4-2011

Glycerol to Propylene Glycol

Kumar Chatterjee
University of Pennsylvania

Kelsey Hall
University of Pennsylvania

Samuel Tell
University of Pennsylvania

Chatterjee, Kumar; Hall, Kelsey; and Tell, Samuel, "Glycerol to Propylene Glycol" (2011). *Senior Design Reports (CBE)*. 26.
http://repository.upenn.edu/cbe_sdr/26

Glycerol to Propylene Glycol

Abstract
A Cu-ZnO-Al_2O_3 catalyst has been observed in laboratory scale tests to effectively produce propylene glycol from glycerol using a liquid phase hydrogenolysis reaction, which occurs at 410 F and 580 psia. A trickle-bed reactor will be used to ensure the full contact of liquid and vapor phases with the solid catalyst. This project aims to successfully scale up this reactor model, which has thus far only been tested in bench scale. The design specification stipulates that this process will produce 100 MM lb/year of propylene glycol. Using crude glycerol harvested from biodiesel production, a final product purity of 99.6% was achieved from a feedstock of 80% glycerol, 15% water, 1% methanol, and 4% sodium chloride by weight, plus trace amounts of organic salts.

The economic analysis that follows assumes a grassroots plant on the US Gulf Coast. The total capital investment was calculated to be \$34.0 million, which includes a working capital of \$9.78 million. Under the assumptions that the prices of crude glycerol, hydrogen, and propylene glycol are \$0.22, \$0.50, and \$1.00 per pound respectively, the net present value (NPV) at the end of the 15 year allotted course of the project is \$88.4 million and the investors' rate of return (IRR) is 58.45%. The price of glycerol is projected to remain stable or decrease in the future and the price of propylene glycol is projected to remain stable or increase suggesting that this project could become even more profitable in the future.

The apparent profitability of this project is largely caused by the efficient and cost effective method of desalting glycerol through electrodeionization. Unfortunately, the proprietary nature of this new process precludes public access to true costing and specifications for the equipment since firms as Dow largely control the technology. Thus, conservative estimations were made in our economic analysis to account for this uncertainty.

Glycerol to Propylene Glycol

April 12, 2011

Kumar Chatterjee

Kelsey Hall

Samuel Tell

Advisor: Dr. Warren Seider

Professor Warren Seider
Professor Leonard Fabiano
Department of Chemical and Biomolecular Engineering
University of Pennsylvania
220 South 33rd Street
Philadelphia, PA 19104

April 12, 2011

Dear Professor Seider and Professor Fabiano,

As proposed by Bruce Vrana, we have designed a plant that will produce one hundred million pounds per year of propylene glycol from crude glycerol, which is a byproduct derivative of biodiesel production. This process integrates electrodeionization, an emerging glycerine refinement technology, with a multiphase reaction in a trickle-bed reactor.

This report includes the design details for the process, an economic analysis, and recommendations and predictions for the extent of its success. Based on the aforementioned analysis, this process is found to be a viable and profitable alternative to current methods of propylene glycol production. Furthermore, the process is environmentally friendly while also complementing the growth of the biodiesel industry that is predicted to surge over the project's lifetime.

Thank you for your consideration and assistance with this endeavor.

Sincerely,

Kelsey Hall Kumardipti Chatterjee Samuel Tell

TABLE OF CONTENTS

Section 1

ABSTRACT

Abstract

A Cu-ZnO-Al_2O_3 catalyst has been observed in laboratory scale tests to effectively produce propylene glycol from glycerol using a liquid phase hydrogenolysis reaction, which occurs at 410 F and 580 psia. A trickle-bed reactor will be used to ensure the full contact of liquid and vapor phases with the solid catalyst. This project aims to successfully scale up this reactor model, which has thus far only been tested in bench scale. The design specification stipulates that this process will produce 100 MM lb/year of propylene glycol. Using crude glycerol harvested from biodiesel production, a final product purity of 99.6% was achieved from a feedstock of 80% glycerol, 15% water, 1% methanol, and 4% sodium chloride by weight, plus trace amounts of organic salts.

The economic analysis that follows assumes a grassroots plant on the US Gulf Coast. The total capital investment was calculated to be $34.0 million, which includes a working capital of $9.78 million. Under the assumptions that the prices of crude glycerol, hydrogen, and propylene glycol are $0.22, $0.50, and $1.00 per pound respectively, the net present value (NPV) at the end of the 15 year allotted course of the project is $88.4 million and the investors' rate of return (IRR) is 58.45%. The price of glycerol is projected to remain stable or decrease in the future and the price of propylene glycol is projected to remain stable or increase suggesting that this project could become even more profitable in the future.

The apparent profitability of this project is largely caused by the efficient and cost effective method of desalting glycerol through electrodeionization. Unfortunately, the proprietary nature of this new process precludes public access to true costing and specifications for the equipment since firms as Dow largely control the technology. Thus, conservative estimations were made in our economic analysis to account for this uncertainty.

Section 2

INTRODUCTION

Introduction

Propylene glycol (also called 1,2-propanediol) is an incredibly versatile compound that is used in a number of industrial applications that range from transportation and construction to food and pharmaceutical production. Pharmaceutical (USP) grade propylene glycol is at least 99.5% pure by weight and is used in health-sensitive products such as food, personal consumer goods, cosmetics, and pharmaceuticals. Due to its highly sensitive applications, USP grade propylene glycol is regulated carefully by the FDA and producers must comply with strict regulations to ensure the quality and purity of their product. Industrial grade propylene glycol is at least 95% pure and is an important player in the transportation industry as it is used in aircraft de-icer, antifreeze, and brake fluid. It is also used in the construction industry as the primary component in unsaturated polyester resins (UPRs) that are used to make fiberglass reinforced plastics.

Propylene glycol's chemical neutrality and nonreactivity make it very useful as a solvent. It can be used as an emulsifier to stabilize mixtures of two or more immiscible liquids. This often occurs in the preparation of cosmetics, where oil and water must be mixed to produce creams or lotions, and in the preparation and processing of some foods. It is a useful excipient, a pharmacologically inactive substance that acts as a carrier for the active ingredients in medication. It can be used for boiling point elevation or freezing point reduction, which makes it an effective de-icer and antifreeze solution.

Historically, propylene glycol has been produced by the hydration of propylene oxide, which occurs at 392 F and 174 psia, or catalytically at 302-356 F, and produces diand tripropylene glycols and small quantities of higher glycols in side reactions (ICIS, 2011). This process has a large negative environmental impact due to pollution and use of valuable resources, so alternative methods, such as production from glycerol, are under investigation worldwide. This option is especially promising in light of the recent surge in biodiesel production. Interest in "greener" technologies has in part been responsible for this boom, creating incentive for companies to invest in research to develop more environmentally friendly methods to produce and distribute their products. In addition to being extremely profitable, the glycerol to propylene glycol manufacturing process described in this report can be marketed as "green" technology, increasing the value of the end product.

The method for propylene glycol production described here consists of three main sections: a pretreatment section, in which crude glycerol purchased from biodiesel manufacturers is desalted by electrodeionization for feed to the reactor; a reactor section, which contains a trickle-bed reactor packed with alumina-supported catalyst for the reaction of glycerol; and a separation section, in which the product is purified to 99.5% (USP grade). Overall, this process describes a profitable, novel way to produce propylene glycol while reducing the negative environmental effects of traditional production methods. It is predicted to eventually become a mainstream process in industry.

Section 3

PROJECT CHARTER

Initial Project Charter

Project Name

Glycerol to Renewable Propylene Glycol

Project Champions

Bruce M. Vrana (DuPont)
Dr. Warren D. Seider (UPenn)
Professor Leonard Fabiano (UPenn)

Project Leaders

Kelsey Hall
Kumar Chatterjee
Samuel Tell

Specific Goals

Develop a process to make 100MM lb/year of propylene glycol from crude glycerol that provides a high Net Present Value and Return On Investment

Project Scope

In Scope:

- Selecting an optimal catalyst for the process
- Designing a trickle-bed reactor model based on reaction kinetics
- Investigating and choosing an efficient and cost-effective pre-treatment equipment for crude glycerol
- Creating a process flow sheet for the overall process
- Conducting a financial analysis of the process to determine the ROI of the project
- Writing a report that summarizes all relevant information

Out of Scope:

- Testing and verifying reaction kinetics, conversions and yields proposed in literature

Deliverables

Business Opportunity Assessment
Technical Feasibility Assessment
Manufacturing Capability Assessment
Safety and Health Assessment
Profitability Analysis

Timeline

The deliverables included above will be completed in 10 weeks. Future implementation of the project proposal will be determined by the Project Champions.

Section 4

TECHNOLOGY READINESS ASSESSMENT

Technology Readiness Assessment

One major limiting factor for the synthesis of propylene glycol from glycerol is the extremely high cost and difficulty of glycerol desalting. In the past, vacuum distillation was the only option and was very expensive, precluding the entry of many proprietors into the market. There are a number of companies that specialize in glycerine desalting, but the purified feed glycerol is expensive and drives up the cost of the process. As membrane and resin technologies improve, the electrodeionization process becomes a low cost alternative to vacuum distillation, which allows the use of crude glycerol in the process feed, making the process much more economically feasible. The popularity of biodiesel has increased in recent years, increasing the availability and decreasing the price of the crude glycerol process input.

Although the kinetic model for the glycerol to propylene glycol reaction used in this process is fairly new, the necessary Cu-ZnO-Al_2O_3 catalyst is available commercially. Alumina-supported catalysts such as this are standard for use in many industrial applications. A catalyst very similar to the one in this process is widely used for methanol synthesis and other applications. It is manufactured and sold by a number of companies worldwide, such as Haldor Topsoe (MK-121 catalyst).

Slight manipulation must be done to prepare the catalyst for use in the propylene glycol manufacturing process, as the reaction kinetics call for the catalyst particles to have a diameter less than 0.22 mm. Since the commercial methanol synthesis catalysts are sold in larger (6x5 mm) pellets, simple manual crushing of the catalyst to achieve the desired size will suffice.

The Cu-ZnO-Al_2O_3 catalyst with a molar metal ratio of 1:1:0.5 was chosen out of a group of similar options with slight variations (Zhou 2010). In activity tests, this showed the highest conversion and selectivity to propylene glycol. It is assumed in the process analysis that a 100% conversion may be reached by extrapolating the mass of catalyst to a large enough value based on the expressions for r_1 and r_2. In reality, this is an optimistic estimate, and the actual conversion will be less than 100%. It is expected that the actual conversion will fall between the 82% achieved in Zhou's activity test and the 100% predicted with the extrapolation model (Appendix B). To account for this, further separation may be necessary following the reactor section in the process.

Prior to beginning plant construction, a midsize pilot plant should be used to determine the reliability of scale-up models used for the reactor. This will also provide a more precise value for the conversion of glycerol in the reactor. The final separation train should not be designed until the reactor product composition can be determined.

Section 5

CONCEPT STAGE

Market Analysis

In the following sections, the various inputs and products of this process are analyzed in the context of their individual markets to determine consumer, technical and financial needs. Propylene glycol historically has been synthesized from a petroleum derivate known as propylene oxide. In recent years, novel reaction routes have been discovered to synthesize propylene glycol from glycerol. In a patent issued to the BASF chemical company, a Cu-ZnO-Al_2O_3 catalyst was identified that converts glycerol to propylene glycol with very high conversion. Crude glycerol, a naturally occurring by-product of biodiesel production, will be used as a feed to this process.

Crude Glycerol Market

For every nine kilograms of biodiesel produced, about one kilogram of glycerol is formed; thus, the market for crude glycerol is intimately linked with the biodiesel industry (Chiu *et al.* 2006). Biodiesel represents a very promising green alternative as it can be used in conventional diesel engines. Furthermore, the synthesis mechanism for biodiesel is well studied and can be carried out using a variety of feed stocks. As of 2009, 148 plants were producing 2 billion gallons of biodiesel a year in the US. As a result, 200 million gallons of glycerol was produced as well (Johnson *et al.* 2007). Although purified glycerol can be sold for \$0.60/lb-\$1.20/lb depending on the grade, crude glycerol is currently sold for \$0.22/lb, and the price is projected to fall as biodiesel production continues to increase.

