need lower regeneration temperature than molecular sieves.

In addition, bio-based adsorbents are cheaper than molecular sieves.

3.2.6 Membrane separation

Membrane pervaporation is one of the most effective and energy-saving processes to separate azeotropic mixtures and also has a small surface area as compared to larger equipment such as distillation columns (Kiss and Suszwalak, 2011). Pervaporation is based on the solution-diffusion mechanism and also its driving force is the gradient of the chemical potential between the feed and the permeate sides of the membrane (Huang, et. al., 2008).

In pervaporation, the mixture to be separated does not need boiling and so it is possible to use low-grade heat. The difference from distillation is that distillation needs multiple separation of the entire mixture but pervaporation consumes energy only for permeate evaporation. In addition to this, pervaporation can be economically more suitable than distillation to recover low concentrations of ethanol from fermentation. Generally, the reachable ethanol concentration in lignocellulosic fermentation is below 5 wt.% (Gaykawad, et. al., 2012).

Although azeotropic and extractive distillation, extraction, and other methods use extra chemicals (separation or extracting agents) and then they need recovery of these chemicals, pervaporation mainly does not need any extra reagents (Frolkova and Raeva, 2009).

There are generally two different pervaporation processes: vacuum and sweep gas pervaporation. Mixture to be separated contacts with the membrane at the feed side, that is retentate or upstream side, in the vacuum pervaporation process. In this side, the holded retentate leaves the unit. On the permeate (downstream) side, the partial pressure of pervaporated permeate is lowered by using a vacuum pump. An inert sweep gas such as N_2 is applied on the permeate side in order to reduce the permeate partial pressure in the sweep gas pervaporation (Wei, et. al., 2013).

Most membranes are hydrophilic or water permselective due to the smaller molecular size of water, some membranes are hydrophobic or ethanol permselective. There are three types of membranes and this depends on materials used for membrane production. These are: inorganic, polymeric and composite membrane.

- Hydrophilic membrane

- Inorganic membrane.

Inorganic pervaporation membranes have important advantages such as superior temperature stability and mechanical strength so they recently become commercially available in industries.

- Polymeric membrane.

The studied polymeric pervaporation membranes are cellulose acetate butyrate membrane, PDMS (polydimethylsiloxane) membrane, polydimethylsiloxanepolystyrene interpenetrating polymer network (PDMS-PS IPN) supported membranes, aromatic polyetherimide membranes.

- Composite or mixed membrane.

Polystyrenesulfonate/alumina, polyelectrolytes multi-layer, KA zeolite-incorporated crosslinked PVA multilayer mixed matrix membranes (MMMMs), and poly(vinyl alcohol) (PVA)-sodium alginate (SA) blend membranes are composite membranes for pervaporation separation of ethanol/water mixtures. Composite membranes are studied to integrate the advantages of inorganic and polymeric membranes.

- Hydrophobic membranes

Hydrophobic membranes are also three types. These are:

-hydrophobic polymeric membranes poly(1-trimethylsilyl-1-propyne) (PTMSP) and poly(dimethyl siloxane) [PDMS] membranes,

-hydrophobic zeolite membranes,

-composite membranes, i.e., silicalite-PDMS membranes which consist of silicatlite-1 particles dispersed in PDMS.

Hydrophobic zeolite membranes are used commercially, but polymeric membranes (PDMS, PTMSP) and composite membranes are still studied.

Zeolite membranes are more costly than polymer membranes, but zeolite membranes have greater separation factors and flux than polymer membranes.

In addition, zeolite membranes may be more cost impressive on per unit ethanol basis (Nomura, et. al., 2001).

3.2.7 Membrane pervaporation-bioreactor hybrid

Fermentation broth mainly includes inhibiting substances which contain ethanol product, flavors (phenolics), and other chemicals. This is a problem and it can be solved by integrating fermentation with hydrophobic membrane pervaporation to remove the inhibitors from the fermentation broth. Figure 3.10 shows the process.

Therefore, the process can be accomplished regularly and the recovered organic VOCs, volatile organic compounds, (ethanol, acetone, butanol, 2-propanol) can be used again in other processes.

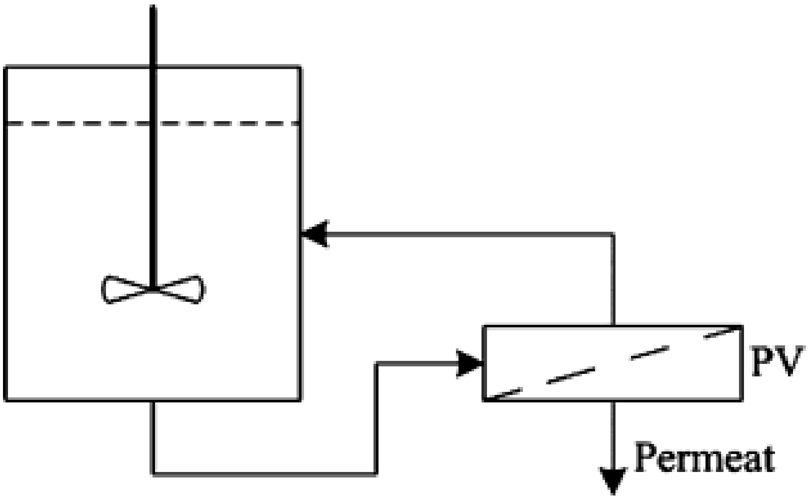


Figure 3.10 Membrane Pervaporation-Bioreactor Hybrid (Huang, et. al., 2008).

Before pervaporation, a microfiltration membrane is added for avoidance fouling of the hydrophobic membrane in actual operations. Therefore, the mixture which enriched with ethanol can be further dehydrated to obtain anhydrous ethanol. Process diagram is shown in Figure 3.11.

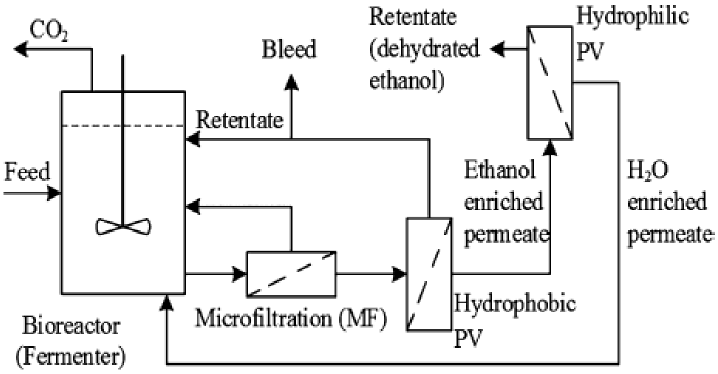


Figure 3.11 Membrane Pervaporation-Bioreactor Hybrid with Microfiltration (Huang, et. al., 2008).

3.2.8 Vacuum Membrane Distillation (VMD) – bioreactor hybrid

Membrane distillation is an appropriate process to separate aqueous mixtures. There are four types of membrane distillation: direct contact membrane distillation, air gap membrane distillation, sweeping gas membrane distillation and vacuum membrane distillation.

Vacuum membrane distillation is very similar to pervaporation and also vacuum membrane distillation -bioreactor hybrid process is suitable like membrane pervaporation-bioreactor hybrid. The only dissimilarity is that in vacuum membrane distillation the separation factor is set up by vapor–liquid equilibrium of the feed.

Vacuum membrane distillation is commercially used because of its high selectivity of ethanol over water, large flux, high thermal efficiency and low energy cost (Huang, et. al., 2008).

3.2.9 Pressure Swing Distillation

Conventional pressure-swing distillation is a dual-column process shown in Figure 3.12. If the composition of the binary azeotrope mixture alters at different external conditions (temperature, pressure), this mixture can be separated using complex distillation columns working at different pressures (Frolkova and Raeva, 2009).

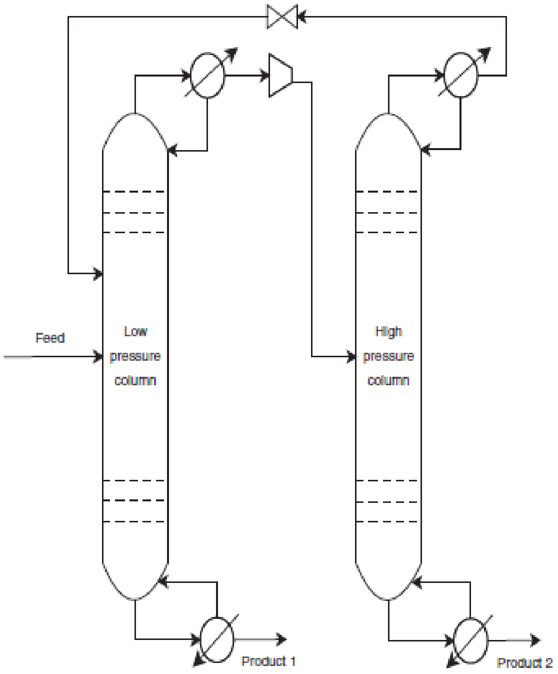


Figure 3.12 Flowsheet of the Conventional Pressure-Swing Distillation Scheme (Mulia-Sotoa and Flores-Tlacuahuacb, 2011).

Conventional pressure-swing distillation has been commonly studied in the literature. In addition to this, it is used commercially to separate tetrahydrofurane/water, acetronitrile/water, methanol/methyl ethyl kenote, and acetone/methanol which are azeotropic mixtures (Mulia-Sotoa and Flores-Tlacuahuacb, 2011).

This method is firstly proposed as early as 1960 and now it is used for dehydration of ethanol obtained from fermentation (Frolkova and Raeva, 2009).

Although the ethanol/water azeotrope has low sensibility to pressure changes, this low sensitivity is large enough for the use of pressure-swing.

The disadvantage of this process is the need of energy and the processing costs because of the use of compression equipment for high-pressure operation (Mulia-Sotoa and Flores-Tlacuahuacb, 2011).

4. EXTRACTIVE DISTILLATION OF ETHANOL – LITERATURE VIEW

Extractive distillation performs the separation in the presence of a miscible, high boiling, relatively non-volatile component that forms no azeotrope with the other components in the mixture (Kiss and Ignat, 2012).

The basic extractive distillation process contains two columns. In the first column, most of the water is obtained from the bottom and also a distillate close to the azeotropic point is obtained (around 96% in weight), during the second stage the breaking of the azeotrope is achieved by using an extractive distillation column where the final ethanol purity is obtained (around 99.5% in weight) (Kiss and Suszwalak, 2011). The first distillation column requires energy in the reboiler to accomplish the separation and the second distillation column requires both energy and a mass separation agent (entrainer) **(**Navarrete-Contreras, et. al., 2014).

An ethanol−water stream is taken from the fermentation unit and generally fed to process. Therefore, this stream contains more dilute ethanol compared to azeotropic composition. For this reason, a preconcentration column is used to concentrate it (Errico, et. al., 2013a).

The conventional extractive distillation separation of ethanol includes three distillation columns depicted in Figure 4.1: first column is for the pre-concentration of ethanol, second column is for extractive distillation and a third column is for solvent recovery and also there are three column shells, three condensers and three reboilers in total (Kiss and Ignat, 2012).

Generally, while water is collected as bottoms stream, ethanol is preconcentrated using a conventional distillation column to the azeotrope of ethanol and water (about 85 wt% ethanol) as distillate, then ethanol-water mixture is sent to an extractive distillation column (Vázquez-Ojeda, et. al., 2012). In the typical extractive distillation, ethylene glycol is used as a solvent to dehydrate ethanol.

Pure ethanol (over 99.8 wt% according to the standards) is obtained as distillate of the extractive distillation column and the bottoms of the column includes solvent and water which are sent to solvent recovery column. The solvent is then recovered in the bottoms of the solvent recovery column, cooled and then recycled back to the extractive distillation column. A small amount of fresh solvent is added as make up to prevent any losses of solvent in the two product streams. A second water stream is obtained as distillate of the solvent recovery column. The flowsheet of the process is shown in Figure 4.2 (Errico and Rong, 2012).

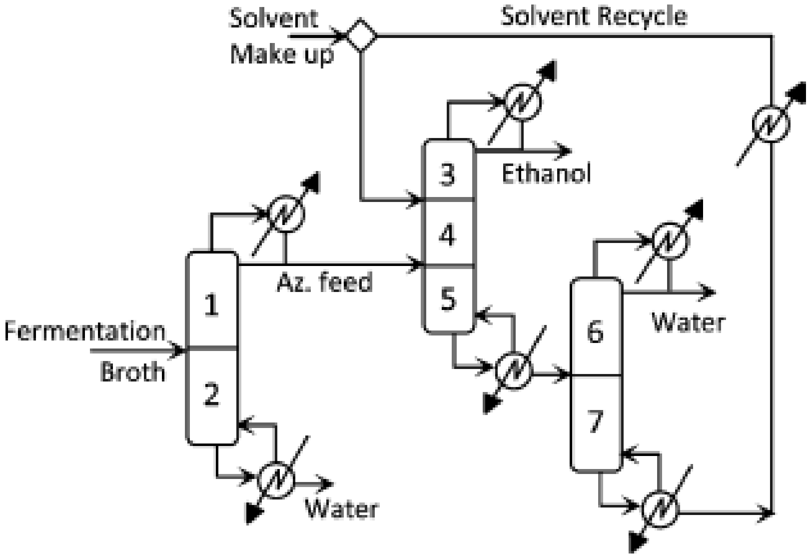


Figure 4.1 The Conventional Extractive Distillation (Errico, et. al., 2013a).

Another flowsheet of the distillation process for ethanol-water separation studied by Li and Bai is given in Figure 4.2. This configuration includes three columns: the extractive distillation column, the solvent recovery column, and the concentrator column, respectively. The azeotropic mixture, containing 85 percent ethanol and 15 percent water, is sent to the extractive column. Ethylene glycol is added as a solvent to extractive column. Pure ethanol is obtained from the distillate and water-solvent mixture is sent to the solvent recovery column. Ethylene glycol is recovered with a high purity through the second column. The distillate of the solvent recovery column is separated as water and an azetropic mixture, and the mixture is turned back to the first column (Segovia-Hernandez, et. al., 2013).

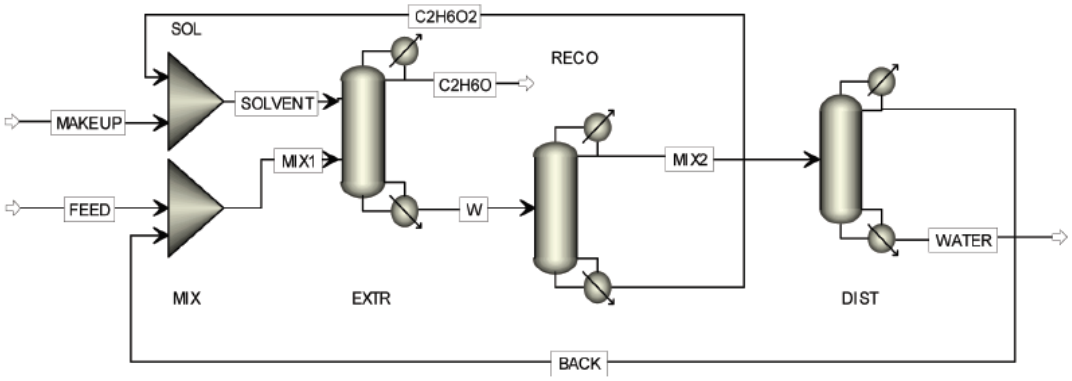


Figure 4.2 The New Three-Column Flowsheet for Ethanol Extractive Distillation (Li and Bai, 2012).