Propylene glycol represents an inherently profitable value-added chemical produced from crude glycerol due to the high margin between the feed and final product. In addition to propylene glycol, however, a number of other alternatives also exist as potential markets for crude glycerol as outlined in the article “Glycerin – Emerging Opportunity”. Solvay Chemicals commercialized a process to reverse the conventional route of making synthetic glycerol from epichlorohydrin. After the success of their pilot plant in 2007, a full scale commercial plant is scheduled to be built in Map Tha Phut, Thailand. Epichlorohydrin can be used to make epoxy resins, paper-reinforcing agents and other similar products. Alkylene carbonate (reactive intermediate or solvent), biomenthanol, acrylic acid are additional examples of potential products produced from glycerol feed material. (Chemical Business 2010).

Companies have also invested in developing cost effective methods to purify crude glycerol. Pure glycerol has a number of uses ranging from consumer goods to food and beverages to industrial chemicals. Pharmaceutical grade glycerol can be sold for up to \$1.20/lb, making it a very profitable venture. Purada Processing and Cargill are two examples of companies that have chosen to invest in glycerol refineries. However, traditional methods of crude glycerol refinement require vacuum distillation and thus are capital and energy intensive. New purification systems, such as elecrodionization (EDI), offer good alternatives to costly and labor intensive vacuum distillation, which could further equalize glycerol supply and demand.

Propylene Glycol

Propylene glycol is a value-added derivative of crude glycerol that has the potential to be a profitable venture. PG is used in a number of markets including unsaturated polyester resins, plastics, antifreeze products, plane de-iceres, industrial solvents, and consumer goods such as detergents, cosmetics and other personal care products. The global demand for propylene glycol was 3.5 billion lb/yr as of 2007 (Shelley 2007). According to a recent report by ICIS, a subsidiary of Reed Business Information and trusted information provider for the chemical and oil industry, the demand in the unsaturated polyester resin (UPR) industry has grown approximately 2.5% per year while demand in the cosmetics and consumer goods industries has grown 3.0% and 3.5% a year, respectively (2010). Because propylene glycol is not toxic, it is gradually replacing ethylene glycol as the primary ingredient in the 2.4 billion lb/yr market of antifreeze de-icing liquids (Suppes 2008).

Although the emergence of the renewable propylene glycol market is relatively new, a number of large industry leaders have already begun to embrace the change. Dow Chemical, currently the world's leading manufacturer of petroleum based propylene glycol, introduced product called renewable propylene glycol (RPG). A successful pilot plant was built at their Dow Halterman Custom Processing Facility in Houston and a full scale plant will soon be implemented at that site. Huntsman Corp. is another major company that has begun producing RPG using a proprietary method. Located in Conroe Texas, the company started to scale up the process to produce 100 million lb/yr (Shelley 2007).

Senergy Chemical famously licensed a novel low temperature, low pressure reaction route developed by two of the most famous researchers in the field, Dr. Suppes and Dr. Sutterlin from the University of Missouri. And finally, Ashland and Cargill have signed a joint venture to build a facility to produce 65,000 tonnes per year of RPG from glycerol. Furthermore, the plant will include a large glycerol refinery that will enable it to simultaneously produce high purity glycerol to be sold in the chemical market. (Chemical Business 2010)

Consumer Requirements

Consumer Requirement Category	**Propylene Glycol Requirement**	**Type (NUD,FTS)**	**Weighting Factor**
Non-Toxic	Non-toxic to both people and animals	FTS	35
High Purity	Non-toxic for food/cosmetics	NUD	35
Low Freezing Point	Appropriate for anti-freeze	FTS	12
Miscibility	Use in detergents	FTS	6
Polar Solvent	Use in paints and detergents	FTS	6
Green Manufacturing	Biodiesel Byproduct	NUD	3
Degradability	Use in detergents and solvents	FTS	2
Ease of Handling	Use as a working fluid	FTS	1

Table 1 Consumer requirements.

The consumer requirements of non-toxicity and high purity were weighted as the most important factors because the food, consumer goods and pharmaceutical industries have been identified as the most profitable target markets. As a result, our process is designed to produce UPS-grade propylene glycol, which is defined as greater than 99.8% purity by mass. The high purity requirement is labeled as New-Unique-Difficult because it relies on new catalysts that have been developed for very high selectivity. Furthermore, these criteria are important when positioning propylene glycol in the antifreeze and de-icing markets as an alternative to the toxic ethylene glycol.

Our process is also designed to accommodate consumers in the industrial chemical market. Low freezing point, miscibility and polarity were all weighted to account for their needs. Finally, a weighting factor of 3 was assigned to “Green Manufacturing” because there is significant marketing potential if the product is characterized as an environmentally friendly chemical. Furthermore, designing a plant with a limited carbon footprint may be advantageous when seeking government subsidies or tax breaks in the future.

Section 6

PRELIMINARY PROCESS SYNTHESIS

Pretreatment Section

The growing biodiesel industry supplies an abundance of crude glycerol products that can be used as the feed for the propylene glycol synthesis process. However, this crude glycerol cannot be fed directly to the process because it contains chloride and sulfate salts and organic alcohols, which must be removed prior to reaction. If they were to enter the reactor, these salts would cause corrosion of the reactor and preclude the success of the process.

Conventional methods for accomplishing this difficult purification require a great deal of energy and resources. A number of companies, such as SRS Engineering Corporation of Murrieta, California (SRS 2010), turn a considerable profit by refining and selling purified glycerol. The conventional method of desalting glycerol involves its distillation under vacuum conditions. Glycerol is extremely stable and nonvolatile, with a normal boiling point of 554 F. Because the polymerization temperature of glycerol (approximately 500 F) is lower than its boiling point, distillation that requires glycerol evaporation is impossible to achieve at atmospheric pressure. In order to maintain the condenser's temperature below the polymerization temperature of glycerol, the separation column must run under vacuum conditions. In this process, the purified glycerol flows out of the column in an overhead stream through the condenser, leaving a highly concentrated salt solution with other heavy components in the bottoms product from the reboiler.

The high temperatures required to achieve this separation result in excessive utility usage in the form of high pressure steam and electricity. The vacuum inside the column necessitates thick walls and effective seals to prevent leakage of gases into the column and a powerful pump to maintain the vacuum. These things are expensive and contribute to the high price of glycerol purification.

Recently, new technologies involving cation/anion selective membranes have been developed. These allow for electricity to be used instead of heat as the separation agent for removal of salts from glycerol. One such technique is electrodeionization, which involves flowing the mixture of glycerol, water, and salt through a mixture of resins bound together with fluoroelastomers. The resins adsorb the free ions, which are then attracted to opposite sides of the EDI device when an electrical current is applied. The ions are transported through an ionically selective semi-permeable membrane and accumulate in a concentrate stream of process water. The concentrate is then disposed of as wastewater.

EDI is a proprietary process, and there are only a few companies that specialize in desalting glycerol through electrodeionization, such as EET and Dow. Due to the competitive nature of this new market, process specifications for EDI equipment are not publicly available. However, from some basic figures provided by EET, it was estimated that the desalting of the crude glycerol stream in this process to 10 ppm salt content should require approximately 200 kW of electricity. This estimation was made using the current efficiency equation (Shaffer 1980).

$$\xi = \frac{zFQ_f(C^d_{inlet} - C^d_{outlet})}{NI}$$

Details of this calculation are located in the Appendix. Additionally, an estimated \$2MM/year was assumed for equipment leasing. Both the capital and annual costs of using the electrodeionization process to desalt the crude glycerol is substantially lower than the cost of vacuum distillation.

Reactor Section

A trickle-bed reactor was selected for use in this process to accommodate the multiphase reaction. Non-negligible volumes of liquid and vapor phase reactants must be able to simultaneously come into contact with the solid surface of the catalyst in order for the reaction to proceed. In a trickle bed reactor, a liquid feed and a vapor feed enter the reactor co-currently at the top of the packed catalyst bed. The liquid "trickles" down over the catalyst and reaction occurs as described by the kinetic model. A more traditional reactor such as a packed bed plug flow reactor is unacceptable for this application due to the impracticality of sufficient contact between the hydrogen gas and the catalyst in the presence of liquid. This effect is amplified by the presence of a large excess of hydrogen gas in the reactor, which is intended to ensure complete conversion of the glycerol input.

Trickle bed reactors are traditionally used in industry for hydrodesulfurization, the kinetics and conditions of which are similar to propylene glycol synthesis from glycerol. Both reactions occur at severe conditions (temperatures above 572 F and pressures above 514 psia) and require a vapor and a liquid to react on a solid catalyst. Using the catalytic hydrodesulfurization of thiophene as described in Chapter Five of *Chemistry of Catalytic Processes* by Gates, Katzer, and Schuit as a basis for comparison, it is expected that the use of an industrial trickle-bed reactor will be successful for propylene glycol manufacture in this process.

Section 7

CHEMICAL DATABASE

Chemical Database

The notable thermophysical and chemical properties of each chemical species present in the process are shown below. Room temperature values are displayed for all temperature-dependent properties (viscosity, thermal conductivity, heat capacity).

Propylene Glycol (1,2 propanediol)	
Molecular Weight (g/mol)	76.09
Melting Point Temp (°C)	-60
Boiling Point Temp (°C)	189
Density (lb/ft^3)	64.207
Standard enthalpy of formation (Btu/lbmol)	-209880
Standard molar entropy (Btu/lbmol-R)	-130.306
Viscosity (cP)	40.4
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.116
Heat Capacity, C_P (Btu/lbmol-R)	38.735

Glycerol	
Molecular Weight (g/mol)	92.1
Melting Point Temp (°F)	64.2
Boiling Point Temp (°F)	554
Density (lb/ft^3)	78.7
Standard enthalpy of formation (Btu/lbmol)	-287069
Standard molar entropy (Btu/lbmol-R)	-146.3
Viscosity (cP)	934
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.169
Heat Capacity, C_P (Btu/lbmol-R)	46.327

Water	
Molecular Weight (g/mol)	18.0
Melting Point Temp (°F)	32
Boiling Point Temp (°C)	212
Density (lb/ft^3)	62.4
Standard enthalpy of formation (Btu/lbmol)	-229.2
Standard molar entropy (Btu/lbmol-R)	38.9
Viscosity (cP)	1
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.335
Heat Capacity, C_P (Btu/lbmol-R)	1.80

Hydrogen (gaseous)	
Molecular Weight (g/mol)	2.01
Melting Point Temp (°C)	-259
Boiling Point Temp (°C)	-253
Density (lb/ft^3)	0.005
Standard enthalpy of formation (Btu/lbmol)	0
Standard molar entropy (Btu/lbmol-R)	22.430
Viscosity (cP)	0.009
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.103
Heat Capacity, C_P (Btu/lbmol-R)	6.873

n-Propanol (1-propanol)	
Molecular Weight (g/mol)	60.1
Melting Point Temp (°C)	-127
Boiling Point Temp (°C)	97
Density (lb/ft^3)	50.255
Standard enthalpy of formation (Btu/lbmol)	-130079
Standard molar entropy (Btu/lbmol-R)	-107.168
Viscosity (cP)	1.952
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.090
Heat Capacity, C_P (Btu/lbmol-R)	37.301

Isopropanol (2-propanol)	
Molecular Weight (g/mol)	60.1
Melting Point Temp (°C)	-89
Boiling Point Temp (°C)	82.5
Density (lb/ft^3)	49.458
Standard enthalpy of formation (Btu/lbmol)	-136421
Standard molar entropy (Btu/lbmol-R)	-109.637
Viscosity (cP)	2.055
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.078
Heat Capacity, C_P (Btu/lbmol-R)	41.309

Acetol	
Molecular Weight (g/mol)	74.1
Melting Point Temp (°C)	-17
Boiling Point Temp (°C)	145
Density (lb/ft^3)	66.939
Standard enthalpy of formation (Btu/lbmol)	-178054
Standard molar entropy (Btu/lbmol-R)	-92.820
Viscosity (cP)	6.701
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.088
Heat Capacity, C_P (Btu/lbmol-R)	29.739

Methanol	
Molecular Weight (g/mol)	32.0
Melting Point Temp (°C)	-98
Boiling Point Temp (°C)	65
Density (lb/ft^3)	49.5
Standard enthalpy of formation (Btu/lbmol)	-102573
Standard molar entropy (Btu/lbmol-R)	-57.5
Viscosity (cP)	0.538
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.116
Heat Capacity, C_P (Btu/lbmol-R)	24.6

Ethylene Glycol	
Molecular Weight (g/mol)	62.1
Melting Point Temp (°C)	-12.9
Boiling Point Temp (°C)	197.3
Density (lb/ft^3)	69.865
Standard enthalpy of formation (Btu/lbmol)	-197205
Standard molar entropy (Btu/lbmol-R)	-107.699
Viscosity (cP)	16.746
Thermal Conductivity (Btu-ft/hr-ft^2-R)	0.147
Heat Capacity, C_P (Btu/lbmol-R)	34.608

The T-xy diagrams for the major separations in the process are shown below. As in column D101, the separation of glycerol and water can be described by the curves shown in Figure 1.

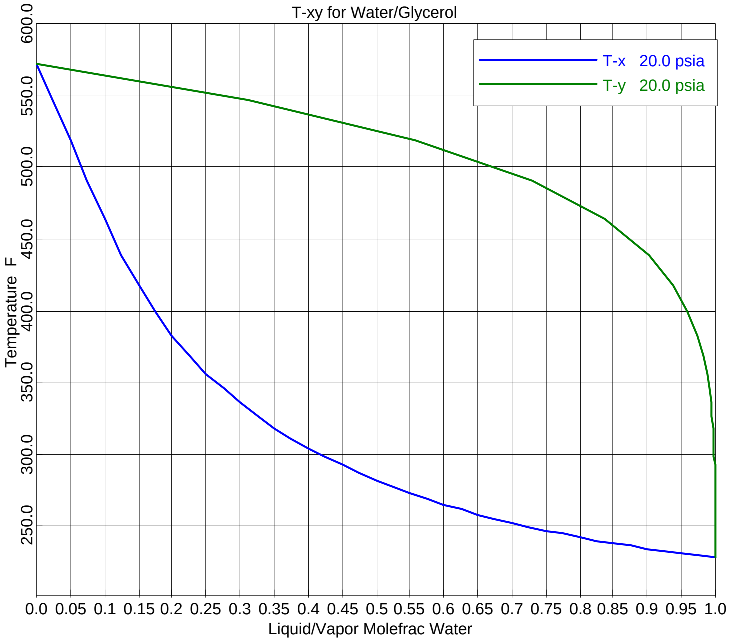


Figure 1 T-xy diagram for the separation of glycerol and water.

The major separation in column D102 is the extraction of propylene glycol from water. This separation, at a pressure of 20 psia as in the column, is described by the curves in Figure 2.

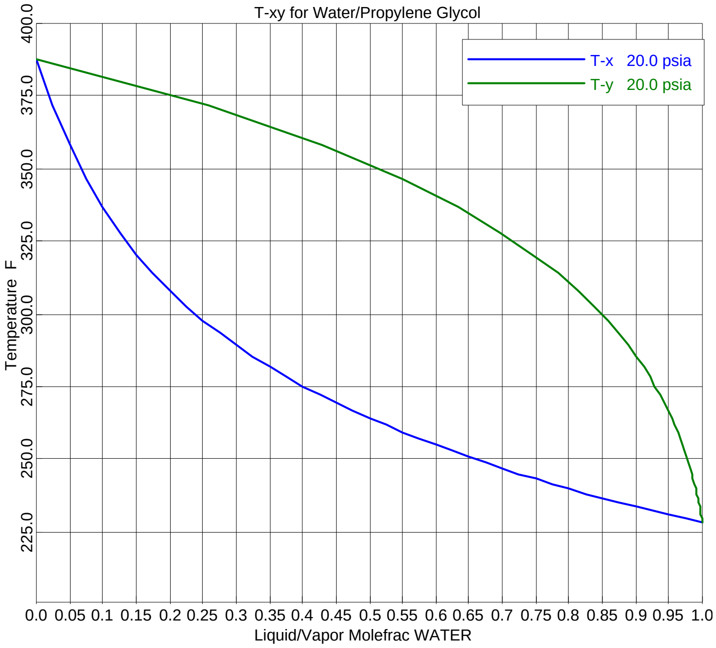


Figure 2 T-xy diagram for the separation of propylene glycol and water.

N-propanol and water exist simultaneously in the system. An azeotrope exists as shown in Figure 3, but it is of very little concern as the mole fraction of water in such mixtures is significantly higher than the point of azeotropy, which in this case is approximately 60% water. The azeotrope only becomes a concern at compositions near this value, which are not present in the process.

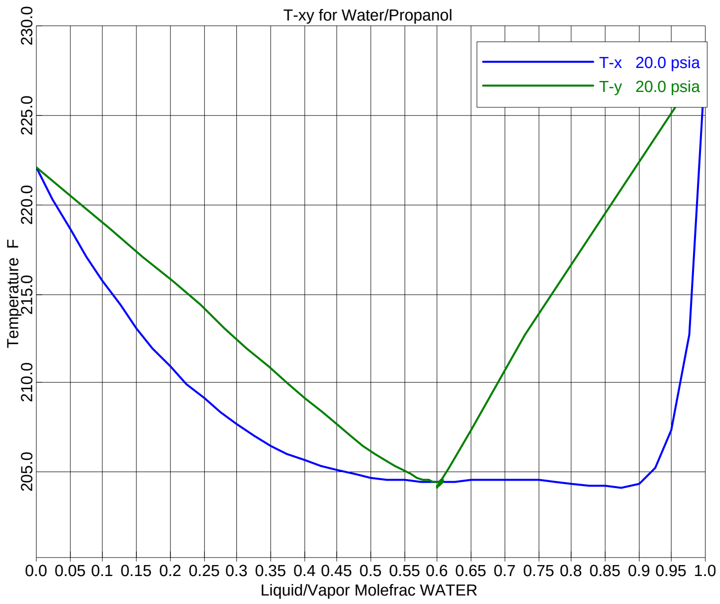


Figure 3 T-xy diagram for the separation of n-propanol and water. An azeotrope exists at a composition of approximately 60% water.

Section 8

REACTION KINETICS

Reaction Kinetics

The kinetics of the reaction of glycerol to propylene glycol used in this process were developed largely in "Kinetics of Hydrogenolysis of Glycerol to Propylene Glycol over Cu-ZnO-Al_2O_3 Catalysts" (Zhou et al. 2010). Their model was developed to enable the simulation and optimization of different-scale reactors for glycerol hydrogenolysis, as used in the propylene glycol production process.

Cu-ZnO- Al_2O_3 catalysts of varying metal compositions were prepared using co-precipitation. Activity tests showed that a molar ratio of 1:1:0.5 Cu:Zn:Al in the catalyst resulted in the highest glycerol conversion as well as the highest selectivity for propylene glycol. Henceforth, this preparation was used in catalytic studies. The experiments were performed over a hydrogen pressure of 431-725 psia and a temperature range of 428-464 K.

A two-step mechanism for the hydrogenolysis of glycerol to propylene glycol, originally proposed by Suppes *et al.,* has been investigated by many researchers and is widely accepted for copper-based catalysts. This mechanism, shown below, consists of the dehydration of glycerol to intermediate acetol, followed by the hydrogenation of acetol to propylene glycol.

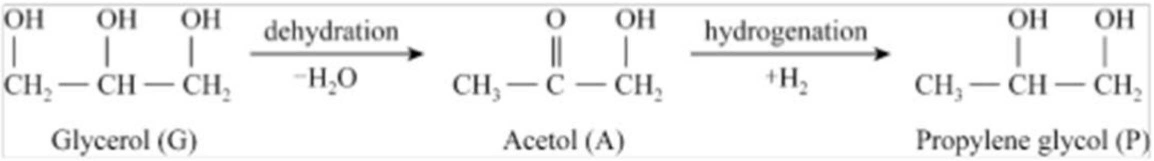


Figure 4 Reaction mechanism of glycerol hydrogenolysis to propylene glycol (Zhou et al. 2010)

From this reaction, a two-site Langmuir-Hinshelwood kinetic model was proposed as follows, and validated by the experimental work of Li, Zhou et al.:

$$H_2 + 2\theta_1 \overset{b_H}{\rightleftharpoons} 2H\theta_1$$

$$G + \theta_2 \overset{b_G}{\rightleftharpoons} G\theta_2$$

$$G\theta_2 \xrightarrow{k_1} A\theta_2 + H_2O$$

$$2H\theta_1 + A\theta_2 \xrightarrow{k_2} P\theta_2 + 2\theta_1$$

$$A\theta_2 \overset{b_A^{-1}}{\rightleftharpoons} A + \theta_2$$

$$P\theta_2 \overset{b_P^{-1}}{\rightleftharpoons} P + \theta_2$$

Figure 5 Langmuir-Hinshelwood kinetics for glycerol dehydrogenation reaction.

Where θ_1 is the active site for hydrogen adsorption, θ_2 is the active site for organic molecule adsorption, k_1 and k_2 are the rate constants for the first and second reaction steps respectively, and b_H, b_G, b_A, b_p are the adsorption constants of each species. The temperature dependence of these parameters is expressed in the following equations.

$$k_i = k_i^0 \exp[\frac{-E_i}{R_g T}], \qquad i=1,2$$

$$b_j = b_j^0 \exp[\frac{Q_j}{R_g T}], \qquad j=G, A, P, H$$

Assuming that a pseudo-steady-state analysis for adsorbed intermediates is valid, the rate expressions for the system are derived and presented below, where r_1 is the consumption of glycerol per mass of catalyst and r_2 is the production of propylene glycol per mass of catalyst, c_i are the molar concentrations of each species and P_H is the hydrogen pressure.

$$r_1 = \frac{k_1 b_G c_G}{1 + b_G c_G + b_A c_A + b_P c_P}$$

$$r_2 = \frac{k_2 b_A c_A b_H P_H}{\left(1 + b_G c_G + b_A c_A + b_P c_P\right)\left(1 + \sqrt{b_H P_H}\right)^2}$$

Figure 6 Rate expressions for propylene glycol formation.

The kinetic model described above was used as a basis for the design of the trickle-bed reactor that appears in the glycerol to propylene glycol process. To determine the mass of catalyst needed, an Excel model was developed to compute the kinetic parameters and species flow rates based on the temperature, hydrogen to glycerol feed ratio, and the feed composition using a Riemann sum over the total catalyst mass. This calculation is shown in the Appendix. The conversion of glycerol is plotted against the mass of catalyst in kilograms in Figure 7. Based on this analysis, it was determined that 4190 kg of catalyst is necessary to achieve a 99.8% conversion of glycerol, for a hydrogen to glycerol feed ratio of 5:1, temperature of 423 F and the specified feed composition.