In extractive distillation, the vapor–liquid equilibrium (VLE) data with solvent is used for the evaluation of the feasibility of the process. When a suitable solvent is used, the azeotropic condition generally disappears. Also, an increase in the ratio of solvent to feed create an increase of relative volatility. But there is a special situation under VLE conditions. When the solvents are added to the mixture, the solvent displays positive deviation with a light component such as ethanol-water with ethylene glycol and also negative deviation with a heavy component such as methanol-acetonitrile with DMF.

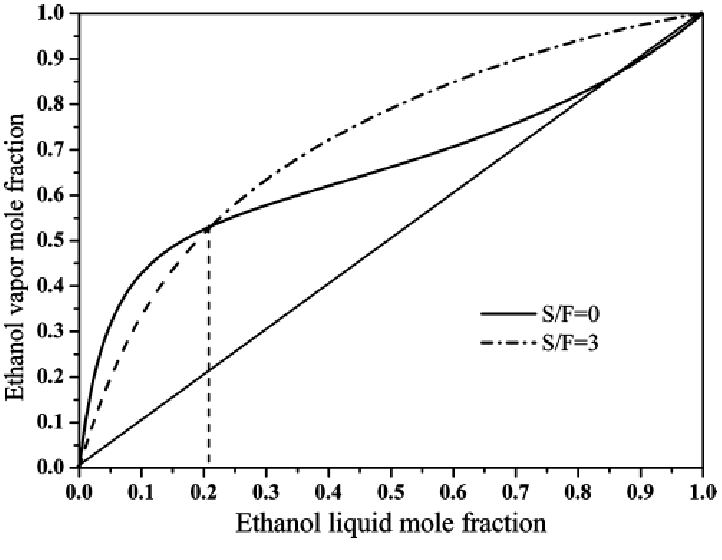
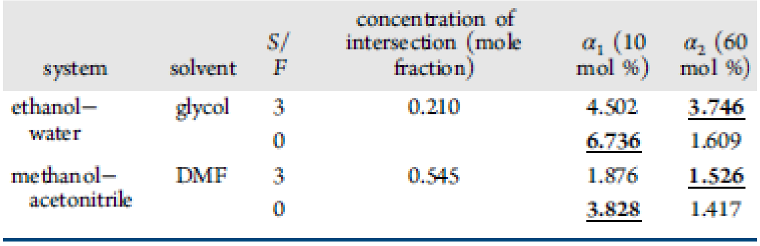


Figure 4.3 VLE of Ethanol−Water with (S/F = 3) and without (S/F = 0) Solvent (Li and Bai, 2012).

In the ethanol-water equilibrium curve of the configuration of Li and Bai, the relative volatility with the solvent is less than that when the system is without solvent, while the ethanol concentration is below 21 mol %. This is the clearly contrary in the higher concentration region. The results about this situation are shown in Figure 4.3 and also Table 4.1. So in this process, the bottom product of the extractive distillation column in Figure 4.3 contains ethanol with a molar proportion of 0.21 (excluding separating agent) (Li and Bai, 2012).

Table 4.1 Relative Volatility in Different Concentration Areas.



system	solvent	S/F	concentration of intersection (mole fraction)	α_1 (10 mol %)	α_2 (60 mol %)
ethanol–water	glycol	3	0.210	4.502	3.746
		0		6.736	1.609
methanol–acetonitrile	DMF	3	0.545	1.876	1.526
		0		3.828	1.417

As shown in Figure 4.4., the new three-column flowsheet for ethanol extractive distillation studied by Li and Bai is modified by adding a preconcentration column. If the concentration of ethanol in the mixture is under 21% mol, the relative volatility of the system with solvent become less than the system without solvent. So, in this process, an amount of 0.21 of ethanol (free solvent basis) is left in the bottom of the extractive column like the flowsheet of Li and Bai and then it is recovered in the solvent recovery column.

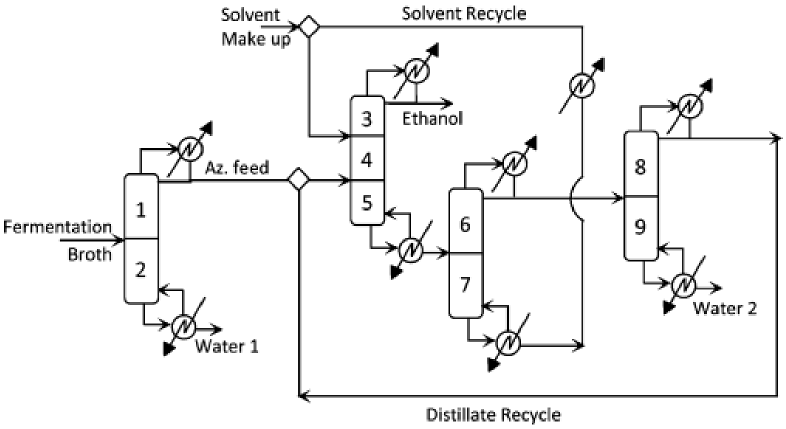


Figure 4.4 The Three-Column Flowsheet for Ethanol Extractive Distillation Studied by Li and Bai Integrated with the Preconcentrator Column (Errico, et. al., 2013a).

Errico et al studied to develop alternative structures by using the structure of Li and Bai as a reference structure. These alternative structures were compared to find the best structure based on the energy consumption, the capital cost investment, and the solvent consumption. The use of a partial condenser proposed for ethanol−water distillation instead of a total condenser is one of the alternative structures. A partial condenser can be applied to columns except extractive column in the four-column system. Because it is used for only the nonproduct streams. These structures provide a higher solvent concentration on the feed tray and on the trays instantly below. The partial condenser can be also used in two or three units simultaneously (Errico, et. al., 2013a).

In four-column system, water is separated twice; one of them is obtained from preconcentrator column and the other one is obtained from the last column. In addition to this, the mixture of distillate of last column is same to azeotropic composition. When the two columns are integrated, the distillate of the solvent recovery column can be liquid or vapor (depending on if a partial or total condenser is used) and it is sent to preconcentrator column and also the bottom of the solvent recovery column is sent to extractive column. Thus, the system is reduced from a column (Errico, et. al., 2013a).

Three-column systems consist of preconcentrator, extractive and solvent recovery colum. In preconcentrator column, fermentation broth is separated until a purity close to the azeotrope is obtained and then the azeotropic mixture is sent to the second column. Pure ethanol is obtained using ethylene glycol as entrainer from the distillate of the column. The solvent is recovered at the bottoms in the last column and is turned to the second column. When the distillate of the solvent recovery column includes a water–ethanol liquid mixture, the structure is called conventional separation sequences with liquid recycle (CLR); when the distillate of the solvent recovery column includes a water–ethanol vapor mixture, the structure is called conventional separation sequences with vapor recycle (CVR). This distillate is recycled to the prefractionator (Segovia-Hernandez, et. al., 2013).

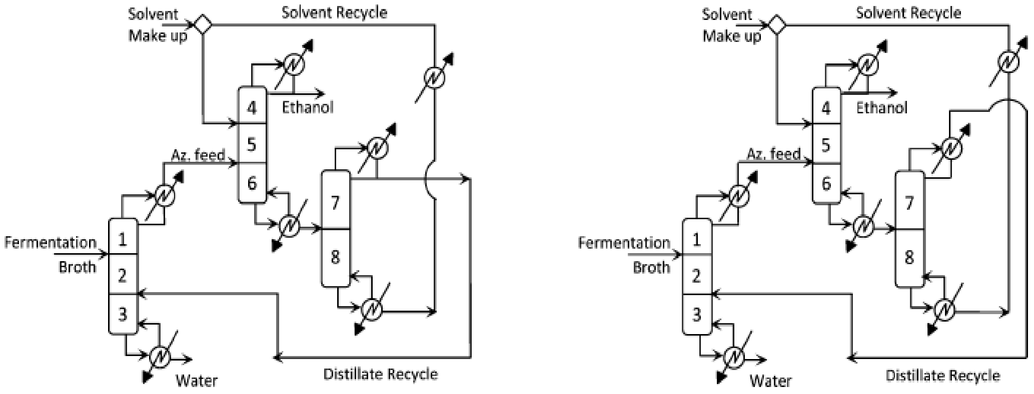


Figure 4.5 Conventional Separation Sequences: (a) CLR with Liquid Recycle and (b) CVR with Vapor Recycle (Errico, et. al., 2013a).

A two-column system is obtained for ethanol-water distillation by improving the three-column system as shown in Figure 4.6. In this configuration, section 7 turns into a vapor side stream and then is recycled to the preconcentrator column (Errico, Rong, Tola, Spano, 2013b). Thus, the configuration, called SSVR, includes two column: preconcentrator column and extractive distillation column.

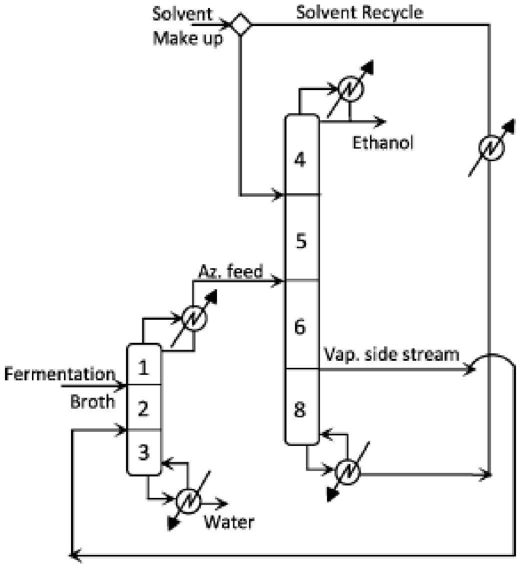


Figure 4.6 Two-Column Configuration with Vapor Side Stream (Errico, et. al., 2013b).

The prefractionator column is fed with the fermentation broth. While the azeotropic mixture is obtained from the distillate of the column, water is obtained from the bottoms. In the extractive column, bioethanol is obtained at the distillate, the solvent is recovered at the bottom. The vapor side stream includes a mixture of water and ethanol and is recycled to the prefractionator column (Segovia-Hernandez, et. al., 2013).

5. CONTROL OF DISTILLATION SYSTEMS

5.1 Control Fundamentals

A simple two-product distillation column system shown in Figure 5.1 has six control valves and so six control degrees of freedom.

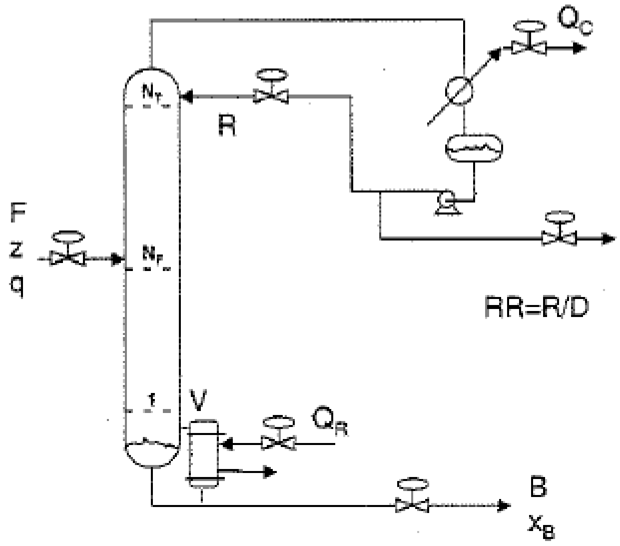


Figure 5.1 A Simple Two-Product Distillation Column System.

One of these is generally applied to set throughput by using the valve of the feed line. Furthermore there are also other possibilities. In some columns, it is applied to product valves (if this product is an on-demand stream) or to the condenser using the valve of the cooling water (if capacity is limited by maximum pressure/maximum cooling conditions) or to the reboiler using the valve of stream (if capacity is limited by heat input or column flooding).

Two of the control degrees of freedom are used to control the reflux drum level and base level in the process. Reflux drum level can be controlled by adjusting the flowrate of the distillate, the reflux, the vapor boilup, the condenser cooling, or the feed (if the feed is partially vapor) because each of these flows has an individually effect on reflux drum level. Column base level (or reboiler level in a kettle reboiler) can be controlled by adjusting the flowrate of the bottoms, the vapor boilup, or the feed (if the feed is partly liquid and the stripping section does not include too many trays).

Fourth degree of freedom is used to control the column pressure. Column pressure can be controlled using the valve of condenser cooling (the most generally used), reboiler heat input or feed (when the feed is partially vapor).

Finally two remaining degrees of freedom can be used to control two other variables, for example, two compositions, two temperatures, or one composition and one temperature. Direct composition controls are applicable on columns, but composition analyzers are costly and often unreliable. Therefore, many columns are controlled using temperatures to inferentially measure compositions. If the separation of an ideal binary mixture is performed, two degrees of freedom are used for composition control. If the separation of a multicomponent nonideal mixture is performed, two degrees of freedom is still used, but there are limitations. For example, we can not freely determine that two compositions in the same stream are to be controlled in a multicomponent system. For this reason, the situation where the feed includes a light key component (LK), a heavy key component (HK), and a heavier-than-heavy key component (HHK) must be evaluated. The impurity levels of both the light key and the heavier-than-heavy key can not determined in the bottoms product. If some of the light key leaves the bottom of the column, essentially all of the heavier-than-heavy key in the feed stream will also leaves the bottom no matter what we do. So the composition of the heavier-than-heavy key can not be controlled. For applying two control degrees of freedom, using one of these to control a composition somewhere in the column and using one of these to control the flow of distillate or bottom is another impossible choice. Because fixing the flowrate of either product stream distillate or bottom limits the possible range of product compositions.

5.1.2 Inferential temperature control

Direct composition analyzers are costly and often unreliable. For this reason, temperature is used in many industries for control of columns. Temperature control is used in approximately 75 percent of all distillation columns. Temperature control is still used on various trays up and down the column to maintain approximate composition control in multicomponent systems. However, it is directly related to the composition only in binary systems at known pressure. There are five methods to select the best tray location for this temperature control.

The conventional procedure for selection of control tray is to look at the steady-state temperature profile in the column at the base-case conditions and then to determine large temperature changes from tray to tray. The tray having the biggest temperature change from tray to tray is chosen as the controlled variable. Generally, the slope of the temperature profile is the steepest in the stripping section of the column. This "steepest slope" criterion is usually used to determine the control tray. This method is effectively works because temperature is influenced by other variables (pressure and other components) but this method determines a tray where the compositions of the LK and HK components importantly influences the temperature and also other variables have small effects.

The second method includes the determination of the control tray which is most sensitive to changes in the manipulated variable. A dynamic program is used to make small open loop changes in the manipulated variable such as heat input. Then, the results are analyzed and the tray showing the largest temperature change is selected. This method shows the largest steady-state gain between the controlled variable and manipulated variable.

A third method determines the control tray based on the similarity in steady-state responses a for both positive and negative changes of manipulated variable. This method is studied to avoid problems about nonlinearity.

In a fourth method, the steady-state rating program is run for different values of feed composition and also a specified tray temperature is kept constant. For example, a control tray close the bottom of the column gives good control of bottoms composition but not the top composition. So the determination of which tray is best depends on which stream composition is more significant about product quality.

A final method is to use singular value decomposition (SVD) techniques. This method is more complex than the others. A steady-state rating program is used to find the gains between the two manipulated variables and the temperatures on all trays. The gain matrix is decomposed to find the most sensitive tray by using SVD.

5.2 Control of Sidestream Columns

Industry uses columns with complex structures such as multiple feeds, sidestreams, combinations of columns, and heat integration to increase the efficiency of the processes. As a result of these complex structures, significant reductions in energy consumption are observed.