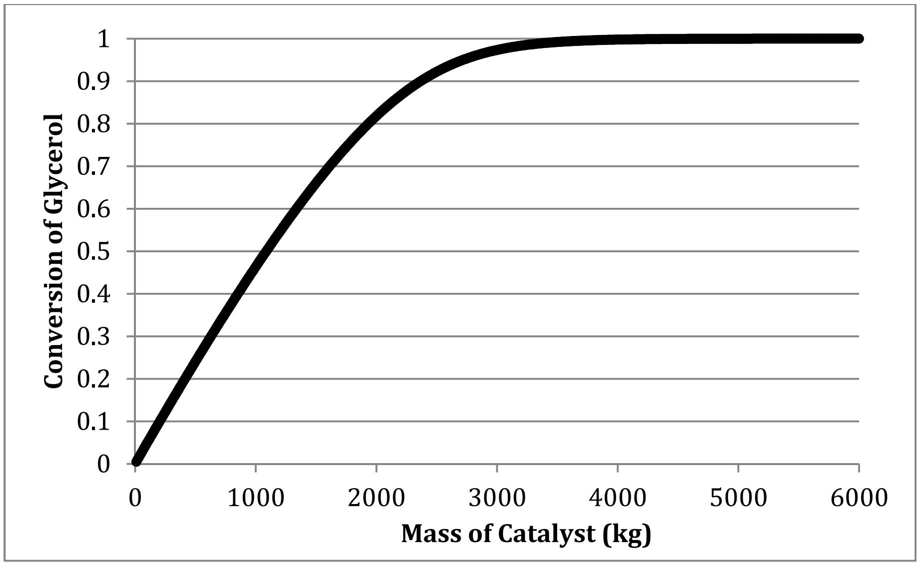
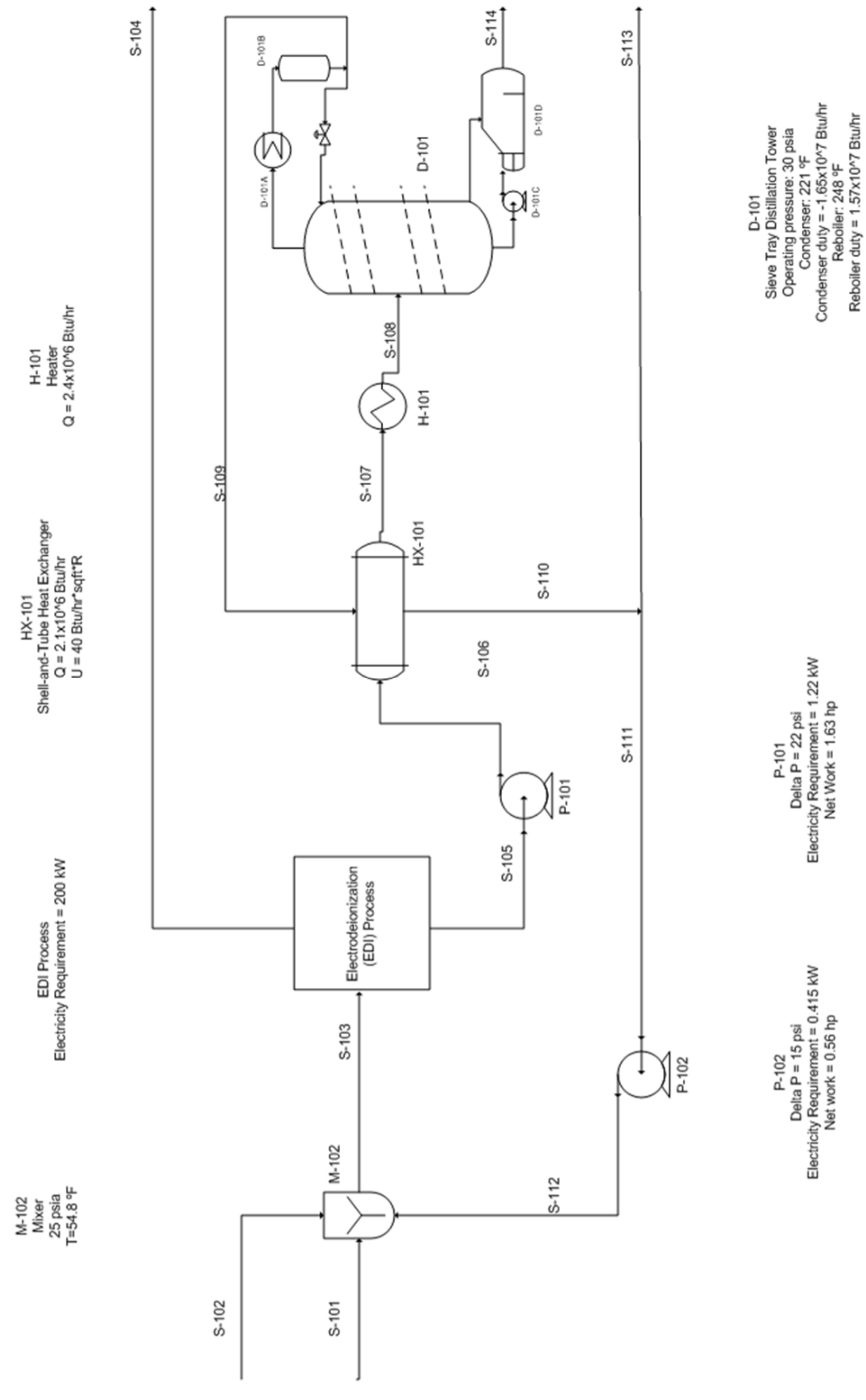


Figure 7 Conversion of glycerol versus mass of catalyst. 4190 kg of catalyst are necessary to achieve 99.8% conversion.

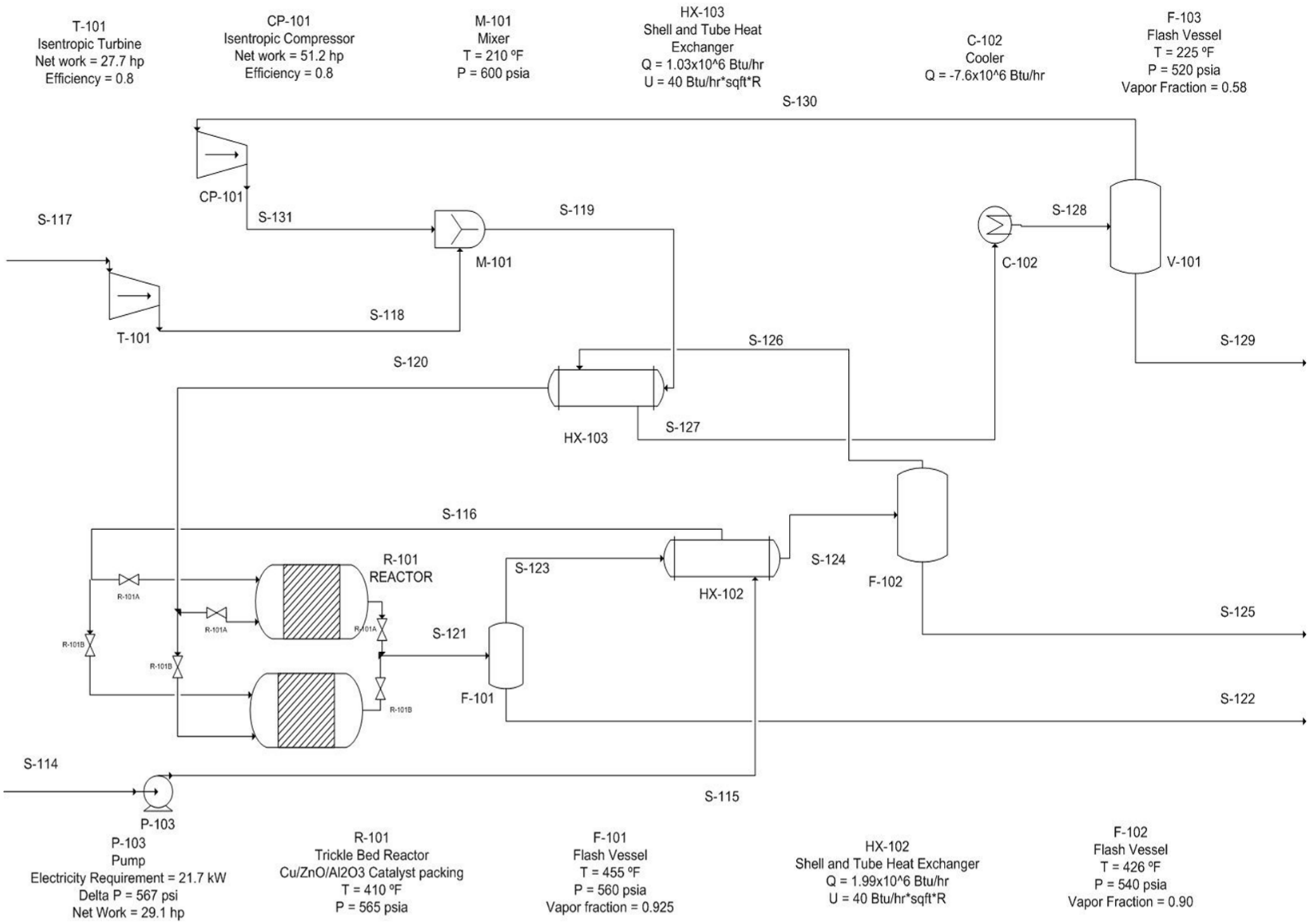
Higher conversions have a very low rate of return. To achieve the remaining 0.1% conversion would require almost 2000 kg of additional catalyst, or an increase of almost 150%, which is not economically justifiable.

Section 9

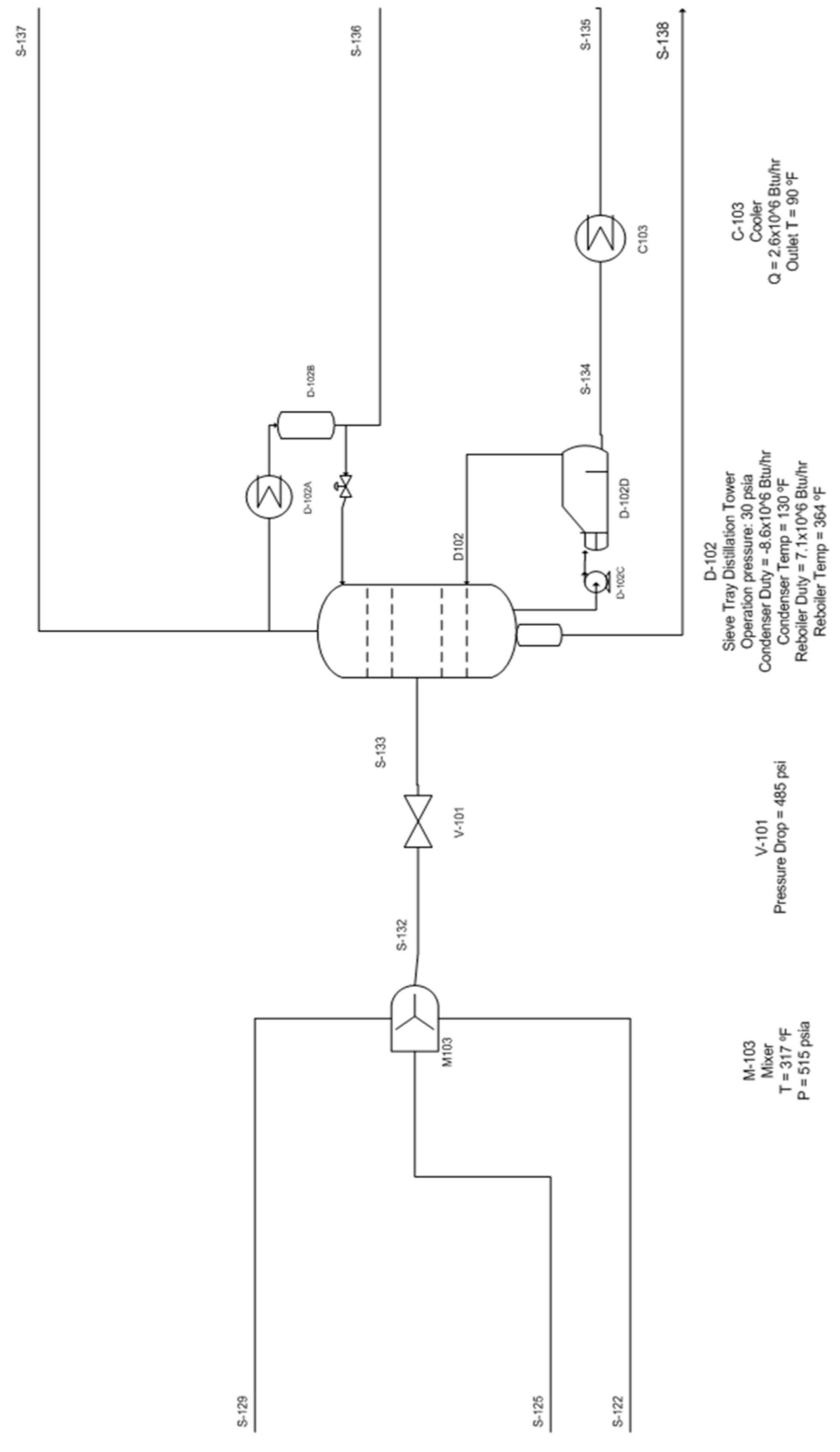
PROCESS FLOW DIAGRAMS AND MATERIAL BALANCES


M-102
Mixer
25 psia
T=54.8 °F
EDI Process
Electricity Requirement = 200 kW
HX-101
Shell-and-Tube Heat Exchanger
Q = 2.1x10^6 Btu/hr
U = 40 Btu/hr*sqft*R
H-101
Heater
Q = 2.4x10^6 Btu/hr
S-102
S-101
M-102
S-103
Electrodeionization (EDI) Process
S-104
S-105
P-101
S-106
HX-101
S-107
H-101
S-108
S-109
D-101
D-101A
D-101B
D-101C
D-101D
S-114
S-110
S-111
S-112
P-102
S-113
P-102
Delta P = 15 psi
Electricity Requirement = 0.415 kW
Net work = 0.56 hp
P-101
Delta P = 22 psi
Electricity Requirement = 1.22 kW
Net Work = 1.63 hp
D-101
Sieve Tray Distillation Tower
Operating pressure: 30 psia
Condenser: 221 °F
Condenser duty = -1.65x10^7 Btu/hr
Reboiler: 248 °F
Reboiler duty = 1.57x10^7 Btu/hr

	S-101	S-102	S-103	S-104	S-105	S-106	S-107	S-108	S-109	S-110	S-111	S-112	S-113	S-114
	LIQUID	LIQUID	LIQUID	SOLID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Temperature F	70.0	70.0	54.8	54.8	69.8	69.9	151.8	242.0	221.4	80.0	80.0	80.1	80.0	247.9
Pressure psia	30.0	30.0	25.0	20.0	20.0	42.0	41.8	36.8	20.0	19.7	19.7	30.0	19.7	20.0
Total Flow lb/hr	19392	5384	34007	5876	33231	33231	33230	33230	13985	13985	9230	9230	4755	19245
Mass Flow														
GLYCEROL	15514	0	15514	0	15514	15514	15514	15514	0	0	0	0	0	15514
WATER	2909	5384	17151	5100	17151	17151	17149	17149	13421	13421	8858	8858	4563	3729
HYDROGEN	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PG	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PROP	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISO-PROP	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SODIU-01	776	0	776	776	0	0	0	0	0	0	0	0	0	0
METHA-01	194	0	566	0	566	566	566	566	564	564	372	372	192	2
Mass Frac														
GLYCEROL	0.800	0.000	0.456	0.000	0.467	0.467	0.467	0.467	Trace	Trace	Trace	Trace	Trace	0.806
WATER	0.150	1.000	0.504	0.000	0.516	0.516	0.516	0.516	0.960	0.960	0.960	0.960	0.960	0.194
HYDROGEN	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PG	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-PROP	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ISO-PROP	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SODIU-01	0.040	0.000	0.023	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
METHA-01	0.010	0.000	0.017	0.000	0.017	0.017	0.017	0.017	0.040	0.040	0.040	0.040	0.040	Trace


T-101
Isentropic Turbine
Net work = 27.7 hp
Efficiency = 0.8
CP-101
Isentropic Compressor
Net work = 51.2 hp
Efficiency = 0.8
M-101
Mixer
T = 210 ºF
P = 600 psia
HX-103
Shell and Tube Heat Exchanger
Q = 1.03x10^6 Btu/hr
U = 40 Btu/hr*sqft*R
C-102
Cooler
Q = -7.6x10^6 Btu/hr
F-103
Flash Vessel
T = 225 ºF
P = 520 psia
Vapor Fraction = 0.58
S-130
CP-101
S-131
S-117
S-119
M-101
T-101
S-118
C-102
S-128
V-101
S-129
S-126
S-120
HX-103
S-127
S-116
R-101
REACTOR
S-123
HX-102
S-124
F-102
R-101A
R-101A
R-101A
R-101B
R-101B
R-101B
S-121
F-101
S-125
S-122
S-114
S-115
P-103
P-103
Pump
Electricity Requirement = 21.7 kW
Delta P = 567 psi
Net Work = 29.1 hp
R-101
Trickle Bed Reactor
Cu/ZnO/Al2O3 Catalyst packing
T = 410 ºF
P = 565 psia
F-101
Flash Vessel
T = 455 ºF
P = 560 psia
Vapor fraction = 0.925
HX-102
Shell and Tube Heat Exchanger
Q = 1.99x10^6 Btu/hr
U = 40 Btu/hr*sqft*R
F-102
Flash Vessel
T = 426 ºF
P = 540 psia
Vapor Fraction = 0.90

	S-114	S-115	S-116	S-117	S-118	S-119	S-120	S-121	S-122	S-123	S-124	S-125	S-126	S-127	S-128	S-129	S-130	S-131
	LIQUID	LIQUID	LIQUID	VAPOR	VAPOR	MIXED	VAPOR	MIXED	LIQUID	VAPOR	MIXED	LIQUID	VAPOR	MIXED	MIXED	LIQUID	VAPOR	VAPOR
Temperature F	247.9	252.1	410.0	70.0	11.7	202.4	416.5	455.8	455.2	455.2	429.0	429.0	429.0	409.0	225.0	225.0	225.0	244.4
Pressure psia	20.0	587.0	581.0	1000.0	600.0	600.0	598.9	566.0	560.0	560.0	559.1	559.1	559.1	558.3	553.3	553.3	553.3	600.0
Total Flow lb/hr	19245	19245	19245	346	346	1952	1952	21197	4317	16880	16880	4876	12004	12004	12004	10398	1606	1606
Mass Flow																		
GLYCEROL	15514	15514	15514	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	3729	3729	3729	0	0	308	308	7117	491	6626	6626	759	5867	5867	5867	5559	308	308
HYDROGEN	0	0	0	346	346	1342	1342	997	1	996	996	1	996	996	996	0	995	995
PG	0	0	0	0	0	18	18	12645	3805	8840	8840	4088	4752	4752	4752	4734	18	18
N-PROP	0	0	0	0	0	60	60	136	9	127	127	12	116	116	116	55	60	60
ISO-PROP	0	0	0	0	0	224	224	300	12	288	288	16	272	272	272	48	224	224
SODIU-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
METHA-01	2	2	2	0	0	0	0	3	0	2	2	0	2	2	2	2	0	0
Mass Frac																		
GLYCEROL	0.806	0.806	0.806	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
WATER	0.194	0.194	0.194	0.000	0.000	0.158	0.158	0.336	0.114	0.393	0.393	0.156	0.489	0.489	0.489	0.535	0.192	0.192
HYDROGEN	0.000	0.000	0.000	1.000	1.000	0.687	0.687	0.047	Trace	0.059	0.059	Trace	0.083	0.083	0.083	0.000	0.620	0.620
PG	0.000	0.000	0.000	0.000	0.000	0.009	0.009	0.597	0.881	0.524	0.524	0.838	0.396	0.396	0.396	0.455	0.011	0.011
N-PROP	0.000	0.000	0.000	0.000	0.000	0.031	0.031	0.006	0.002	0.008	0.008	0.002	0.010	0.010	0.010	0.005	0.037	0.037
ISO-PROP	0.000	0.000	0.000	0.000	0.000	0.115	0.115	0.014	0.003	0.017	0.017	0.003	0.023	0.023	0.023	0.005	0.139	0.139
SODIU-01	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
METHA-01	Trace	Trace	Trace	0.000	0.000	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace


S-137
S-136
S-135
S-138
C103
C-103
Cooler
Q = 2.6x10^6 Btu/hr
Outlet T = 90 ºF
D-102B
D-102A
S-134
D-102D
D102
D-102C
D-102
Sieve Tray Distillation Tower
Operation pressure: 30 psia
Condenser Duty = -8.6x10^6 Btu/hr
Condenser Temp = 130 ºF
Reboiler Duty = 7.1x10^6 Btu/hr
Reboiler Temp = 364 ºF
S-133
V-101
V-101
Pressure Drop = 485 psi
S-132
M103
M-103
Mixer
T = 317 ºF
P = 515 psia
S-129
S-125
S-122

	S-129	S-130	S-131	S-132	S-133	S-134	S-135	S-136	S-137	S-138
	LIQUID	VAPOR	VAPOR	MIXED	MIXED	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID
Temperature F	225.0	225.0	244.4	317.3	254.8	364.0	90.0	130.0	130.0	364.0
Pressure psia	553.3	553.3	600.0	548.3	30.0	20.0	15.0	20.0	20.0	20.0
Total Flow lb/hr	10398	1606	1606	19591	19591	12380	12380	7075	136	Trace
Mass Flow										
GLYCEROL	0	0	0	0	0	0	0	0	0	0
WATER	5559	308	308	6809	6809	38	38	6765	6	Trace
HYDROGEN	0	995	995	2	2	0	0	0	2	0
PG	4734	18	18	12626	12626	12342	12342	285	0	Trace
N-PROP	55	60	60	76	76	0	0	21	55	0
ISO-PROP	48	224	224	76	76	0	0	2	74	0
SODIU-01	0	0	0	0	0	0	0	0	0	0
METHA-01	2	0	0	2	2	0	0	2	0	0
Mass Frac										
GLYCEROL	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
WATER	0.535	0.192	0.192	0.348	0.348	0.003	0.003	0.956	0.043	Trace
HYDROGEN	0.000	0.620	0.620	Trace	Trace	Trace	Trace	Trace	0.012	0.000
PG	0.455	0.011	0.011	0.644	0.644	0.997	0.997	0.040	Trace	Trace
N-PROP	0.005	0.037	0.037	0.004	0.004	Trace	Trace	0.003	0.404	0.000
ISO-PROP	0.005	0.139	0.139	0.004	0.004	Trace	Trace	Trace	0.540	0.000
SODIU-01	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
METHA-01	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	0.000

Section 10

BENCH SCALE LABORATORY WORK

Bench-Scale Laboratory Work

The kinetic model described in the work of Zhou, Li, et al. was tested in a very small bench scale reactor with inner diameter 10 mm and length 450 mm. One major concern in the development of the propylene glycol production process is the plausibility of scaling this process up to the large industrial reactors that are necessary to accommodate the desired 100 million lb/year throughput. The process-scale reactor has a projected diameter of 5.3 feet ($1.6\text{x}10^3$ mm), which is over 100 times larger than the bench-scale reactor.

Most models used to describe the scale-up of trickle bed reactors make the following assumptions (Dudukovic 1984):

i. The gaseous reactant is limiting;
ii. Internal particle diffusion resistance is present;
iii. Catalyst particles are completely externally and internally wetted;
iv. Gas solubility can be treated by Henry's law;
v. Isothermal operation;
vi. Axial dispersion model can be used to describe deviations from plug flow;
vii. Intrinsic reaction kinetics exhibit first order behavior.

The glycerol to propylene glycol reaction is novel among reactions of its kind because it is not vapor phase reactant limiting; the hydrogen gas is flowing at a 5:1 molar excess in the reactor, so the limiting reactant is liquid glycerol. Because of this, the existing models must be modified considerably for use with this reaction.

One method to approach this challenge might be to, with a considerable amount of additional bench-scale lab work, develop a new correlation and model to fit the reaction's parameters, and use it to determine the size of an industrial-scale reactor.

However, the lack of the necessary time and materials to perform this research precluded this as an option.

Instead, a model was built to calculate the conversion achieved in the reactor as a function of catalyst mass, using the reaction kinetics to couple the reaction rate to the input flow rates and compositions (see Appendix). An assumption was made that it is possible to reach 100% conversion of glycerol by extrapolating the catalyst's mass to a large enough value. However, this assumption is highly optimistic. In the work of Zhou et. al., the actual conversion of 81.5% was achieved using the Cu-ZnO-Al_2O_3 catalyst with a 1:1:0.5 molar metal ratio. A more precise value of the conversion should be determined using an intermediate scale reactor prior to plant construction. It can be expected that the actual value of conversion in the reactor should fall between the 81.5% in the activity test and the 99.8% that was extrapolated using the Excel model.

The financial risk involved with undertaking an endeavor such as this process calls for a very high degree of confidence in the plant's scalability, which can be provided by a pilot plant test of a mid-size reactor. This is recommended prior to plant construction to ensure the reliability of the scale-up model described above.

Section 11

PROCESS DESCRIPTION

Pretreatment

The first step in the process involves removing the salt and volatile organic compounds from the crude glycerol. Crude glycerol arrives at our plant directly from biodiesel refineries. It contains by mass, 1% methanol, 4% sodium chloride, 15% water, and trace amounts of organic salts. Almost 20000 lbs/hr of crude glycerol are required, which equates to about one tanker truck each hour. Depending on specific plant geography and transportation networks, rail and ship options are viable; however, 24 tanker trucks per day for raw material and finished product shipment is a reasonable estimate.