A sidestream column is one of the structures created as an alternative to conventional distillation structure for the ternary mixtures. It can have two situations: a liquid sidestream or a vapor sidestream. In a liquid sidestream, stream is removed from a tray somewhere above the feed tray; while in a a vapor sidestream, stream is removed from a tray somewhere below the feed tray. These two conditions are shown in Figure 5.2.

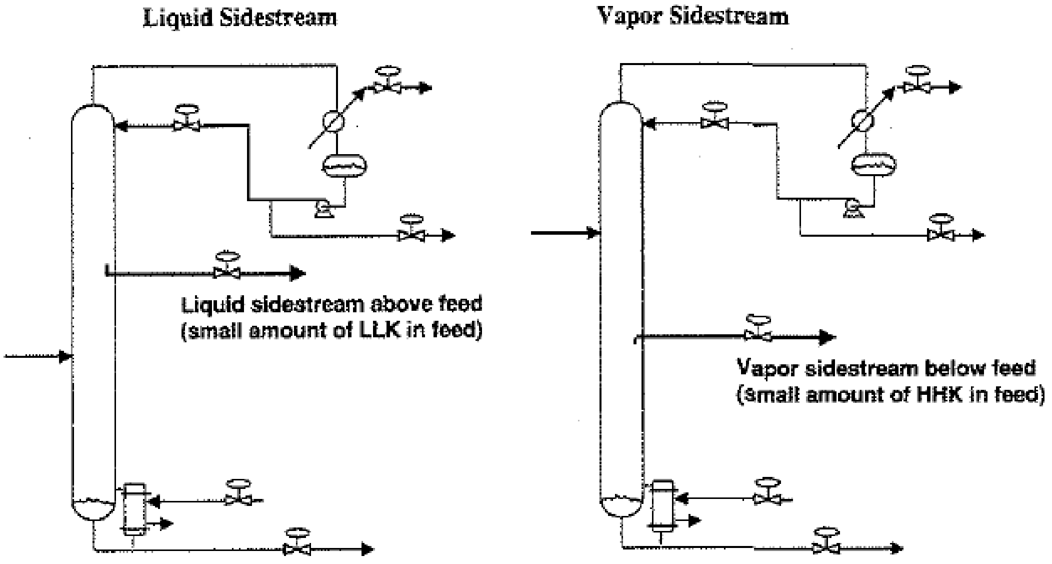


Figure 5.2 Liquid Sidestream Columns and Vapor Sidestream Columns.

There is a ternary mixture containing components A, B, and C, and assume that their relative volatilities decrease respectively. So component A is obtained from the distillate of column, component B is obtained from the sidestream, and component C is obtained from the bottoms.

Figure 5.3 shows a control scheme for a sidestream column. An additional control degree of freedom is used in the sidestream columns because sidestream flow can be manipulated. The impurity of B in the distillate, the purity of B in the sidestream and the impurity of B in the bottoms can be controlled in the sidestream columns.

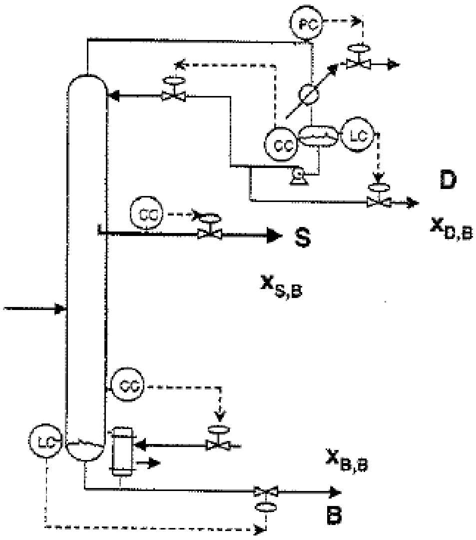


Figure 5.3 The Control of the Sidestream Column.

Sidestream columns can be integrated with other columns such as strippers, rectifiers, or prefractionators. Figure 5.4 shows a complex configuration designed with sidestream column and prefractionator column for a ternary feed. The aim of this structure is to remove the heaviest component C by the help of the first column. Thus, when the distillate of the first column is sent above the sidestream drawoff of the second column called sidestream column, the heaviest component C appears a little and so it must flow down past the sidestream tray. This provides a high-purity sidestream product. In addition, the prefractionator also produces small amount of the lightest component A in the bottom so the vapor stream of the sidestream column has little component A. This also provides high sidestream purities.

Reflux flowrate is used to control flow in the first column and also in the second column it is used to control the impurity of component B in the distillate product. The purity of the sidestream product is controlled by sidestream flowrate. While heat input prevents component A from dropping out the bottom in the first column, it controls the impurity of component B in the bottoms product in the second column.

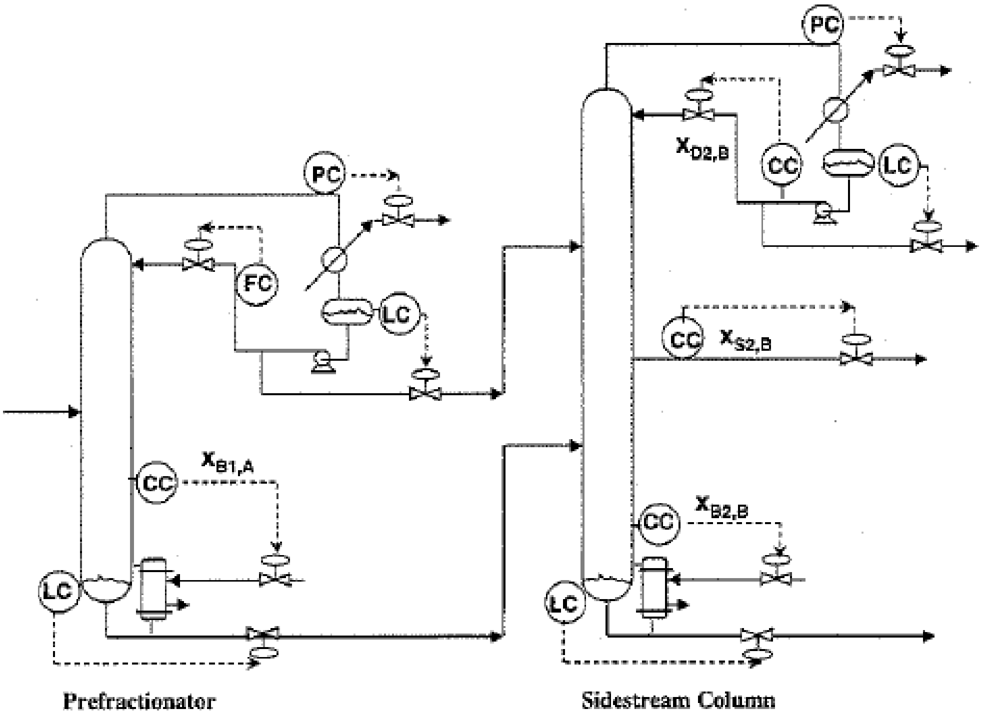


Figure 5.4 The Control Structure of Sidestream Column with Prefractionator.

5.3 Control of Extractive Distillation Columns

Extractive distillation is applied either when the separation is very complicated such as close relative volatilities or when azeotropes appear.

Control of extractive distillation columns is shown in Figure 5.5. The tray temperature, which is selected using one of five methods to find best tray, is usually controlled by manipulating heat input. The reflux flowrate or the reflux ratio is rationed to the feed flowrate. The reflux drum level is controlled by manipulating distillate flowrate and the column base level is controlled by manipulating bottoms flowrate. This structure gives good results for the column because the proportional-only level controller setting both products provide gradual smooth flowrate changes to downstream sections of the plant.

The flowrate of distillate can be used for two parameters: to control distillate product composition or to control a constant reflux ratio.

When composition or temperature is controlled by distillate, there may be significant fluctuations in the distillate flowrate to provide good quality control. In this configuration, the reflux drum level loop must be tuned with PI control. So an additional lag is not added in the composition loop, for example changes in distillate flowrate will result in immediate changes in reflux flowrate.

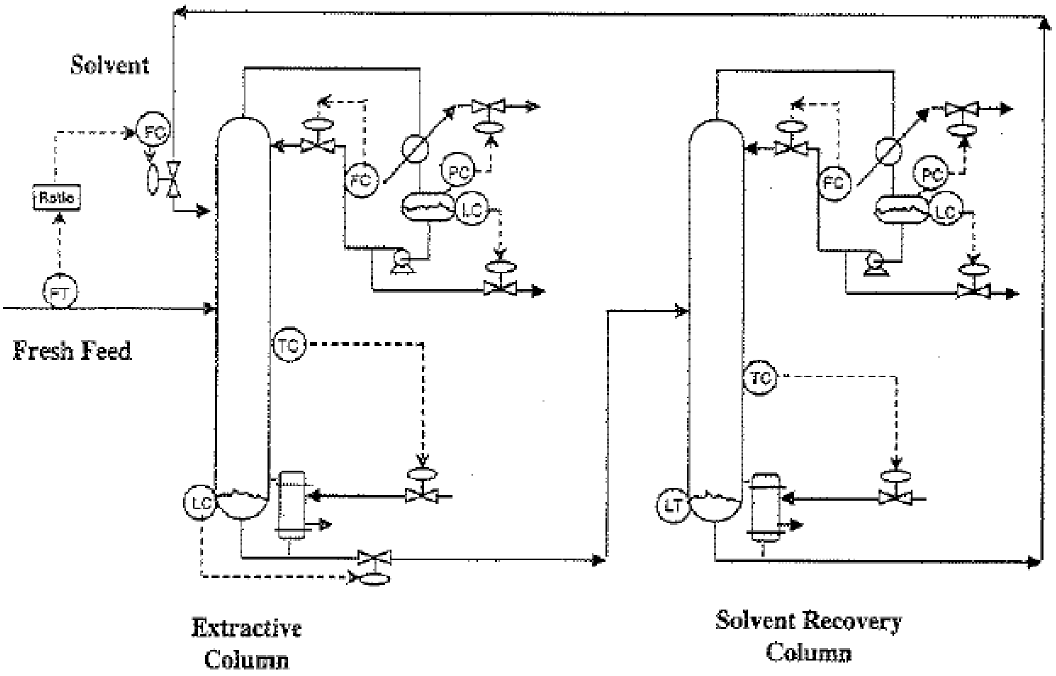


Figure 5.5 Control of Extractive Distillation Columns.

When reflux ratio is controlled by distillate, the changes in distillate flow decreases well. In this configration, the reflux drum level is controlled by manipulating reflux flowrate using a P-only controller. The aim of this is to provide small changes in reflux flowrate and so this gives small changes in distillate flowrate (Luyben, Tyreus, Luyben, 1999).

6. RESULTS AND DISCUSSIONS

In this thesis, three configurations proposed by Errico et al (2013a, 2013b) have been considered. The first one is a four-column distillation sequence. The second configuration is a three-column system, called conventional separation sequences with liquid recycle (CLR), which has a preconcentrator column, an extractive column and a solvent recovery column. The last one is a two-column system, called SSVR (side stream vapor recycle), including a preconcentrator column and an extractive distillation column.

6.1 Steady State Design

For all configurations, a fermentation broth is used as the feed stream. A flowrate of 1700 kmol/h including 5% mol of ethanol and 95% mol of water is fed to the preconcentrator column. The composition and the physical properties of the feed stream are reported in Table 6.1. All the simulations have been performed by the process simulator Aspen Plus. The NRTL method has been applied to evaluate the activity coefficients. Ethylene glycol has been used as solvent due to its low volatility and low boiling point. A solvent to feed ratio of 1 has been utilized for extractive distillation columns of all the configurations simulated.

Table 6.1 Feed Characterization.

Parameters	**value**
feed mole flow (kmol/h)	1700
mole fraction	
ethanol mole fraction	0.05
water mole fraction	0.95
feed temperature (°C)	78.14
Solvent mole flow (kmol/hr)	100
solvent feed temperature (°C)	20
pressure (atm)	1

All the simple columns in the sequences have been first simulated using the Winn−Underwood−Gilliland short-cut method. Then the number of stages, feed location, and reflux ratio have been optimized using the sensitivity analysis tool implemented in the RadFrac rigorous method (Errico, et. al., 2013a).

The solvent recovery column was designed in order to obtain minimum makeup flow rate and also in each sequence, the solvent recovered is cooled to 20˚C. For all columns, "the strongly non-ideal convergence method" is selected.

The four-column system includes: the preconcentrator column, the extractive distillation column, the solvent recovery column, and the concentrator column (Figure 6.1). In preconcentrator column, fermentation broth is separated until a purity close to the azeotrope is obtained. The azeotropic mixture, containing 85 percent ethanol and 15 percent water, is sent to the extractive column. Ethylene glycol is added as the solvent to extractive column. Pure ethanol is obtained from the distillate and water-solvent mixture is obtained from the bottom which is sent to the solvent recovery column. In this process, the bottom product of the extractive distillation column contains ethanol with a molar proportion of 0.21 (excluding separating agent) (Li and Bai, 2012). Ethylene glycol is recovered with a high purity through the extractive distillation column. The distillate of the solvent recovery column is separated as water and azetropic mixture in the concentrator column where the mixture is recycled back to the second column (Errico, et. al., 2013a).

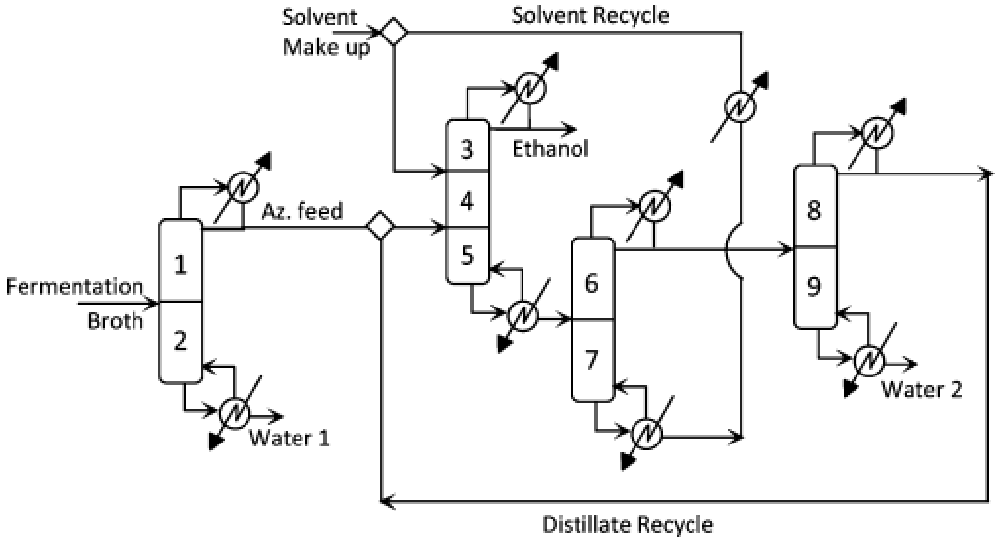


Figure 6.1 The Four-Column System Flowsheet (Errico, et. al., 2013a).

The design parameters for all columns are reported in Table 6.2. Results of the simulation shown in Figure 6.2 such as mass and energy balances and stream compositions are given in Table 6.3.

Table 6.2 Design Parameters, Energy Requirement, and Capital Cost of the Four-Column Configuration.