The crude glycerol is then mixed with process water in order to reduce the viscosity of the mixture to put through the EDI machine. The resultant mix is 50% wt. glycerol. Process water requirements are 5390 lb/hr from a source, and the rest is the recycle from the distillate from column D-101 in S-112.

The glycerol and water are mixed in M-102. This mixer contains a paddle and electrical input because while glycerol and water are readily miscible, the difference in viscosity requires agitation to achieve homogeneity.

The resultant stream, S-103, is then fed into the electrodeionization (EDI) machine, which proceeds to remove the NaCl and trace sulfates and phosphates. The salt is concentrated in a concentrate H_2O stream, S-104 which is usually 15% of the total mass flow flow through the EDI device in stream S-103. This is about 5100 lb/hr of process water. The assumption for the project is that the amount of organic salt is negligible, and so the salt water concentrate can be disposed of at normal sewerage rates for commercial enterprises in Louisiana. However, if organic salts are higher than expected, or the plant is located in a marshland or other salinity sensitive zone, than sewerage rates will be higher as the salt cannot simply be sent into the environment.

The desalted glycerol in S-105 is then pumped to replace the head loss across the mixer and EDI device. This is then heated in a feed-product heat exchanger with the distillate from D-101, S-109. The glycerol stream is then heated further with medium pressure steam. This preheating reduces the duty requirement on the reboiler in the column.

The glycerol stream, S-108, enters column D-101 in order to both remove the methanol and reduce the water content to 20% wt, which is the optimal concentration to use in the trickle bed reactor, due to viscosity concerns. The column contains 4 theoretical trays, a total condenser, and a reboiler. The tray efficiency is approximately 9.3% due to the viscosity of glycerol, so the actual column requires 43 trays to operate. The condenser uses cooling water from 80 F to 130F.

This is a relatively easy separation. The water is the light key and it, with methanol, concentrate in the distillate. The distillate, S-109, exits as a saturated liquid at 20 psia and 221 F. The flow rate is 14000 lb/hr and 4% MeOH by weight. This liquid is cooled to 80 F in HX-101 and then 34% of the total flow is purged in S-113 in order to prevent methanol buildup in the pretreatment section. The rest of the flow is then pumped in P-102 to restore pressure to 15 psig in order to flow freely through the mixer and EDI. The purge stream is combined with the propanol/water distillate, S-136, at the end of the process and sent to wastewater treatment. Since this stream contains organic material, we used the Vrana organic wastewater correlation to determine the cost of treatment.

$$Cost\ \left[\frac{\$}{lb}\right] = 0.044 + 0.048 * (\%\ organic\ impurities\ by\ weight)$$

The clean glycerol and 15% water exits the reboiler at 5 psig and 248 F in S-114. The reboiler is heated with medium pressure steam.

Reactor Section

The refined glycerol from the separation column D-101in S-114 is pumped to 585 psia in P-103 and heated in HX-102 with the reactor vapor effluent, S-123, to 416 F. Hydrogen gas is drawn from a pipeline at 1000 psig in S-117, and is depressurized in the turbine T-101 to reach the operating pressure, 600 psia. This hydrogen stream is mixed with the stream of recycled hydrogen, S-131, to maintain a 5:1 molar ratio of hydrogen to glycerol in S-119. The combined hydrogen stream is heated to process temperature (416.5 F) by condensing the vapor effluent, S-126, from the second flash vessel, F-102.

In order to achieve the maximum conversion of glycerol to propylene glycol in a multiphase system, a trickle-bed reactor was selected. The trickle bed reactor is the simplest reactor type for performing multiphase catalytic reactions, and is used widely in industry for such applications as liquid-phase hydrogenation and oxidation of harmful chemicals in waste streams. Trickle-bed reactors are used industrially for hydrodesulfurization processes, which lends credibility to the use of scale-up from the bench-scale analysis. The reactor, R-101, consists of a packed bed of solid catalyst particles, over which streams of gas (S-120) and liquid (S-116) flow down the reactor.

The catalyst that was selected for this process is Cu-ZnO-Al_2O_3 in a 1:1:0.5 molar ratio of Cu:Zn:Al, as it was determined to exhibit the best performance for glycerol hydrogenolysis by (Zhou 2010). The catalyst particles that showed optimal performance in studies by Zhou, Li, et al. had a diameter of 0.17 mm.

The overall goal of this process is to achieve 100% conversion and 98.5% selectivity of the incoming glycerol to propylene glycol. Based on this specification, it was determined that a mass of 4190 kg of catalyst is necessary. The small diameter of the catalyst pellets allows for the assumption of a void fraction in the bed of 0.35, a typical value for catalyst pellets of small diameter. 21,000 lb/hr of reactants are fed to the reactor. Professor Leonard Fabiano suggested the assumption of a flux of 1000 lb/ft^2*hr through the packed bed, and using this assumption, a 21 ft^2 cross section is required to accommodate the flow. In a cylindrical vessel, this corresponds to a diameter of 5.2 feet. Based on the fluid properties of the liquid and vapor streams, trickle bed reactor of these dimensions, the Ergun equation can be used to calculate a pressure drop of 20 psi along the length of the reactor (See Appendix for sample calculation).

Additionally, a 5:1 molar excess of hydrogen gas must be accounted for in the reactor sizing. At the operating temperature (455.8 F) and pressure (556 psia), the excess volume of hydrogen is 11,112 ft^3/hr. Assuming a retention time of 1 minute in the vessel, calculated based on the effluent flow rate, the total volume of the reactor vessel must be 240 ft^3, an increase of almost double the volume for stoichiometric reactants of 142 ft^3. Accounting for the hydrogen excess, the new reactor vessel requires a diameter of 6 ft and height of 11 ft.

For the economic analysis of the reactor, catalyst prices were assumed equivalent to those of MK-121, a Cu-Zn-Al high activity catalyst for methanol synthesis that is prepared by Haldor Topsoe, a leading manufacturer of commercial catalysts. Consultations with company representative Mr. Henrik Rasmussen of Haldor Topsoe revealed that this prepared catalyst is sold for $27/kg in 6 x 4 mm tablets. The commercial catalyst has dimensions too large for use with the chosen kinetic model; the pellets must have a diameter of 0.22 mm or smaller to eliminate the internal diffusion limitation effects of the transport of fluid around the catalyst. To crush the tablets into small-diameter catalyst particles of diameter approximately equal to 0.17 mm for use in the reactor, an additional \$3/kg surcharge is assumed for processing, for a total of \$30/kg. Therefore, the total purchase cost of one load of 4190 kg catalyst is \$125,700. To account for replacing the catalyst for the main reactor and alternate reactor every two years over the project's life, the total purchase cost of \$1.97 million was used in the economic analysis.

Cu/ZnO/Alumina catalysts have a typical life of approximately 2-3 years and cannot be reliably regenerated by burning. To ensure that there is negligible loss in catalyst performance throughout the plant's lifetime, the catalyst mass will be replaced every year. Two reactor vessels of equal size will be purchased for the plant and connected in parallel. The reactor section process flowsheet displays two sets of valves, labeled R-101A and R-101B corresponding to each reactor vessel. It is relatively simple to switch the reactor vessel that is in operation by alternating which set of valves is open and which is closed. At all times, only set of either R-101A or R-101B will be open. When a reactor is not operational, it may be detached from the plant and repacked with new catalyst. Each year, the plant operators will alternate which reactor is active in the process, to allow the second vessel to be cleaned and packed with new catalyst. This setup also allows for fast and relatively easy introduction of the replacement reactor in case of any kind of malfunction during the operational year.

Both the refined glycerol and mixed hydrogen streams, S-116 and S-120, enter the trickle bed reactor, where the glycerol is completely converted into propylene glycol and some propanol. The heat of reaction varies slightly with temperature. The reactor is assumed to operate adiabatically, as the heat released is relatively small, and it can be removed through bulk transport in the vapor stream.

The mixed-phase effluent flowing out of the reactor, S-121, is collected in a flash vessel, F-101, where the liquid stream, S-122, is sent to the refinement section. The vapor, S-123, is then partially condensed in heat exchanger HX-102 and then flows to another flash vessel, F-102. The liquid stream from the flash vessel, S-125, becomes one of the input streams to the separation section for refinement and purification. The vapor, S-126, that exits the flash vessel is partially condensed in HX-103 and further cooled in C-102 until the vapor phase contains pure hydrogen. This stream is sent to a third flash vessel, F-103. The vapor is then recompressed in CP-101 to the operating pressure, 600 psia, and recycled, and the liquid in S-129 is fed to the separation section.

Separation Section

The separation section purifies the propylene glycol to 99.8% purity by weight. There is only one 2-product distillation column, D-102, required because the propanol/water mixture, S-136, is sent to wastewater treatment. The incoming feed to the separation column, S-133, contains propylene glycol, propanol, and water. Since the patent suggested that there would be 100% conversion, no glycerol will be present in the reactor effluent, and the only design constraint other than product purity was keeping the reboiler temperature, 364 F, below the degradation temperature of propylene glycol, which is 369 F.

The RADFRAC block in ASPEN suggested that 14 theoretical trays would be required to obtain the desired separation. In order to calculate the overall efficiency of the column, the O'Connell correlation was used. This relates the ratio of the number of theoretical trays to the total number of trays, η, as a function of the feed viscosity (in cP) and relative volatility of the key components.

$$\eta = 0.492(\mu_F \alpha)^{-0.245}$$

The O’Connell correlation suggested that the efficiency was 9.8%, therefore the total number of trays required for this column was 70. This is the upper limit on column height. The condenser is a partial condenser, with a vapor pilot flame of hydrogen (S-137) and a liquid water/propanol distillate (S-136). The bottoms product is 99.6% pure propylene glycol at 364 F, which is then cooled in C-103 to handling temperature.

At the bottom of the column there will be a boot attached in order to collect the heavy compounds produced, such as ethylene glycol. The bottoms product will be drawn off as a vapor which will increase the cooling load on C-103. The boot residue will be drawn off periodically in S-138 to prevent contamination.

Section 12

HEAT INTEGRATION: ENERGY BALANCE AND UTILITY REQUIREMENTS

Heat Integration

Because EDI was used for the glycerol pretreatment, the overall utilities required for the process are less than the requirements for other processes on this scale. Additionally, no heater or reboiler is required to operate above 365 F, which is the saturation temperature of 150 psig steam. Since it is less expensive, low to medium pressure steam can be used. Heat integration was achieved primarily through feed/product heat exchange, and required just 2.41 million Btu/hr of heating and 10.08 Btu/hr of cooling utilities, excluding the condensers and reboilers.

In the pretreatment section, the hot water/methanol distillate, S-109, is exchanged with the stream fed to the distillation column, S-106, in HX-101. S-109 is cooled to room temperature, and S-106 receives additional heat in H-101. This design was chosen in order to reduce the size of the reboiler in the first distillation column, D-101. HX-101 exchanges 2.14 million Btu/hr and has an area of 2052 sq. ft.

In the reactor section, the design objectives are to heat the incoming glycerol and hydrogen streams (S-114 and S-120) to the reactor inlet temperature of 416 F, and to recover all of the propylene glycol from the reactor outlet. Since a substantial amount of PG is in the vapor phase at the outlet of the reactor, we decided to design a system of flash vessels and heat exchangers in order to condense PG from hydrogen. The reactor effluent at 456 F is sent to F-101, which collects the PG and water that is liquid in S-122. The vapor (S-123) is then used to heat the incoming glycerol stream to the reactor inlet temperature in HX-102, exchanging 1.99 million Btu/hr. This heat exchange condenses more PG, which is collected in a second flash vessel, F-102, operating at 426 F. The vapor from this vessel in S-126 is then used to heat the incoming hydrogen in S-119 to the reactor inlet temperature in HX-103, exchanging 1.13 million

Btu/hr. The vapor stream, S-127, is then cooled further to 225 F in C-102, at which all of the PG is found in the liquid phase. C-102 exchanges 7.50 million Btu/hr. The reason that we were able to eliminate external heating requirements for the reactor is because hydrogen has a very high heat capacity, and the latent heat of condensation for propylene glycol is also high, which means that there is a lot of available thermal energy stored in the reactor effluent.

In the refinement section, the feed stream is sufficiently hot not to require preheating, and the only requirement is that pure PG be cooled to handling temperature which is approximately 90 F. This occurs in C-103, which has a duty of -2.08 million Btu/hr. The liquid distillate, S-136, is mixed with the methanol purge from the pretreatment section in order to prevent flash boiling once the liquid is sent to the organic wastewater storage tank.