	C1	**C2**	**C3**	**C4**
number of stages	44	25	12	25
reflux ratio (molar)	2.42	0.2278	0.5	3
feed stage	30	22	6	16
solvent feed stage		7		
distillate rate (kmol/hr)	100	85	20	3.75
column diameter (m)	1.3582	0.7975	0.5283	0.3135
design pressure (kPa)	101.325	101.325	101.325	101.325
condenser duty (W)	-3755.8	-1136.4	-348.0	-206.8
reboiler duty (W)	4863.4	1672.1	630.2	214.3
total condenser duty	-5447			
total reboiler duty	7380			

Table 6.3 Mass, Energy Balance and Stream Composition for the Configuration.

	Feed	**Ethanol**	**Solvent recycle**	**Solvent makeup**	**Distillate recycle**	**Prewater**	**Water**
Temperature (°C)	78.18	79.11	20.72	20	79.02	107.62	104.77
Vapor fraction	0	0	0	0	0	0	0
Enthalpy (kW)	-7558	-6382	-12752	-0.06	-378.8	-124151	-1167
Mole flow (kmol/hr)	100.1	85	100	$5x10^{-4}$	5.0122	1599.9	15.032
Mole fraction							
-ethanol	0.849	0.9998	$9x10^{-10}$	-	0.84	$6x10^{-6}$	$8x10^{-5}$
-water	0.151	$2x10^{-4}$	$9x10^{-5}$	-	0.16	1	0.9999
-ethylene glycol	-	$3x10^{-6}$	0.9999	1	-	-	$1x10^{-5}$

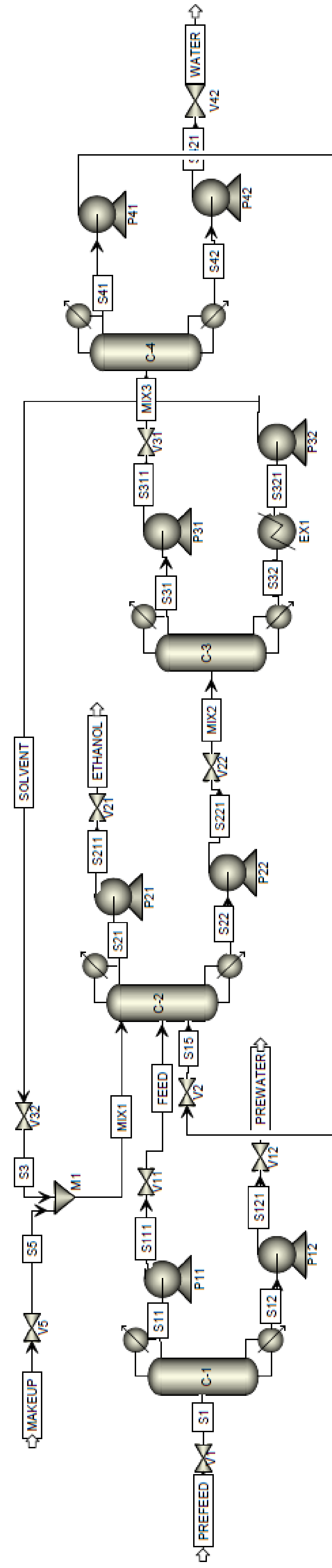


Figure 6.2 The Four-Column System in Aspen Plus.

The three-column system includes a preconcentrator, an extractive column and a solvent recovery column. The concentrator column used in the four-column system is integrated with the preconcentrator column and so new configuration includes three columns. In preconcentrator column, fermentation broth is separated until a purity mixture which is close to the azeotrope is obtained and then the azeotropic mixture which is vapor distillate unlike the four-column system is sent to the second column.

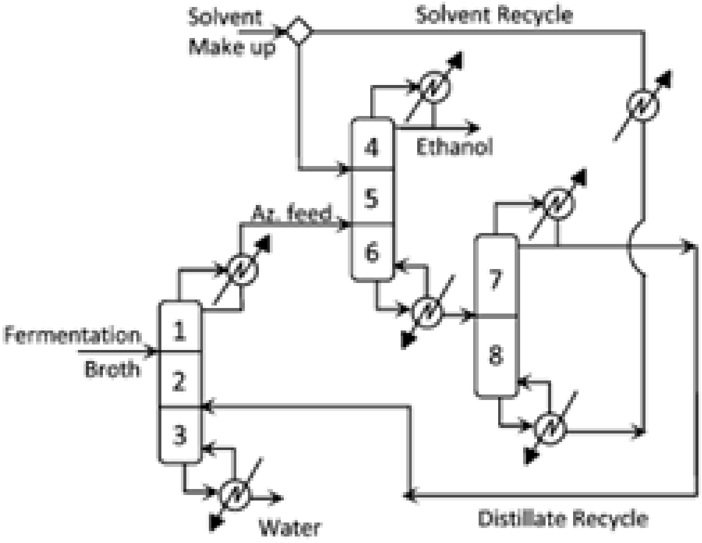


Figure 6.3 The Three-Column Structure.

Pure ethanol is obtained using ethylene glycol as entrainer from the top section of the column. The solvent is recovered from the bottom in the last column and is turned to the second column. When the distillate of the solvent recovery column includes a water–ethanol liquid mixture shown in Figure 6.3, the structure is called conventional separation sequences with liquid recycle (CLR). This distillate is recycled to the prefractionator. The design parameters for all the columns are reported in Table 6.4.

In Figure 6.4, the structure of the three column system is shown in Aspen Plus, and mass and energy balances and stream composition results for the configuration are given in Table 6.5.

Table 6.4 Design Parameters of the Three-Column Configuration.

	PRE-C	C1	C2
number of stages	44	28	17
reflux ratio (molar)	2.335	0.246	0.39
feed stage	30	25	7
distillate feed stage	30		
solvent feed stage		5	
distillate rate(kmol/hr)	103.375	85	18.5
column diameter (m)	1.3747	0.8038	0.4885
design pressure (kPa)	101.325	101.325	101.325
condenser duty (W)	-2722.1	-1151.4	-294.1
reboiler duty (W)	4968.1	340.3	546.9
total condenser duty	-4167.6		
total reboiler duty	5855.3		

Table 6.5 Mass, Energy Balance and Stream Composition for the Configuration.

	Feed	**Ethanol**	**Solvent recycle**	**Solvent makeup**	**Distillate recycle**	**Water**
Temperature (°C)	195	79	20.7	20	84.6	107.5
Vapor fraction	1	0	0	0	0	0
Enthalpy (kW)	-6407	-6372	-12751	-0.6364	-1417	-125331
Mole flow (kmol/hr)	103.1	84.8593	100	4.9×10^{-3}	18.2	1615.1
Mole fraction						
-ethanol	0.85	0.9998	9×10^{-13}	-	0.1535	9×10^{-5}
-water	0.15	2×10^{-4}	1×10^{-4}	-	0.8464	0.9999
-ethylene glycol	-	5×10^{-5}	0.9999	1	1×10^{-5}	1×10^{-7}

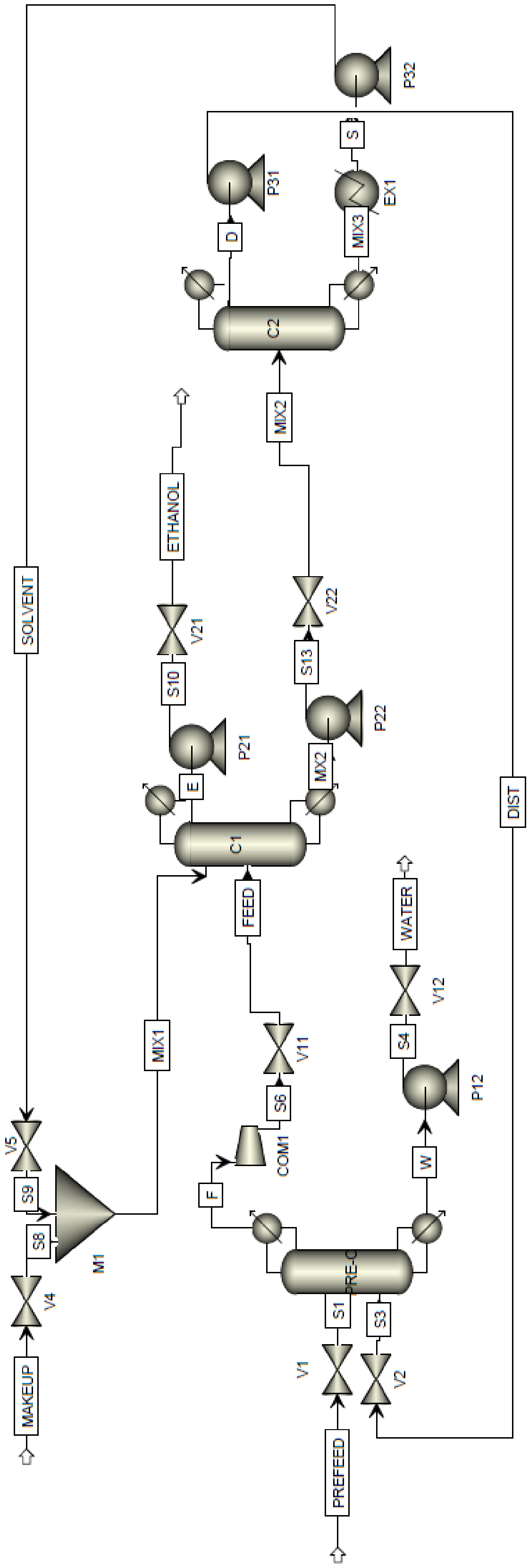


Figure 6.4 The Three-Column Structure in Aspen Plus.

The two-column system is obtained by removing the section 7 which is shown in the three-column system. Section 7 is substituted with a vapor side stream. The prefractionator column is fed with the fermentation broth. While the azeotropic mixture is obtained from the distillate of the column, water is obtained from the bottoms. The azeotropic mixture is vapor like the three-column system. In the extractive column, bioethanol is obtained from the distillate, the solvent is recovered from the bottom. The vapor side stream shown in Figure 6.5 includes a mixture of water and ethanol and is recycled to the prefractionator column. The design parameters for all columns are reported in Table 6.6.

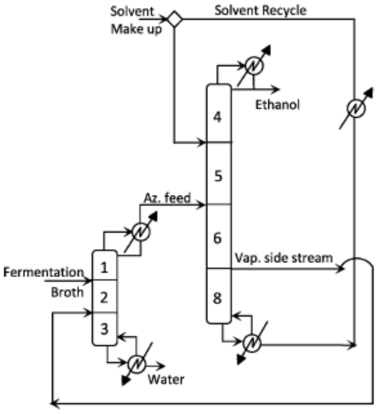


Figure 6.5 Two-Column Configuration with Vapor Sidestream.

Table 6.6 Design Parameters of the Two-Column Configuration.

	C1	**C2**
number of stages	44	41
reflux ratio (molar)	2.325	0.39
feed stage	30	25
distillate feed stage	31	
solvent feed stage		5
sidestream stage		28
distillate rate(kmol/hr)	100.216	85
column diameter (m)	1.3558	0.8784
design pressure (kPa)	101.325	101.325
condenser duty (W)	-2650.6	-1457.7
reboiler duty (W)	4624.3	277.1
total condenser duty	-4108.3	
total reboiler duty	4901.4	

Table 6.7 Mass Balance and Stream Composition for the Configuration.

	Feed	**Ethanol**	**Solvent recycle**	**Solvent makeup**	**Vapor sideatream**	**Water**
Temperature (°C)	195	79	20.7	20	388.6	107.6
Vapor fraction	1	0	0	0	1	0
Enthalpy (kW)	-6226.6	-6382.3	-12650.4	-102.1	-1044.3	-125415.6
Mole flow (kmol/hr)	100.2	84.9984	99.2	0.8	16	1615.8
Mole fraction						
ethanol	0.85	0.9999	$2.5\text{x}10^{-17}$	-	$1.1\text{x}10^{-2}$	$4.8\text{x}10^{-6}$
water	0.15	$6.6\text{x}10^{-5}$	$9.7\text{x}10^{-5}$	-	0.9390	0.9995
ethylene glycol	-	$7.7\text{x}10^{-6}$	0.9999	1	$5\text{x}10^{-2}$	$4.9\text{x}10^{-4}$

Table 6.7 gives the steady state results of the flowsheet, and Figure 6.6 shows Aspen Plus configuration.

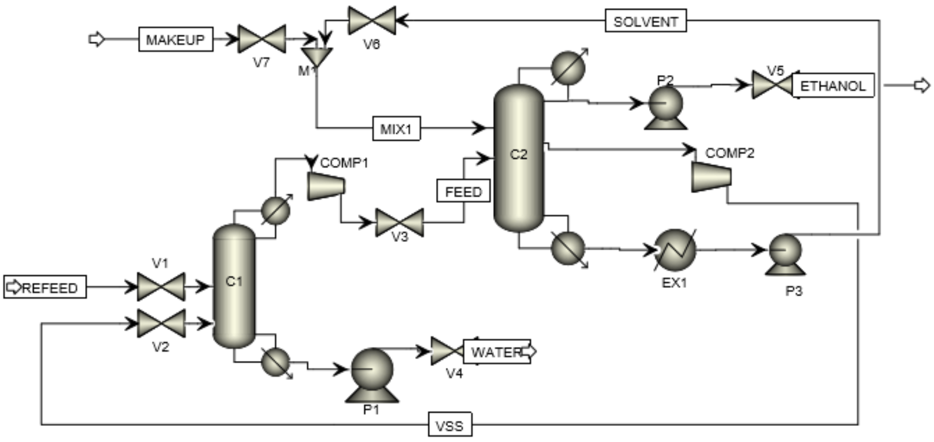


Figure 6.6 Two-Column System in Aspen Plus.

6.2 Control Structure Design

Before being sent to Aspen Dynamics, column sizing is applied to the columns of these three flowsheets to calculate the size of the reflux drum and the column base. Column sizing is necessary because it filters the disturbances of the flow and composition and also allows the column to use large disturbances (Luyben and Chien, 2010). Then, the flowsheets are exported.

The control scheme of the four-column configuration shown in Figure 6.7 is determined by various control loops:

- Reflux drum levels of all columns are controlled by manipulating distillate flow rates.
- Base levels of preconcentrator column, extractive column and concentrator column are controlled by manipulating bottoms flow rates.
- Base level of recovery column is controlled by manipulating makeup flow rate.
- Operating pressures of all columns are controlled by manipulating the corresponding condenser duties.
- Entrainer flow rate is rationed to the azeotropic feed and the ratio is controlled by manipulating bottoms flow rate of the recovery column.
- Reflux ratios are held constant in each column at their nominal values during disturbances. This is set by using a multiplier block. The “Input 1” of this block is the mass flowrate of the distillate (D) and the “Output” is the mass flowrate of the reflux (R). Nominal R/D ratio is calculated and then this is entered as “Input 2”.
- Fresh feed to the preconcentrator column is flow controlled in order to guarantee the constant flowrate.
- Entrainer feed temperature is controlled by manipulating cooler duty.
- Reboiler duties of all columns are used to control the temperature in a particular stage of each column.

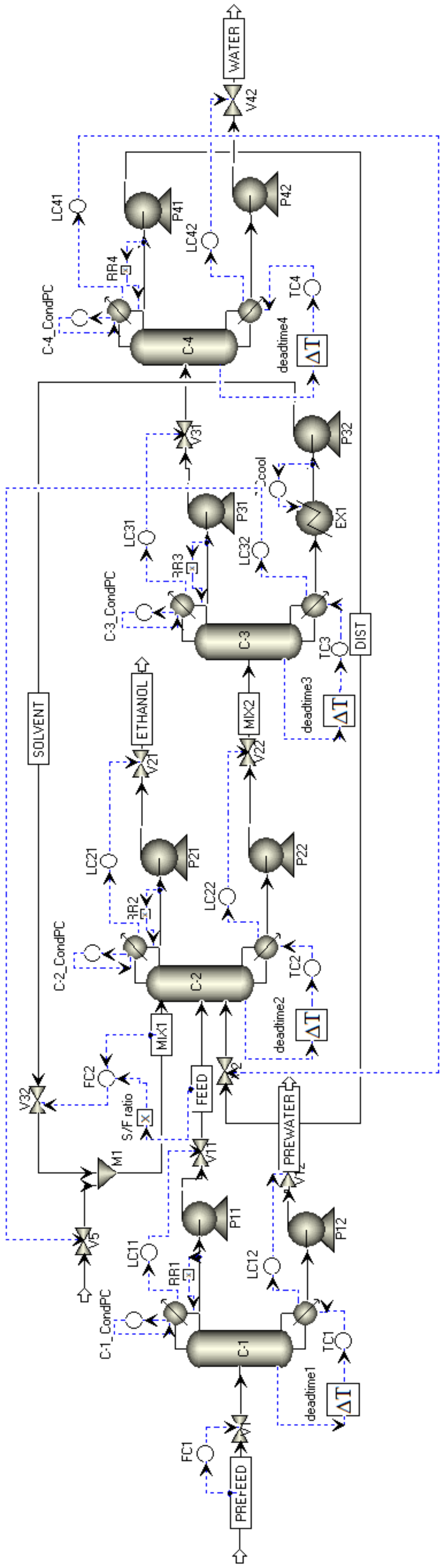


Figure 6.7 Control Structure of the Four-Column System.

The temperature profiles are used to select temperature control stage location for each column. Temperature profiles of columns are shown in Figure 6.8. The temperature of the stage which has highest slope is selected as the controlled variable. So the temperature at the 36th stage is selected as the controlled tray for the preconcentrator column. In extractive column, 24th stage has the highest slope so this is chosen for temperature control. For solvent recovery column and concentrator column, stage 5 and stage 22 are chosen, respectively.

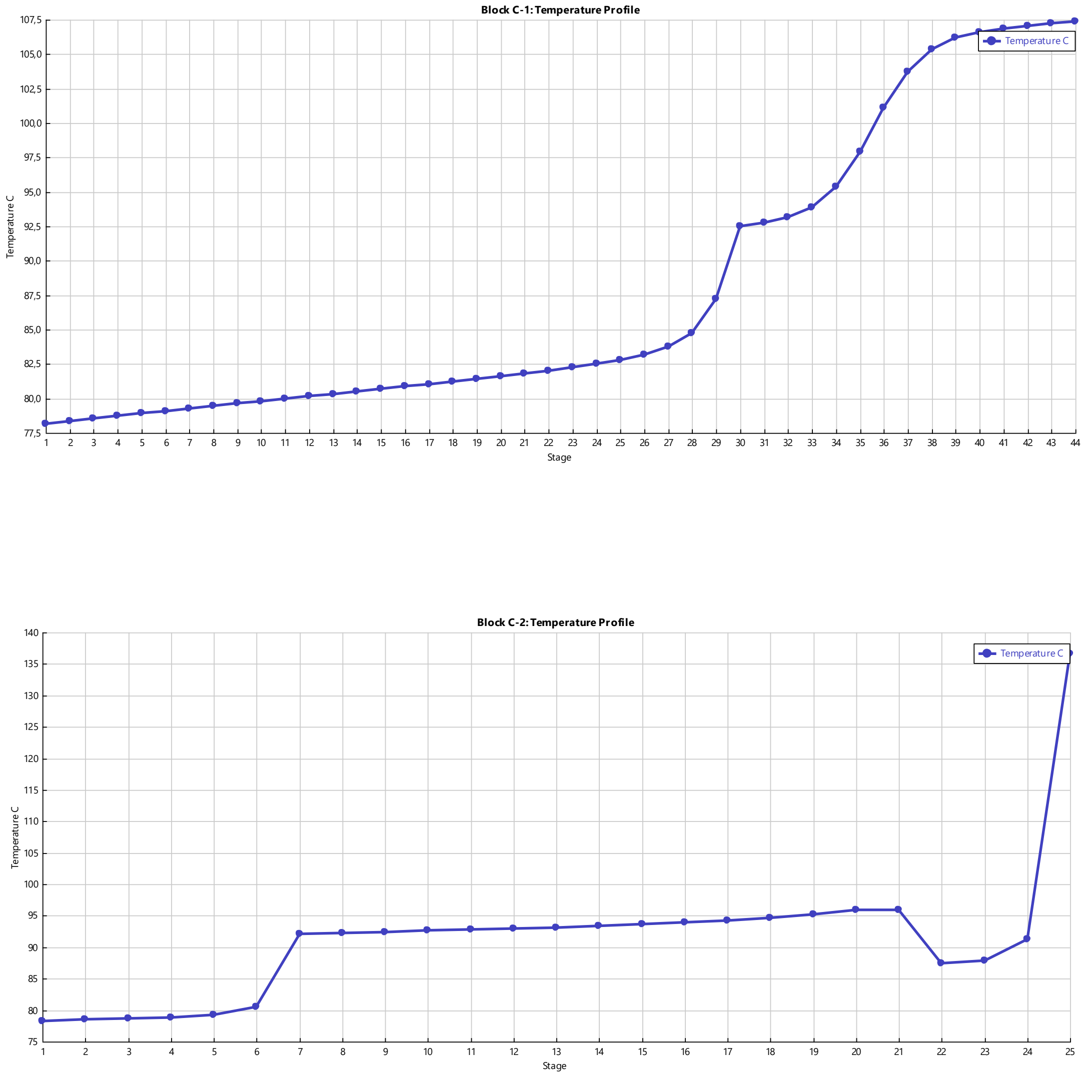


Figure 6.8 The Temperature Profiles of All Columns in the Four Column Structure.

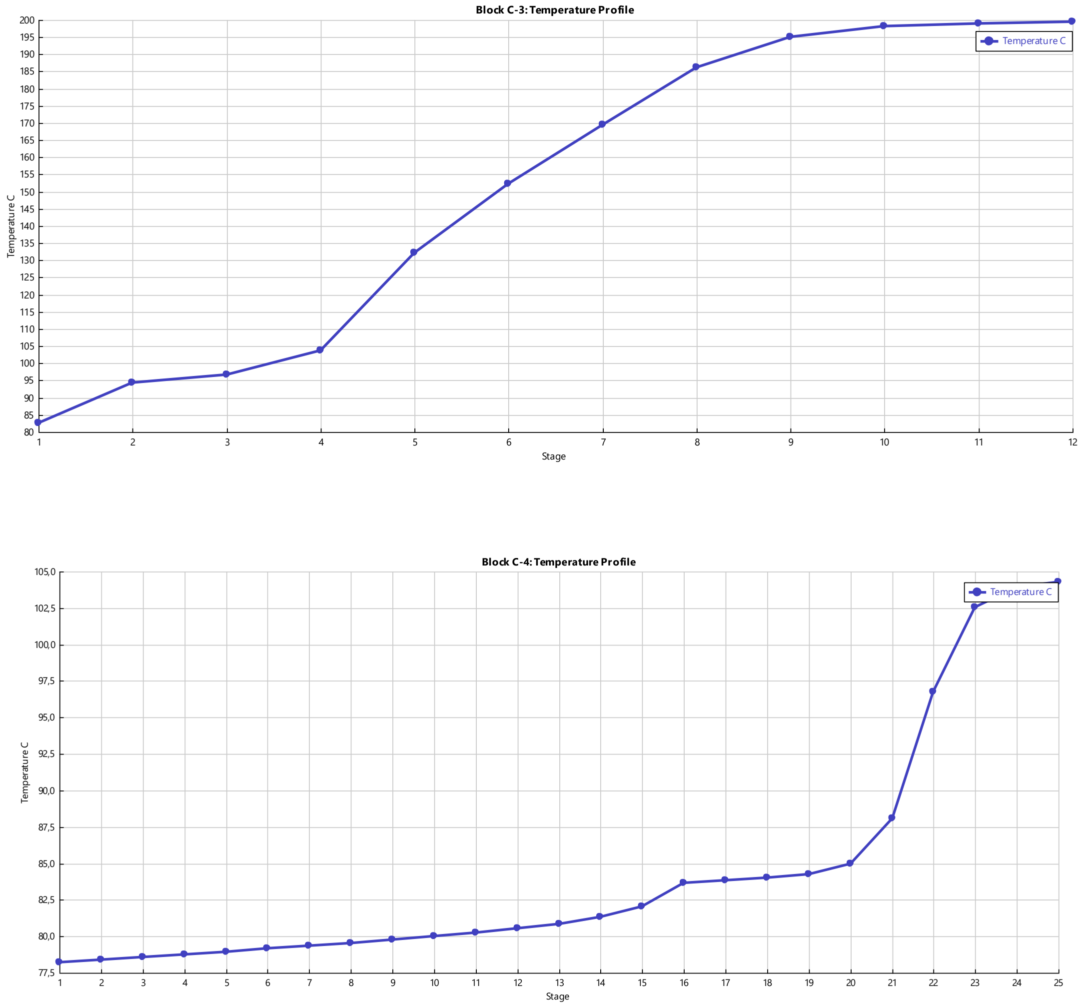


Figure 6.8 The Temperature Profiles of All Columns in the Four Column Structure (continued).

All level control loops use proportional controllers with K_c=2. The pressure controllers are proportional-integral with K_C=20 and τ_I=12 min. All flow controllers are proportional-integral with $K_C = 0.5$, $\tau_I = 0.3$ min and a filter time constant $\tau_F = 0.1$ min. For the temperature controllers, a deadtime of 60 sec is entered. The relay-feedback tests are applied to all temperature loops to find the ultimate gains and periods, and Figure 6.9 gives the relay-feedback test results. Then, Tyreus–Luyben tuning rule is used to determine the controller gain and integral time. For the cooler temperature control loop, open loop tests are performed for determining the PI tuning constants following the IMC-PI tuning rule. The results of those calculations and the final controller tuning parameters are shown in Table 6.8.

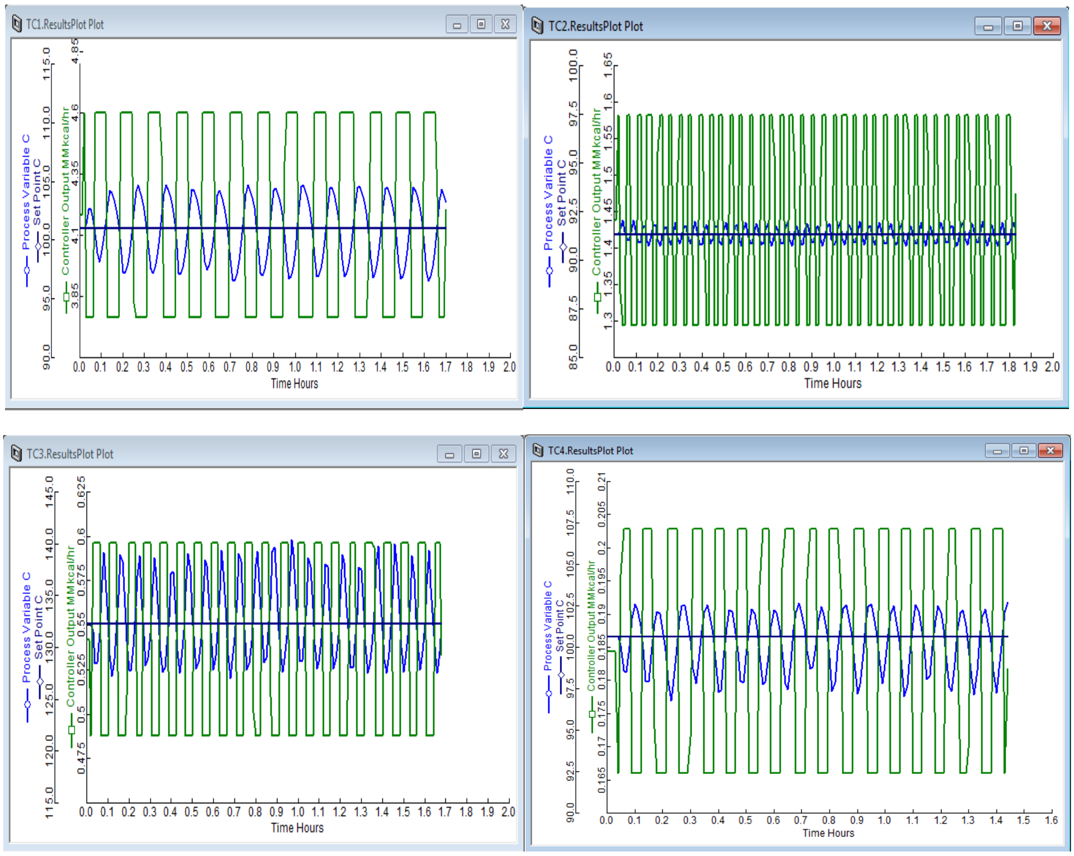


Figure 6.9 ATV Test Results.

Table 6.8 Temperature Controllers Tuning Parameters.

	TC1	**TC2**	**TC3**	**TC4**
Ultimate gain	0.901947	5.966489	0.541961	1.433798
Ultimate period	7.8 min	3 min	4.8 min	4.2 min
Kc	0.281858	1.864528	0.169363	0.448062
τ_I	17.16 min	6.6 min	10.56 min	9.24 min
	TCcool			
Open loop gain	10.00003			
Time constant	0.629993 min			
Dead time	1.8 min			
Kc	0.05			
τ_I	1.529993 min			

The control scheme of the three-column configuration displayed in Figure 6.10 is determined through the control loops as follows:

- Reflux drum levels for extractive and solvent recovery columns are controlled by manipulating distillate flow rates.

- Reflux drum level for preconcentrator column is controlled by manipulating reflux.
- Base levels for preconcentrator column, extractive column are controlled by manipulating bottoms flow rates.
- Base level for solvent recovery column is controlled by manipulating makeup flow rate.
- Operating pressures of all columns are controlled by manipulating the corresponding condenser duties.
- Entrainer flow rate is rationed to the azeotropic feed and the ratio is controlled by manipulating the bottoms flow rate of the recovery column.
- Reflux ratios are held constant in extractive column and solvent recovery column at their nominal values during disturbances.
- Distillate flow rate of the preconcentrator column is rationed to the reflux flow rate.
- Fresh feed to the preconcentrator column is flow control in order to guarantee the constant flowrate.
- Entrainer feed temperature is controlled by manipulating cooler duty.
- Reboiler duties of all columns are used to control the temperature in a particular stage of each column.

In the three-column configuration, preconcentrator column has a partial condenser. Control of partial condenser columns is more complicated due to the connection between the pressure, reflux drum level, and tray temperature control loops. Three alternative control structures are studied. In the first control structure (CS1), reflux is ratioed to the feed flowrate, pressure is controlled by distillate flowrate, and level is controlled by condenser heat removal. In the second strucure (CS2), condenser heat removal is fixed, pressure is controlled by distillate flowrate, and level is controlled by reflux. In the last strucure (CS3), pressure is controlled by condenser heat removal, level is controlled by reflux, and distillate flowrate is ratioed to the reflux flowrate. The performances of structures CS1 and CS2 are really similar because the reflux flowrate is fixed and only feed composition is altering. But some steady-state deviation from the desired product purities occurs. The response of structure CS3 shows some significant results, both steady-state and dynamic. So, CS3 is selected for partial condenser column control (Luyben, 2004).