Energy balances, computed by ASPEN PLUS, are in the Appendix.

Section 13

EQUIPMENT LIST AND UNIT DESCRIPTIONS

Unit Number	Unit Type	Function	Material	Size	Temperature (F)	Pressure (psia)
Pre-Treatment Section						
M-102	Mixer	Mixes crude Glycerol, fresh H20 and recyle H20	Stainless Steel	1 HP		
S-101	EDI Equipment	Extracts all chloride and organic salts				
P-101	Pump	Transports clean glycerol	Stainless Steel	75 HP		
HX-101	Heat Exchanger	Raise temp of liquid stream	Carbon Steel	2052 sqft.	221	35
H-101	Fired Heater	Raise temp of liquid stream	Carbon Steel		242	30
D-101	Tower	H20 LK, Glycerol HK	Carbon Steel	3.9ft x 100ft		20
D-101a	Heat Exchanger	Column Condensor	Carbon Steel	654 sqft.	221	20
D-101b	Reflux Accumulator	Reflux Accumulator	Carbon Steel	3.21ft x 1.61ft		
D-101c	Pump	Pumps bottoms into Reboiler	Carbon Steel	75 HP		
D-101d	Heat Exchanger	Column Reboiler	Carbon Steel	2438 sqft.	248	20
P-103	Pump	Transports clean glycerol	Stainless Steel	250 HP	252	587
P-102	Pump	Transports H20 recycle	Stainless Steel	75 HP	80	30
Reactor Section						
R-101a	Reactor	Contains catalyst	Stainless Steel	5.2ft x 11.5ft	455	565
R-101b	Reactor	Contains catalyst	Stainless Steel	5.2ft x 11.5ft	455	565
F-101	Flash	Separates liquid PG from H2	Stainless Steel	1.7ft x 6.75ft	455	560
HX-102	Heat Exchanger	Raise temp of Glycerol feed	Stainless Steel	73 sqft.	455	587
F-102	Flash	Separates liquid PG from H2	Stainless Steel	1.51ft x 5.36ft	426	540
HX-103	Heat Exchanger	Raise temp of H2 feed	Stainless Steel	165 sqft.	426	585
C-102	Heat Exchanger	Cools PG/H2 mixture	Stainless Steel	256 sqt.	225	520
F-103	Flash	Separates liquid PG from H2	Stainless Steel	0.74ft x 1.5ft	225	520
CP-101	Compressor	Repressurize H2 Recycle	Stainless Steel	123 HP	225	520
TR-100	Turbine	Reduces pressure of fresh H2	Stainless Steel	27.7 HP	12	400 psia drop
M-101	Mixer	Mix fresh H2 and recycle H2	Stainless Steel	7 HP	600	210
Separation Section						
M-103	Mixer	Mix PG product streams	Stainless Steel	1 HP	317	515
V-101	Valve	Decrease pressure of product stream				485 pressure drop
D-102	Tower	H20 LK, PG HK	Carbon Steel	2.8ft x 154ft		20
D-102a	Heat Exchanger	Column Condensor	Carbon Steel	538 sqft.	130	20
D-102b	Reflux Accumulator	Reflux Accumulator	Carbon Steel	1.58ft x 3.15ft		
D-102c	Pump	Pumps bottoms liquid into Reboiler	Carbon Steel	75 HP		
D-102d	Heat Exchanger	Column Reboiler	Carbon Steel	419 sqft.	364	20
C-103	Heat Exchanger	Cools final PG stream	Carbon Steel	191 sqft.	90	15
Storage Vessels						
T-101	Floating Roof Tank	Store 2-wks of Glycerol Feedstock	Carbon Steel	724,559 gal		30
T-102	Floating Roof Tank	Store 2-wks of NaCl/H20 EDI Concentrate Streams	Carbon Steel	424,453 gal		20
T-103	Floating Roof Tank	Store 2-wks of Methanol/H20 Purge	Carbon Steel	25,907 gal		15
T-104	Floating Roof Tank	Store 2-wks Propanol/H20 Product	Carbon Steel	8,400 gal		20
T-105	Floating Roof Tank	Store 8-hr of PG Product	Carbon Steel	11,607 gal		15
T-106	Floating Roof Tank	Store 8-hr of PG Product	Carbon Steel	11,607 gal		15
T-107	Floating Roof Tank	Store 2-wks of PG Product	Carbon Steel	482,718 gal		15

Detailed Equipment Descriptions

The following bare-module costs were calculated using correlations, calculations and heuristics were taken from the text Product & Process Design Principles by Sader, Seider and Lewin. The price index for all calculations were based on CE Index = 560.4 from the most recent reported value from December 2010 (Chemical Engineering 2011). This index was used to account for inflation and provide the most accurate estimation possible for the financial analysis presented later in the report.

M-102 (Mixer)

Bare-Module Cost: $3,699

The crude glycerol feed, fresh water feed and water recycle are mixed in M-102. The water concentration in the resultant stream, S-103 is increased to 50% by weight. This specification is required for the electrodeionization process.

EDI (Electrodionization Equipment)

Bare-Module Cost: $4,483,200

The EDI machine strips the salts from the glycerol/water mixture and transports the ions to a concentrate stream (S-104) for disposal into the sewer system. It uses approximately 200 kW of electricity.

P-101 (Pump)

Bare-Module Cost: $13,993

The pump P-101 is used to raise the pressure of output stream from the EDI by 22 psia. The break horsepower is 1.63 HP to process 471 cuft/hr. Stainless steel is used for construction.

HX-101 (Heat Exchanger)

Bare-Module Cost: $77,519

This heat exchanger is used to cool the distillate (S-109) back to room temperature, as well as to preheat the 33230 lb/hr feed to column D-101. It exchanges 1990000 Btu/hr with a surface area of 2052 sq ft. Carbon steel is used on both sides.

H-101 (Heater)

Bare-Module Cost: $222,840

The heater H-101 is used to give additional heating to stream S-107 in order to reduce the duty requirements on the reboiler in D-101. It uses medium pressure steam to raise the temperature to 242 F, and has a duty requirement of 2410000 Btu/hr. Carbon steel is used on both sides.

D-101 (Distillation Column)

Bare-Module Cost: $1,166,781

The feed stream into distillation column D-101 is S-108, which is composed of water, methanol, and glycerol. D-102 has 4 theoretical trays and an O'Connell efficiency of 0.093, giving 43 trays. The height of the column is 100 ft and the diameter is 3.9 ft. Carbon steel is used in construction. The molar reflux ratio is 0.2 and the feed enters halfway up the column. The column operates at 20 psia and the temperature of the reboiler and total condenser are 248 F and 221 F respectively. The purpose of this separation is to remove 70% of the water and all of the methanol from the glycerol stream. Since methanol is lighter than water, both of these requirements can be accomplished at once. The condenser and reboiler duties are 16480000 and 15740000 Btu/hr respectively.

P-102 (Pump)

Bare-Module Cost: $14,847

P-102 is used to raise the pressure of the water recycle stream to compensate for pressure losses through the machinery. It is made of stainless steel and has a brake horsepower of 0.38 hp.

P-103 (Pump)

Bare-Module Cost: $15,097

Pump P-103 is used to raise the pressure of the refined glycerol to the reactor operating pressure of 581 psia. It is made of stainless steel and moves 267.0 cu ft of liquid with a brake power of 29.01 hp.

HX-102 (Heat Exchanger)

Bare-Module Cost: $67,135

HX-102 raises the temperature of the refined glycerol to the reactor operating temperature of 410 F by cooling and condensing the hot vapor effluent from the reactor. ASPEN suggested that the surface area of this heat exchanger is 73 sq ft. The reason why this is low is because of the very high heat capacity of hydrogen and the additional heating that occurs due to condensation of the propylene glycol. It is made of stainless steel due to the presence of hydrogen.

TR-100 (Turbine)

Bare-Module Cost: $57,089

Turbine TR-100 is an attempt to recover some of the energy as the hydrogen feed pressure is lowered to the reactor operating pressure of 580 psia. It is made of stainless steel and produces 28 hp of power.

CP-101 (Compressor)

Bare-Module Cost: $258,602

Compressor CP-101 repressurizes the hydrogen recycle to the reactor operating pressure of 580 psia. It is made of stainless steel, moves 6947 cu ft/hr and requires a brake power of 28.67 hp.

M-101 (Mixer)

Bare-Module Cost: $20,233

M-101 is a mixer that brings the hydrogen recycle and the hydrogen feed together in a small, stainless steel vessel.

HX-103 (Heat Exchanger)

Bare-Module Cost: $67,421

Heat exchanger HX-103 heats the combined hydrogen in stream S-119 to the reactor operating temperature of 410 F. It uses the vapor from the second flash vessel (F-102) as the hot stream. It exchanges 1130000 Btu/hr and is made of stainless steel. It has a surface area of 165 sq ft.

R-101 (Reactor)

Bare-Module Cost: $796,642

Reactor R-101 is a trickle bed reactor made out of stainless steel and is 5.2 ft x 11.5 ft (DxL). It contains 4800 kg of Cu-ZnO-Al_2O_3 catalyst and converts 100% of the glycerol to propylene glycol and propanol. The reactor operates adiabatically since the heat of reaction can be effectively removed solely through bulk transport of the effluent. See the reactor section for more information.

F-101 (Flash Vessel)

Bare-Module Cost: $111,058

Flash vessels were found to be the most effective way to separate the hydrogen from the propylene glycol product. F-101 is placed directly after the reactor to collect the hot liquid product. The vessel is 6.75 ft x 1.7 ft. The vapor outflow contains 52% propylene glycol by mass.

F-102 (Flash Vessel)

Bare-Module Cost: $89,031

The vapor from F-101 is cooled in HX-102 to 429F, which allows for liquid to form. This stream is separated in F-102, a stainless steel 1.51 ft x 5.36 ft vessel. The vapor outflow from here contains 39.6% propylene glycol by mass.

C-102 (Cooler)

Bare-Module Cost: $85,504

Cooler C-101 is designed to cool the vapor from F-102 to 225 F, which at the design pressure of 553 psia, results in a vapor-liquid equilibrium that has virtually all of the propylene glycol in the liquid phase. The cooler is made of stainless steel and uses cooling water with a required duty of 7497000 Btu/hr.

F-103 (Flash Vessel)

Bare-Module Cost: $31,808

F-103 separates the effectively pure hydrogen vapor from the 10398 lb/hr propylene glycol and water liquid. It is made of stainless steel and is 0.74 x 1.5 ft. The vapor is sent to the recycle compressor.

M-103 (Mixer)

Bare-Module Cost: $3,699

M-103 combines the three liquid effluents from the flash vessels and then depressurizes the mixture to 30 psia, which is the feed to column D-102. The total flow rate is 19591 lb/hr.

D-102 (Distillation Column)

Bare-Module Cost: $2,477,162

The feed stream into distillation column D-121 is S-133, which is composed of water, propanol, and glycerol at 34.7%, 0.7%, and 64.5% propylene glycol by mass. D-102 has 14 theoretical trays and an O'Connell efficiency of 0.198, giving 70 trays. The height of the column is 154 ft and the diameter is 2.8 ft. Carbon steel is used in construction. The molar reflux ratio is 0.13 and the feed enters halfway up the column. The column operates at 20 psia and the temperature of the reboiler and total condenser are 364 F and 130 F respectively. The reboiler operates at a temperature that is low enough to use medium pressure steam. The condenser and reboiler duties are 8590000 and 7110000 Btu/hr respectively. The condenser is a partial condenser. The liquid condensate is sent to wastewater treatment while the vapor is hydrogen which is combusted in a pilot flame.

C-103 (Cooler)

Bare-Module Cost: $75,539

Cooler C-103 reduces the temperature of the final product to a safe handling temperature of 90 F. It is made of carbon steel and the duty is 2580000 Btu/hr. The product has 99.7 % purity.