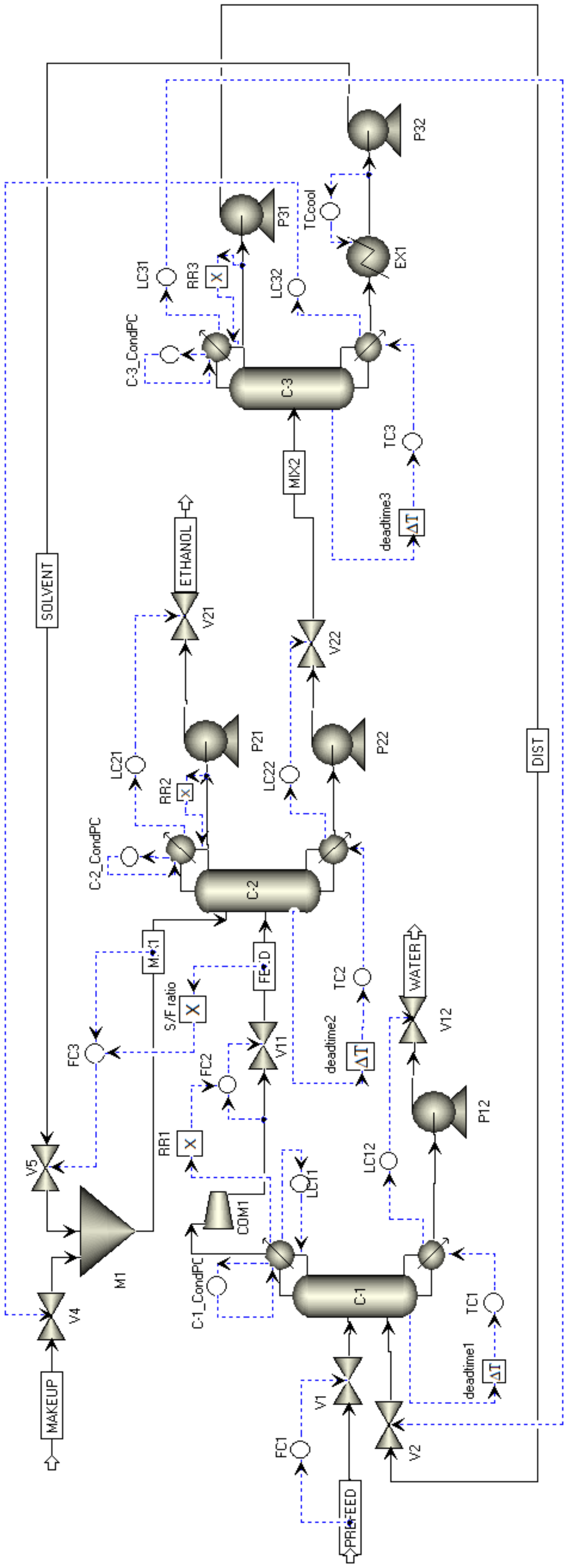


Figure 6.10 Control Structure of the Three-Column System.

Temperature profiles of columns are shown in Figure 6.11. The temperature at the 38th stage is selected as the controlled variable for the preconcentrator column. For extractive column and solvent recovery column, stage 27 and 12 are chosen, respectively.

All level, pressure and flow controllers are set like the four-column control configuration. For the temperature controllers, the relay-feedback tests are applied to the columns to determine the ultimate gains and periods, and Figure 6.12 gives the relay-feedback test results. For the cooler temperature control loop, the controller is set like the previous structure. The results of those calculations and the final controller tuning parameters are shown in Table 6.9.

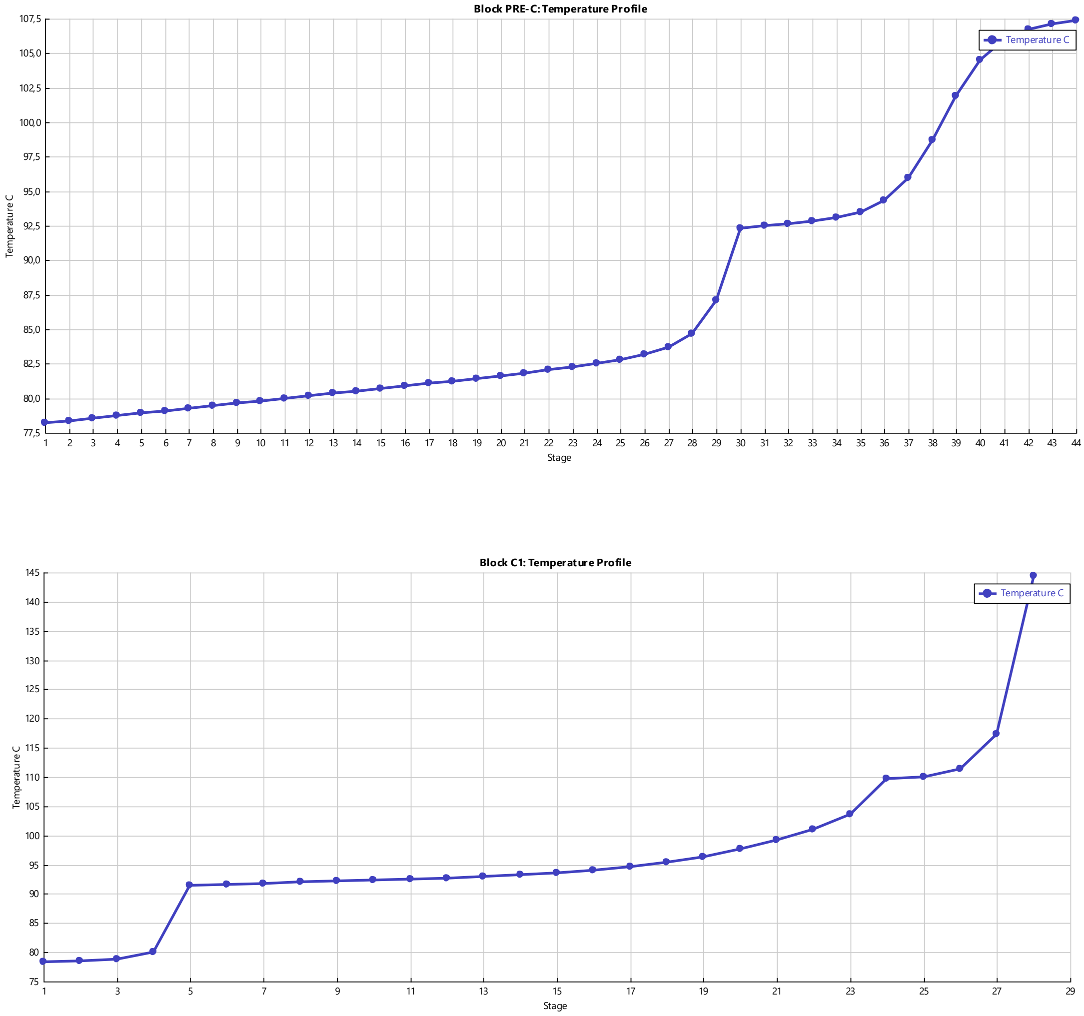


Figure 6.11 The Temperature Profiles of All Columns in Three Column Configuration.

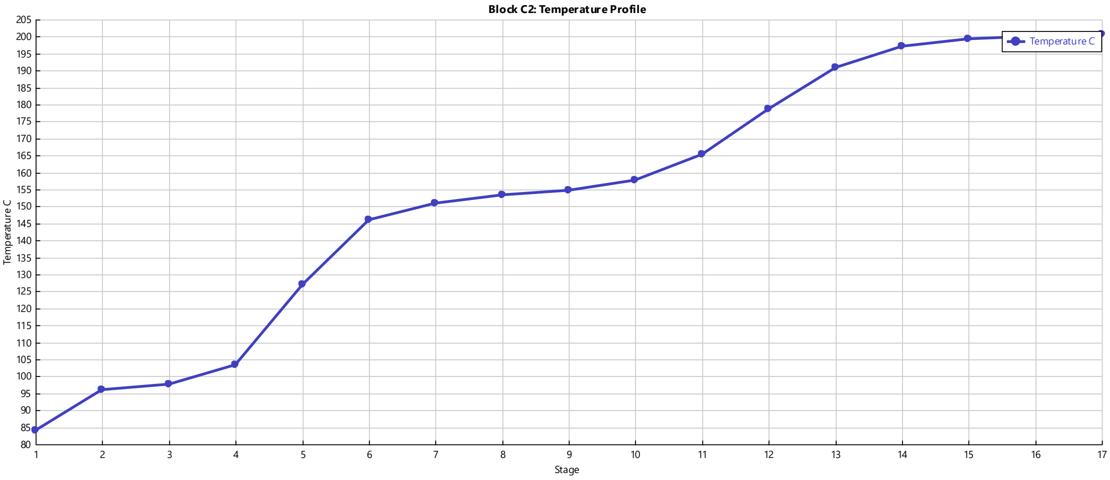


Figure 6.11 The Temperature Profiles of All Columns in Three Column Configuration (continued).

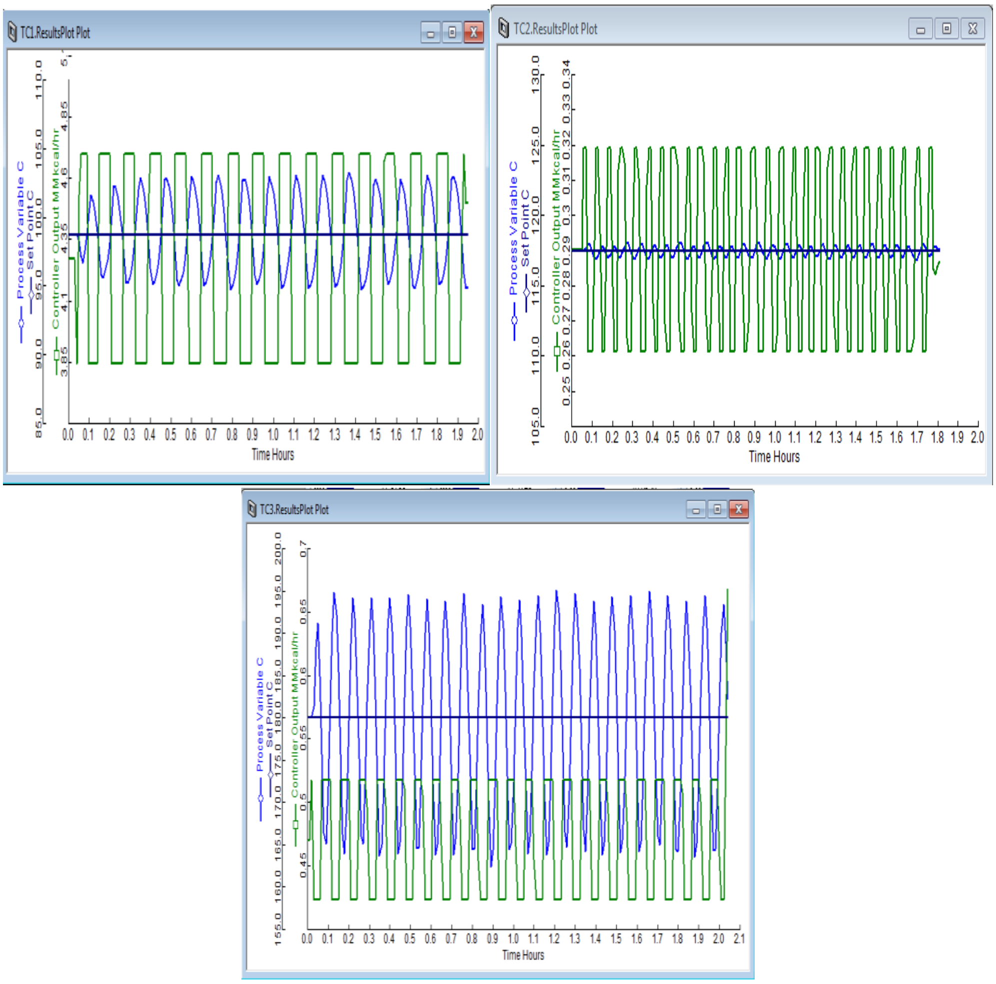


Figure 6.12 ATV Test Results of the Three Column Configuration.

Table 6.9 Temperature Controllers Tuning Parameters.

	TC1	**TC2**	**TC3**
Ultimate gain	0.817214	5.575205	0.211549
Ultimate period	7.2 min	3.6 min	4.8 min
Kc	0.25538	1.742252	0.066109
τ_I	15.84 min	7.92 min	10.56 min

	TCcool
Open loop gain	10.00002
Time constant	0.623777 min
Dead time	0.6 min
Kc	0.090566
τ_I	0.923777 min

Control scheme of the two-column configuration shown in Figure 6.13 is determined through the control loops as follows:

- Reflux drum level for extractive column is controlled by manipulating distillate flow rate.
- Reflux drum level for preconcentrator column is controlled by manipulating reflux.
- Base level for preconcentrator column is controlled by manipulating bottoms flow rates.
- Base level for second column is controlled by manipulating makeup flow rate.
- Operating pressures of both columns are controlled by manipulating the corresponding condenser duties.
- Entrainer flow rate is rationed to the azeotropic feed and the ratio is controlled by manipulating bottoms flow rate of the recovery column.
- Reflux ratio is held constant in extractive column at their nominal values during disturbances.
- Distillate flow rate of the preconcentrator column is rationed to reflux flow rate.
- Fresh feed to the preconcentrator column is flow controlled in order to guarantee the constant flowrate.
- Entrainer feed temperature is controlled by manipulating cooler duty.

- Reboiler duties of both columns are used to control the temperature in a particular stage of each column.
- The temperature of the vapor sidestream is controlled by manipulating bottom flow rate of the second column.

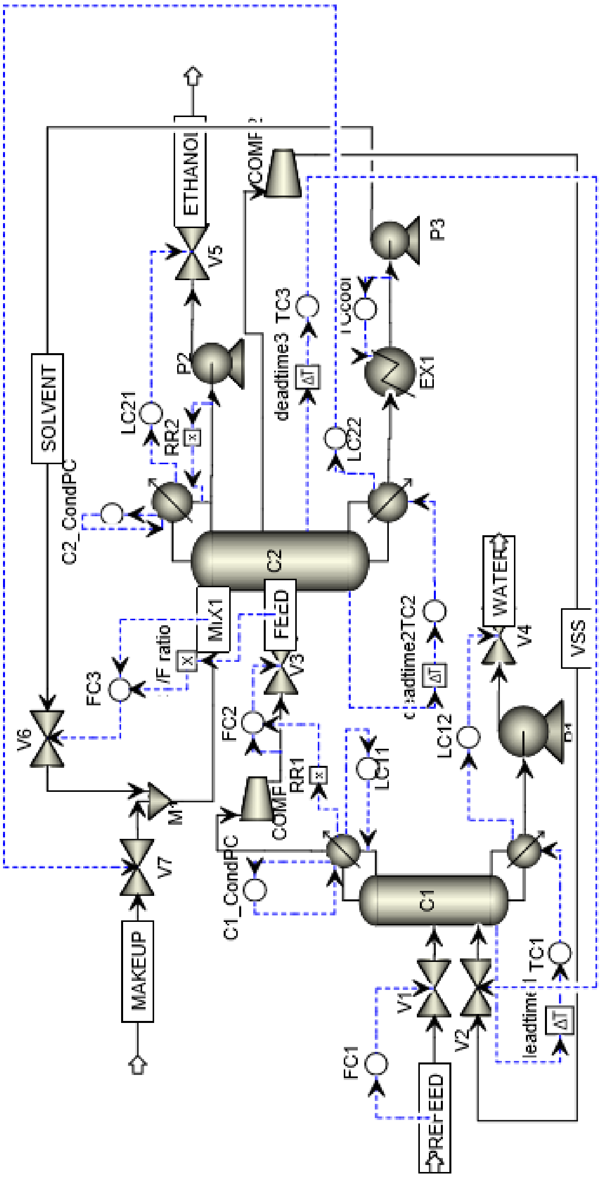


Figure 6.13 The Control Structure of the Two-Column System.

Temperature profiles of both columns are shown in Figure 6.14. The temperature of the 35th stage is selected for the preconcentrator column, while stage 37 is chosen for the temperature control of the extractive column.

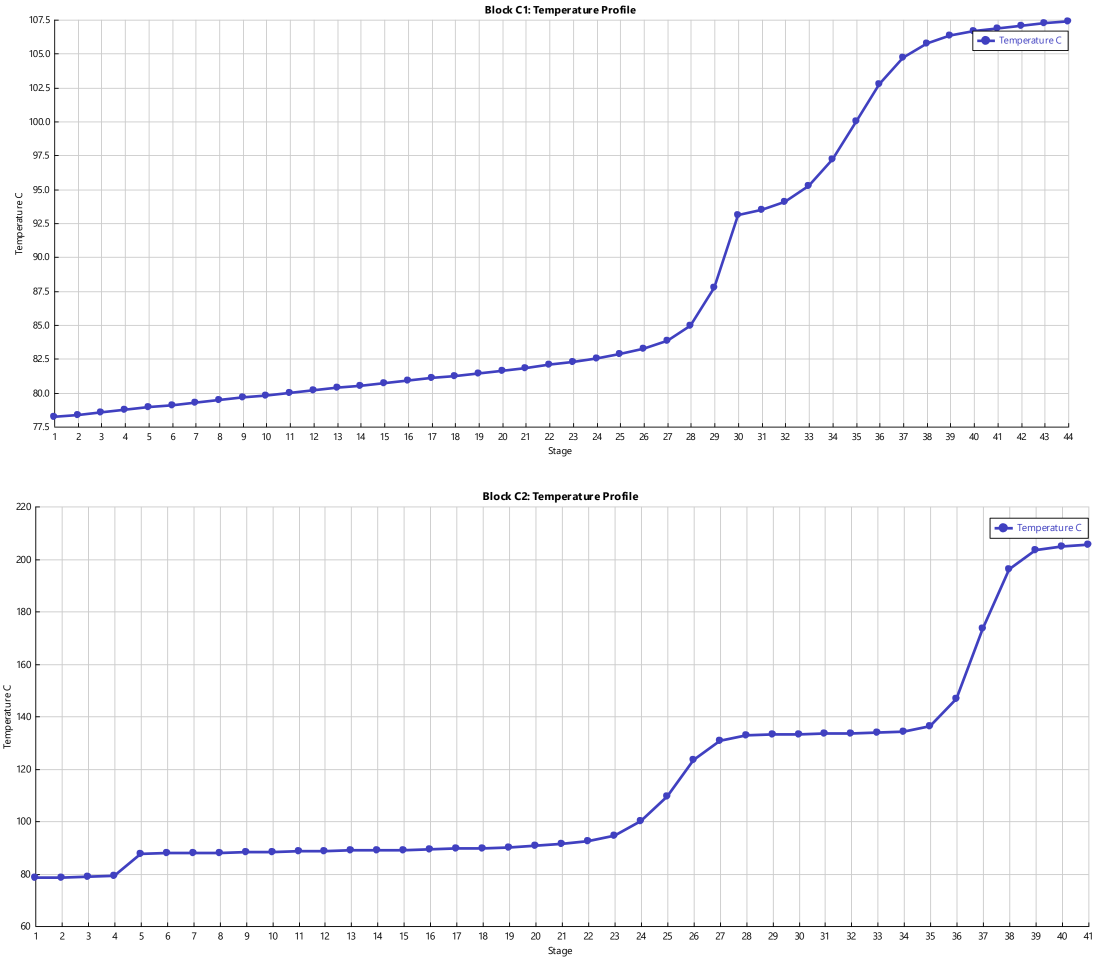


Figure 6.14 The Temperature Profiles of All Columns in the Two Column configuration.

All level, pressure and flow controllers are set like the four column and three column structures. The relay-feedback tests are applied to both columns and Figure 6.15 give the relay-feedback test results. Then, Tyreus–Luyben tuning rule is used. For the cooler temperature control loop, open loop tests are performed following the IMC-PI tuning rule. The results of those calculations and the final controller tuning parameters are shown in Table 6.10.

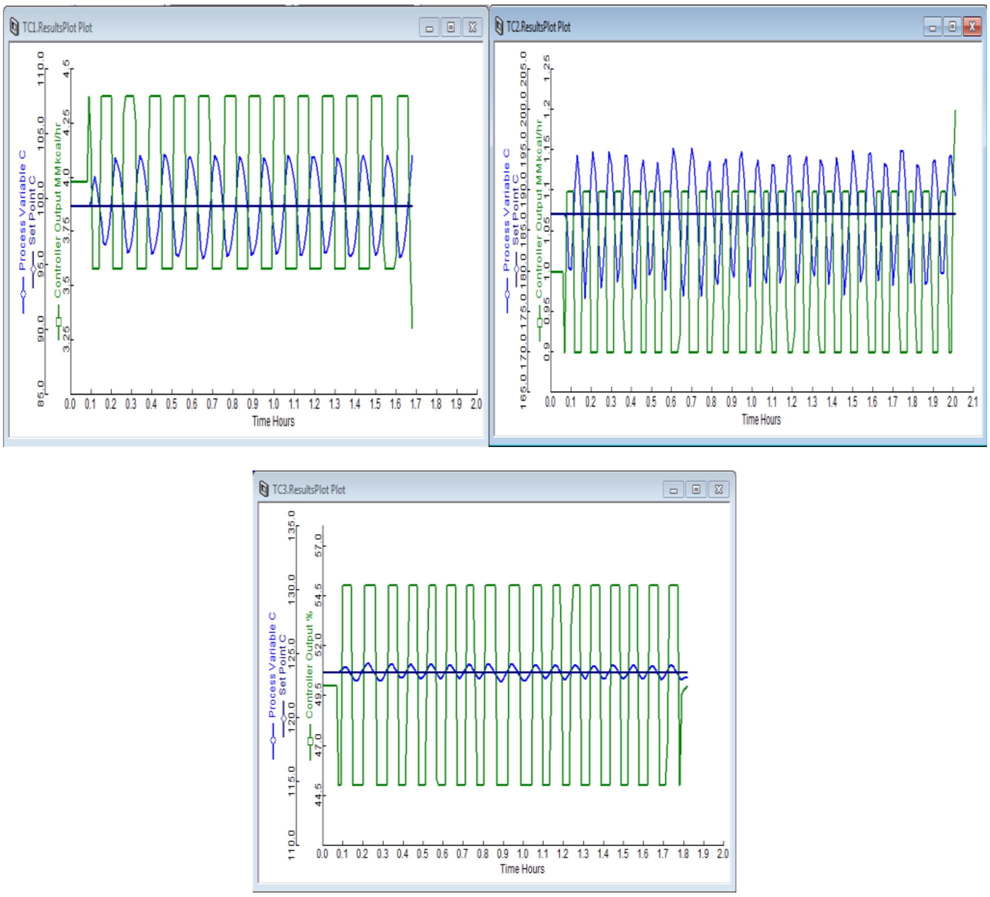


Figure 6.15 ATV Test Results of the Two Column System.

Table 6.10 Temperature Controllers Tuning Parameters.

	TC1	**TC2**	**TC3**
Ultimate gain	0.834096	0.410483	5.967587
Ultimate period	7.8 min	4.8 min	6 min
Kc	0.260655	0.128276	1.864871
τ_I	17.16 min	10.56 min	13.2 min

	TCcool
Open loop gain	10
Time constant	0.604098 min
Dead time	1.2 min
Kc	0.059024
τ_I	1.204098 min

6.3 Dynamic Test Results

Fresh feed flow disturbances of ±20% at 1 hr and also two ethanol composition disturbances, from 5 to 6 mol% ethanol and from 5 to 4 mol% ethanol, at time = 1 hr have been considered for each control configurations. The closed-loop results are shown for these disturbances for each configurations.

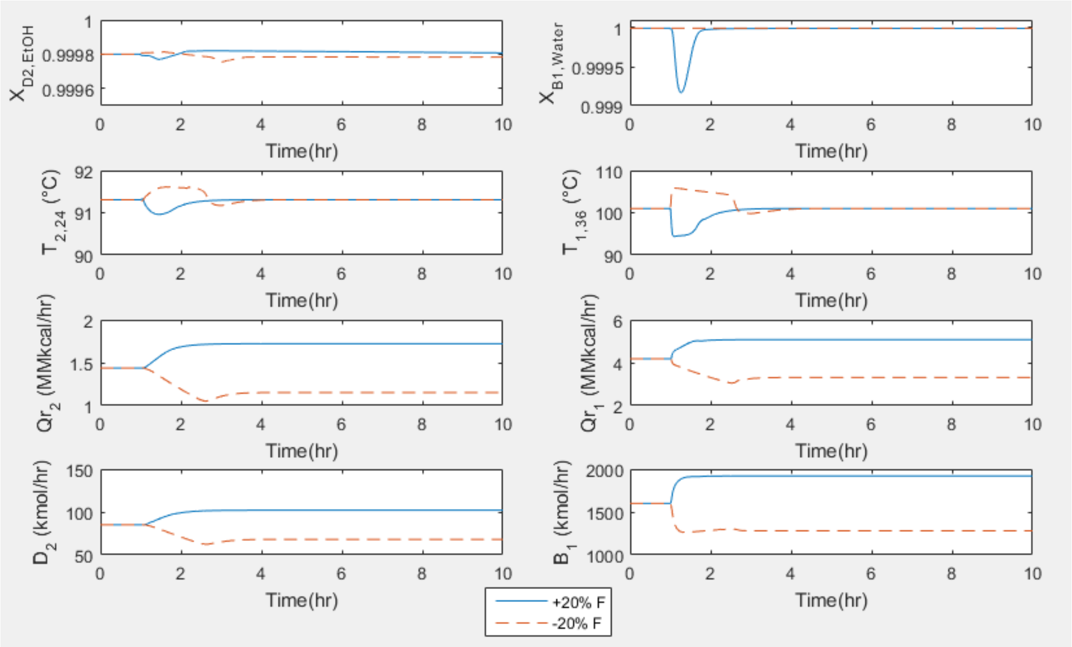


Figure 6.16 Dynamic Responses for Feed Flow Disturbances for the Four Column Configuration.

Ethanol composition is 0.9998 as shown in Figure 6.16 and becomes steady state with a very small change at 2 hr for a positive 20% disturbance and at 4 hr for a negative 20% disturbance. Temperature is reached the steady state with 1°C change at 4 hr. While water composition of the preconcentrator column is not affected by -20% feed flow disturbance, it is affected with a small change by +20% disturbance, but it reaches to steady state quickly in 1 hour. Temperature change is observed in approximately 5°C. Besides, in the dynamic responses of the temperature, reboiler duty and also distillate flow rate of the extractive column and preconcentrator column, steady state are reached at 4 hr.

Figure 6.17 shows the dynamic responses of the solvent recovery and concentrator column. All control and manipulated variables reache steady state conditions approximately at 4 hr except solvent composition for +20% disturbance. Solvent and water compositions show very little changes but in the temperature for the third and forth column the change is about 7°C and 3°C, respectively.

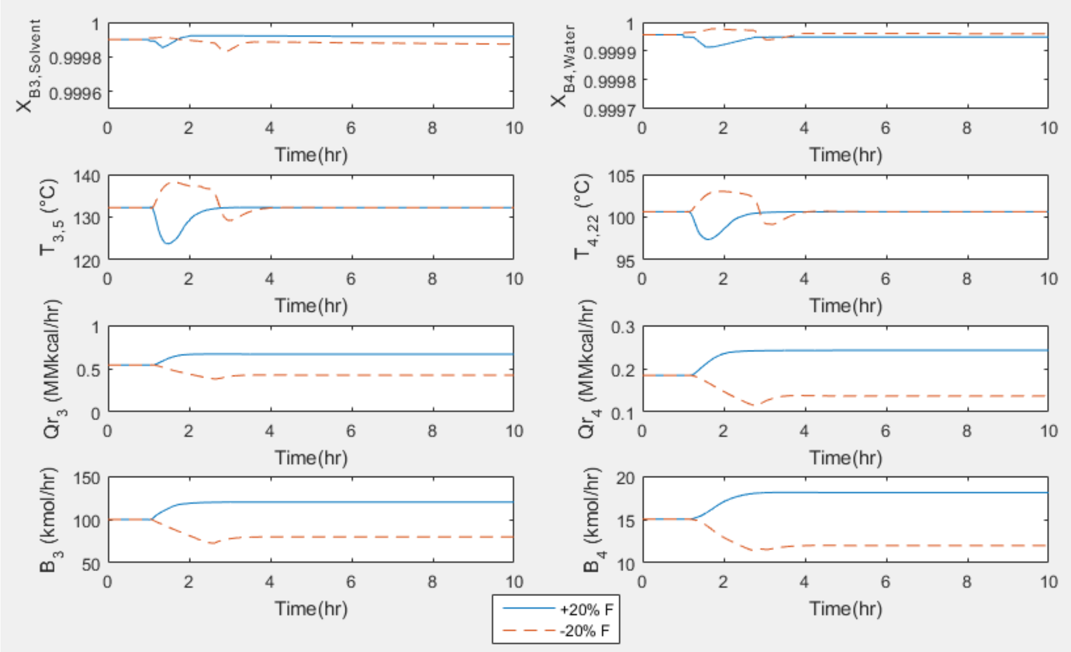


Figure 6.17 Dynamic Responses for Feed Flow Disturbances for the Four Column Configuration.

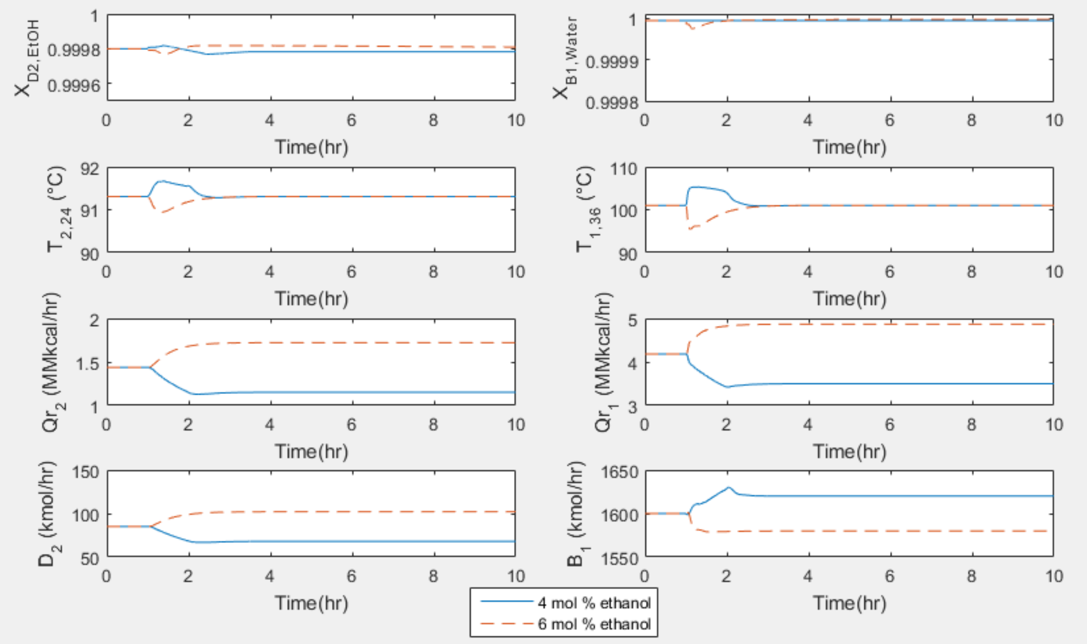


Figure 6.18 Dynamic Responses for Feed Composition Disturbances for the Four Column Configuration.

The compositions of the four-column system are hardly ever affected from feed composition disturbances (Figure 6.18 and 6.19) and also ethanol compositions are 0.9998 and 0.9999, respectively in distillate of extractive column. All of the dynamic responses of the system reach steady state approximately at 3 hr. In feed composition disturbances, the control loops are stabilized quickly than in feed flow disturbances.

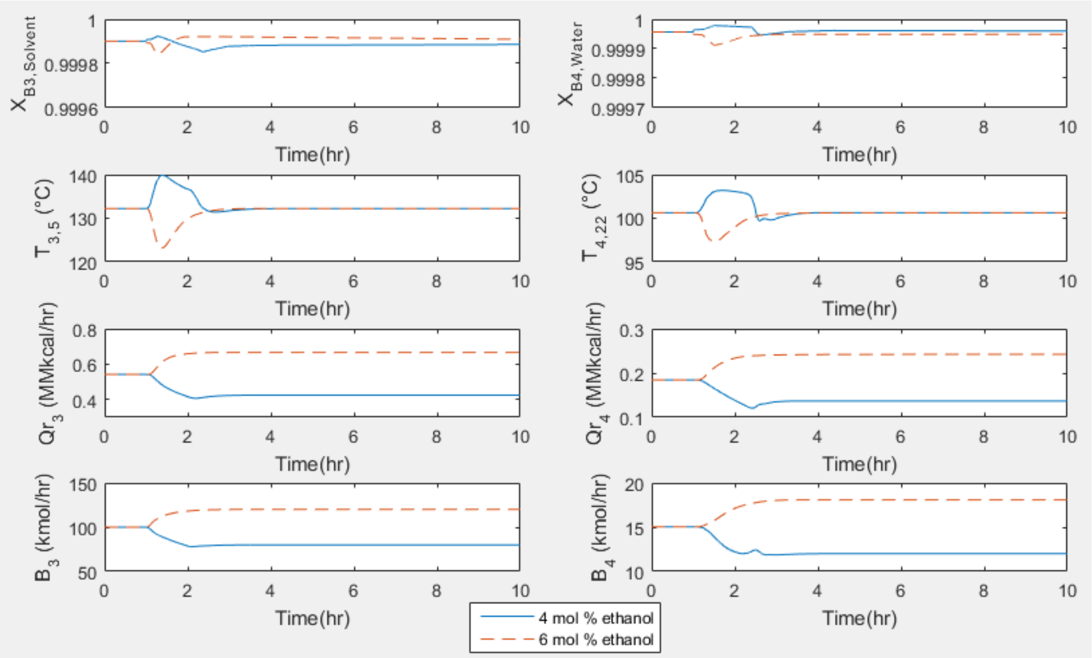


Figure 6.19 Dynamic Responses for Feed Composition Disturbances for the Four Column Configuration.

Dynamic responses of feed flow disturbance of the three-column system are shown in Figure 6.20. Ethanol and solvent compositions stabilize before at 4 hr. Although water composition is not affected by -20% feed flow disturbance, it is affected by +20% feed flow disturbance with small change and then it reaches the steady state at 3 hr. Although the preconcentration and extractive column show very small changes in temperature control, the solvent recovery column temperature variation is about 20 °C. While in 6 mol% feed composition disturbance, very small changes is observed in the compositions; in 4 mol% feed composition disturbance, almost no change is observed in the compositions. Temperature controllers give the same dynamic responses in feed flow disturbances. All control and manipulated variables are stabilized at 3 hr as seen in Figure 6.21.

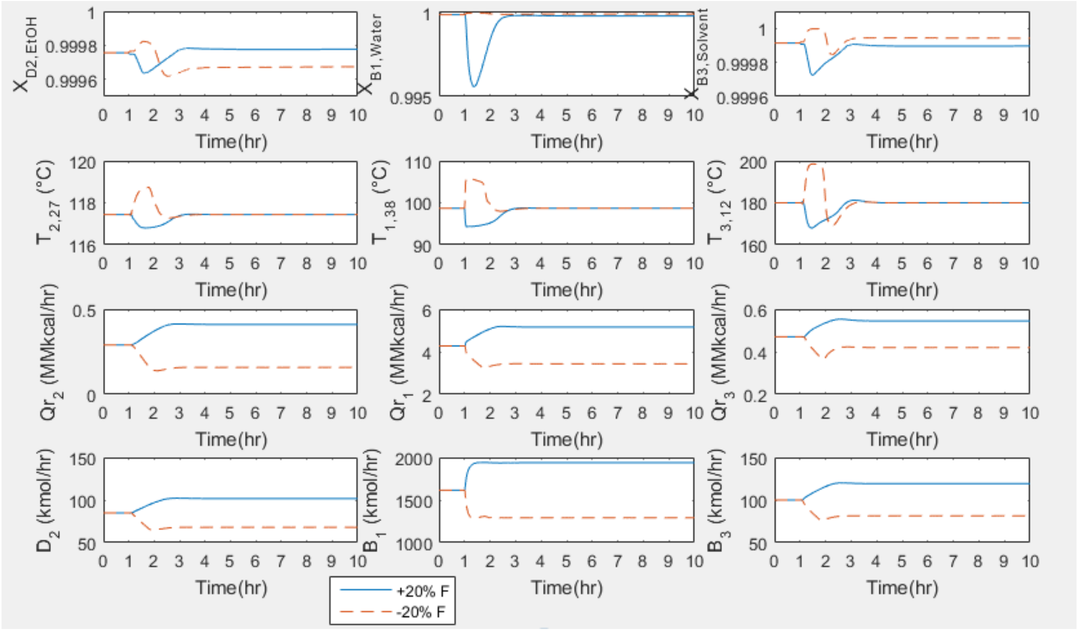


Figure 6.20 Dynamic Responses for Feed Flow Disturbances for the Three Column Configuration.

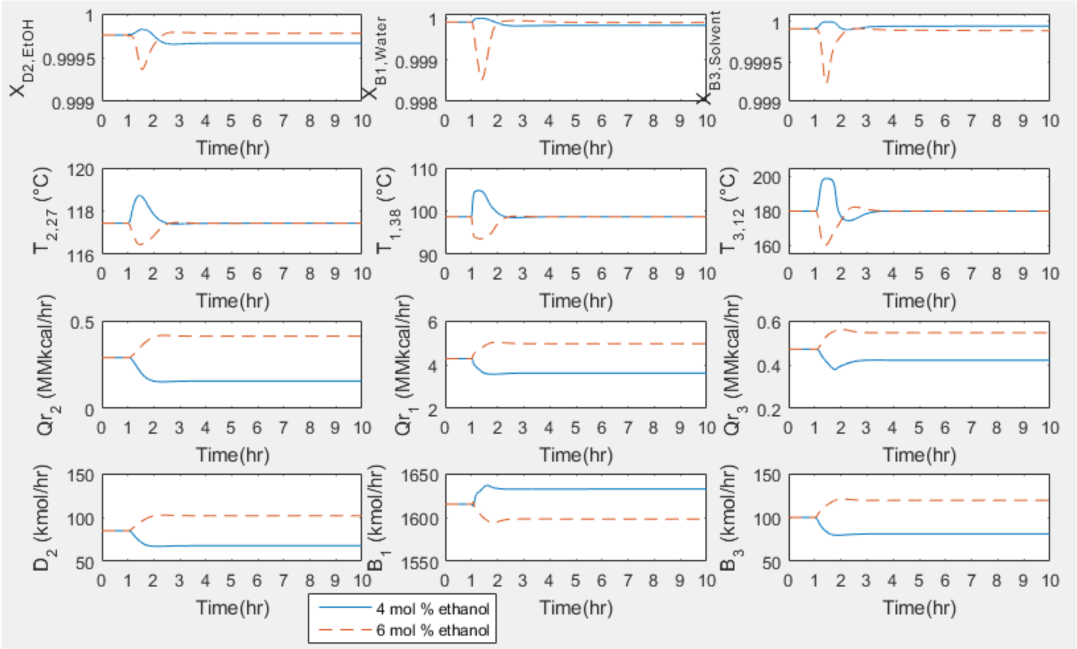


Figure 6.21 Dynamic Responses for Feed Composition Disturbances for the Three Column Configuration.

After the implementation of feed flow and feed composition disturbances, the dynamic responses of the two-column systems are very similar. In less than 3 hr, the controllers have reached steady state. The results of the system are given in Figure 6.22 and Figure 6.23.

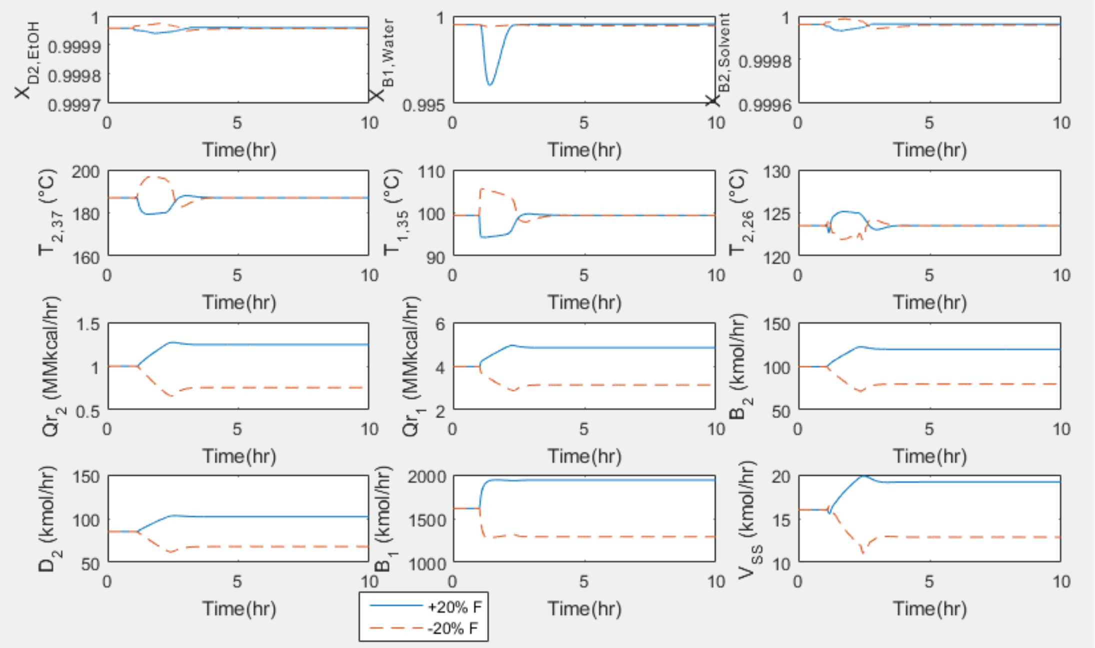


Figure 6.22 Dynamic Responses for Feed Flow Disturbances for the Two Column Configuration.

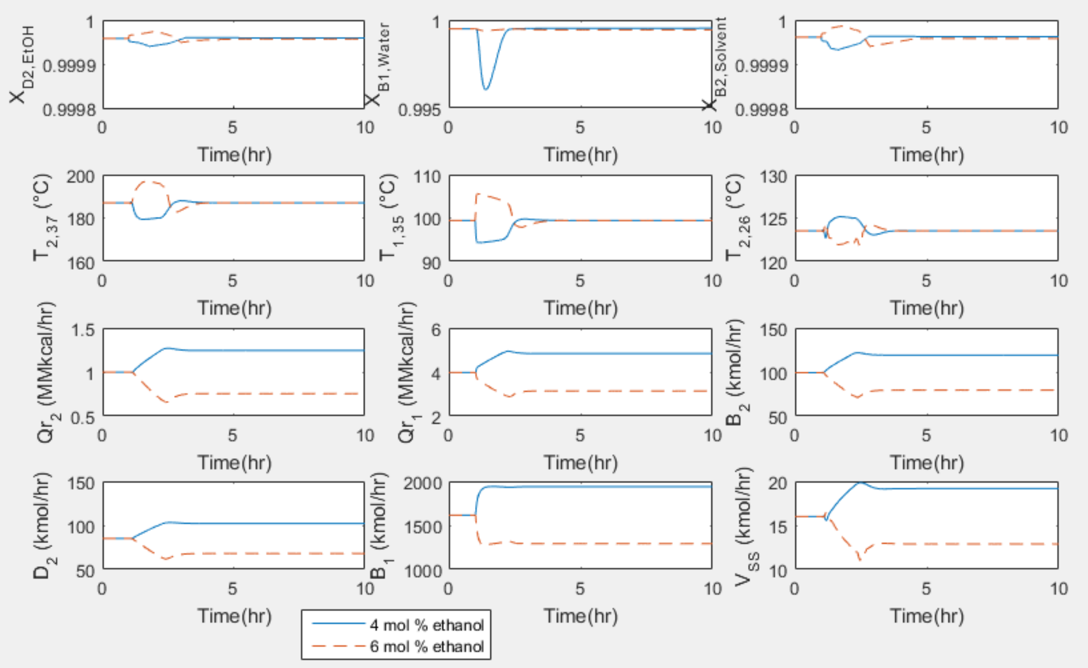


Figure 6.23 Dynamic Responses for Feed Composition Disturbances for the Two Column Configuration.

7. CONCLUSIONS

This thesis represents the design and control of an ethanol dehydration process with extractive distillation using ethylene glycol as entrainer. Three design flowsheets have been represented: the four-column, three-column and the two-column flowsheets. The purity of ethanol, otal reboiler duty and the solvent consumption have been considered for all the structures. Two-column structure overcomes all the others by reducing the total reboiler duties.

In the control of the flowsheets, ethanol , water and solvent concentrations stay close to their nominal values. The ethanol composition is higher than 99.5 mol% for each disturbance types of all configurations. So this provides suitable fuel process applications for ethanol. Temperature changes is very small and in addition temperature controllers are achieved the disturbance well by turning the temperatures back to their setpoints.

As a result, the control structures showed robust controllability against the disturbances in the production rate handles and feed compositions. Two-column structure with a vapor side stream can provide a significant alternative in integrated bioethanol and biodiesel plants.

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Dönem İçi Proje – Biyomalzemeler ve Biyouyumluluk

Dönem İçi Proje - Asetik Anhidrit Üretimi

Dönem İçi Proje - Fosil Yakıtların Yakılmasından Kaynaklanan Sera Etkisi ve Kontrolü

Dönem İçi Proje – Reaktör Tasarımı

Tasarım Projesi - Distilasyon, Gaz Absorbsiyonu ve Sıvı Sıvı Ekstraksiyonu

Tasarım Projesi - Oksalik Asit Üretimi

Tasarım Projesi - Tekstil Endüstrisi Atık Sulardaki Boyar Maddelerin Giderilmesi

Laboratuar Projesi / Çalışması - Barbunya Fasulyesinin Su Alma Özelliklerinin Belirlenmesi

Lisans Tezi - Remozal Navy RGB Reaktif Mavi Tekstil Boyarmaddesinin Aktif ve İnaktif Kefir Taneleri ile Biyosorpsiyon Kinetiğinin İncelenmesi

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MATLAB

CHEMCAD

Aspen Plus

Aspen Dynamics

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