Section 14

SPECIFICATION SHEETS

COOLER

Identification:	**Item**	*Cooler*			
	Item No.	*C-103*		Date:	4-Apr-11
	No. required		1	By:	KMH

Function: To cool the propylene glycol product for storage.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-134	***S-135***
Quantity (lb/hr):	12380	12380
Composition: (mass fraction)		
Water	0.003	0.003
Hydrogen	0	0
Propylene glycol	0.997	0.997
N-propanol	0	0
Isopropanol	0	0
Methanol	0	0

Design Data: Outlet temperature: 90 F
Outlet pressure: 15 psia
Vapor fraction: 0
Tube length: 20 ft
Surface area: 183 sqft.

Utilities: Heat duty: -2581912 Btu/hr
Controls:
Tolerances:
Comments and drawings: See process flow sheet, separation section

Equipment Base f.o.b. Cost: $18,252
Bare Module Factor: 1.0
Bare Module Cost: $85,504

COMPRESSOR

Identification:	**Item**	*Isentropic Compressor*		
	Item No.	CP-101	Date:	11-Apr-11
	No. required	1	By:	KMH

Function: To increase the pressure of stream S130.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-130	***S-131***
Quantity (lb/hr):	1606	1606
Composition: (mass fraction)		
Water	0.192	0.192
Hydrogen	0.620	0.620
Propylene Glycol	0.011	0.011
N-Propanol	0.037	0.037
Isopropanol	0.139	0.139
Methanol	trace	trace

Design Data: Net work required: 28.67 hp
Efficiency: 0.80
Discharge pressure: 600 psia
Outlet temperature: 244 F
Isentropic outlet temperature: 241 F
Vapor fraction: 1.0

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section.

Equipment base f.o.b. cost: $92,292
Bare Module Factor: 1
Bare Module Cost: $258,603

DISTILLATION COLUMN

Identification:	**Item**	*Distillation Column*		
	Item No.	D-101	Date:	30-Mar-11
	No. required	1	By:	KMH

Function: To separate glycerol from water to purify reactor feed stream.

Operation: Continuous

Materials handled:	***Feed***	***Vapor Dist***	***Bottoms***
	S-108	***S-109***	***S-114***
Quantity (lb/hr):	33230	13985	19245
Composition: (mass fraction			
Glycerol	0.467	0.960	0.806
Water	0.516	0	0.194
Methanol	0.017	0.040	trace

Design Data:

Number of theoretical trays: 4
Pressure: 20 psia
Functional height: 100 ft
Material of construction: Carbon steel
Recommended inside diameter: 3.8 ft
Tray efficiency: 0.093
Feed stage: 22

Molar reflux ratio: 0.2
Tray spacing: 2.0 ft
Skirt height: 14.5 ft
Vessel weight: 8507 lb
Wall thickness: 1/4 in

Utilities: Condenser duty: -16479327 Btu/hr, Reboiler duty: 15739914 Btu/hr
Controls:
Tolerances:
Comments and drawings: See pretreatment section process flow sheet

Equipment base f.o.b. cost:	$125,546
Bare-Module Factor:	4.16
Bare Module Cost:	$522,271

DISTILLATION COLUMN

Identification:	**Item**	*Distillation Column*		
	Item No.	D-102	Date:	30-Mar-11
	No. required	1	By:	KMH

Function: Purify propylene glycol product stream by separating water, PG, and propanol.

Operation: Continuous

Materials handled:	***Feed*** ***S-133***	***Vapor Dist.*** ***S-137***	***Liquid Dist.*** ***S-136***	***Bottoms*** ***S-135***
Quantity (lb/hr):	19591	136.1	7075	12380
Composition: (mass frac)				
Glycerol	0	0	0	0
Water	0.348	0.043	0.956	0.003
Hydrogen	trace	0.012	trace	0
Propylene Glycol	0.644	trace	0.040	0.997
N-propanol	0.004	0.404	0.003	trace
Isopropanol	0.004	0.540	trace	trace
Methanol	0	trace	trace	trace

Design Data:

Number of theoretical trays: 14
Pressure: 20 psia
Functional height: 156 ft
Material of construction: Carbon steel
Recommended inside diameter: 2.8 ft
Tray efficiency: 0.198
Feed stage: 46

Molar reflux ratio: 0.13
Tray spacing: 2.0 ft
Skirt height: 14.5 ft
Vessel weight: 6025 lb
Wall thickness: 1/4 in

Utilities: Condenser duty: -8588644 Btu/hr, Reboiler duty: 7106169 Btu/hr

Controls:

Tolerances:

Comments and drawings: See process flow sheet, separation section

Equipment base f.o.b. cost: $112,587

Bare-Module Factor: 4.16

Bare Module Cost: $468,362

FLASH VESSEL

Identification:	**Item**	*Vertical Pressure Vessel*		
	Item No.	*F-101*	Date:	4-Apr-11
	No. required	1	By:	KMH

Function: To purify propylene glycol reactor product.

Operation: Continuous

Materials handled:	***Feed***	***Distillate***	***Bottoms***
	S-121	***S-123***	***S-122***
Quantity (lb/hr):	21197	16880	4317
Composition: (mass fraction)			
Water	0.336	0.393	0.114
Hydrogen	0.047	0.059	trace
Propylene glycol	0.597	0.524	0.881
N-propanol	0.006	0.008	0.002
Isopropanol	0.014	0.017	0.003
Methanol	trace	trace	trace

Design Data: Pressure: 560 psia
Vapor fraction: 0.927
Functional height: 6.8 ft
Inside diameter: 1.7 ft
Material of construction: Carbon steel
Vessel weight: 1188 lb
Wall thickness: 0.65 in

Utilities: Heat duty: 0
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section

Equipment base f.o.b. cost: $26,697
Bare-Module Factor: 4.16
Bare Module Cost: $111,058

FLASH VESSEL

Identification:	**Item**	*Vertical Pressure Vessel*		
	Item No.	*F-102*	Date:	4-Apr-11
	No. required	1	By:	KMH

Function: To purify propylene glycol reactor product.

Operation: Continuous

Materials handled:	***Feed*** ***S-124***	***Distillate*** ***S-126***	***Bottoms*** ***S-125***
Quantity (lb/hr):	16880	12004	4876
Composition: (mass fraction)			
Water	0.393	0.489	0.156
Hydrogen	0.059	0.083	trace
Propylene glycol	0.524	0.396	0.838
N-propanol	0.008	0.01	0.002
Isopropanol	0.017	0.023	0.003
Methanol	trace	trace	trace

Design Data:
Pressure: 560 psia
Vapor fraction: 0.902
Functional height: 5.4 ft
Inside diameter: 1.5 ft
Material of construction: Carbon steel
Vessel weight: 766 lb
Wall thickness: 0.583 in

Utilities: Heat duty: 0
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section

Equipment base f.o.b. cost: \$21,402
Bare Module Factor: 4.16
Bare Module Cost: \$89,031

FLASH VESSEL

Identification:	**Item**	*Vertical Pressure Vessel*		
	Item No.	*F-103*	Date:	4-Apr-11
	No. required	1	By:	KMH

Function: To purify propylene glycol reactor product.

Operation: Continuous

Materials handled:	***Feed* *S-128***	***Distillate* *S-130***	***Bottoms* *S-129***
Quantity (lb/hr):	12004	1606	10398
Composition: (mass fraction)			
Water	0.489	0.192	0.535
Hydrogen	0.083	0.619	trace
Propylene glycol	0.396	0.011	0.455
N-propanol	0.008	0.037	0.005
Isopropanol	0.023	0.139	0.005
Methanol	trace	trace	trace

Design Data: Pressure: 553 psia
Vapor fraction: 0.581
Functional height: 1.5 ft
Inside diameter: 0.8 ft
Material of construction: Carbon steel
Vessel weight: 77 lb
Wall thickness: 0.375 in

Utilities: Heat duty: 0
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section

Equipment base f.o.b. cost: $7641
Bare Module Factor: 4.16
Bare Module Cost: $31,786

HEATER

Identification:	**Item**	*Heater*			
	Item No.	*H-101*		Date:	4-Apr-11
	No. required		1	By:	KMH

Function: To increase the temperature of the glycerol/water outlet stream from the EDI prior to distillation.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-107	***S-108***
Quantity (lb/hr):	34007	34007
Composition: (mass fraction)		
Glycerol	0.467	0.467
Water	0.516	0.516
Methanol	0.017	0.017

Design Data: Outlet temperature: 242 F
Outlet pressure: 36.8 psia
Vapor fraction: 0

Utilities: Heat duty: 2410557 Btu/hr
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section

Equipment base f.o.b. cost: $106,893
Bare Module Factor: 1.86
Bare Module Cost: $222,839

HEAT EXCHANGER

Identification:	**Item**	*Heat exchanger*			
	Item No.	HX-101		Date:	4-Apr-11
	No. required	1		By:	KMH

Function: To integrate heat between streams.

Operation: Continuous

Materials handled:	***Hot Stream*** ***S-109, S-110***	***Cold Stream*** ***S-106, S-107***
Quantity (lb/hr):	13985	33231
Composition: (mass frac		
Glycerol	trace	0.467
Water	0.960	0.516
Methanol	0.040	0.017

Design Data: Hot side: Tube side, Cold side: shell side
Hot stream temperature, Inlet: 221.4 F Outlet: 80.0 F
Cold stream temperature, Inlet: 69.9 F Outlet: 151.8 F
Material of construction: Carbon steel
Heat duty: 2136340 Btu/hr
Heat transfer coefficient (U): 33.97
Area: 2052 sqft

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section.

Equipment base f.o.b. cost: $21,818
Bare Module Factor: 3.17
Bare Module Cost: $77,519

HEAT EXCHANGER

Identification:	**Item**	*Heat exchanger*		
	Item No.	HX-102	Date:	4-Apr-11
	No. required	1	By:	KMH

Function: To integrate heat between streams.

Operation: Continuous

Materials handled:	***Hot Stream*** ***S-123, S-124***	***Cold Stream*** ***S-115, S-116***
Quantity (lb/hr):	16880	19245
Composition: (mass frac		
Glycerol	0	0.806
Water	0.393	0.194
Hydrogen	0.059	0
Propylene glycol	0.524	0
N-propanol	0.008	0
Isopropanol	0.017	0
Methanol	trace	trace

Design Data: Hot side: Tube side, Cold side: shell side
Hot stream temperature, Inlet: 455 F Outlet: 429 F
Cold stream temperature, Inlet: 252 F Outlet: 410 F
Material of construction: Carbon steel
Heat duty: 1990194 Btu/hr
Heat transfer coefficient (U): 344.8
Area: 72.8 sqft

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section.

Equipment base f.o.b. cost: $9404
Bare Module Factor: 3.17
Bare Module Cost: $67,136

HEAT EXCHANGER

Identification:	**Item**	*Heat exchanger*		
	Item No.	HX-103	Date:	4-Apr-11
	No. required	1	By:	KMH

Function: To integrate heat between streams.

Operation: Continuous

Materials handled:	***Hot Stream*** ***S-126, S-127***	***Cold Stream*** ***S-119, S-120***
Quantity (lb/hr):	1952	12004
Composition: (mass fraction)		
Water	0.158	0.489
Hydrogen	0.687	0.083
Propylene glycol	0.009	0.396
N-propanol	0.031	0.010
Isopropanol	0.115	0.023
Methanol	trace	trace

Design Data: Hot side: Tube side, Cold side: shell side
Hot stream temperature, Inlet: 429 F Outlet: 409 F
Cold stream temperature, Inlet: 202 F Outlet: 416 F
Material of construction: Carbon steel
Heat duty: 11132628 Btu/hr
Heat transfer coefficient (U): 145.3 Btu/hr*sqft*R
Area: 164.4 sqft

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section.

Equipment Base f.o.b. cost: $9428
Bare Module Factor: 3.17
Bare Module Cost: $67,420

MIXER

Identification:	**Item**	*Mixer*			
	Item No.	M-101		Date:	30-Mar-11
	No. required		1	By:	KMH

Function: Combine recycled and fresh hydrogen streams for feed to reactor.

Operation: Continuous

Materials handled:	***Feed 1***	***Feed 2***	***Outlet***
	S-118	***S-131***	***S-119***
Quantity (lb/hr):	346.4	1605.7	1952
Composition: (mass fraction)			
Water	0	0.192	0.158
Hydrogen	1	0.620	0.687
Propylene glycol	0	0.011	0.009
N-propanol	0	0.037	0.031
Isopropanol	0	0.139	0.115
Methanol	0	trace	trace

Design Data: Pressure: 600 psia
Outlet temperature: 202.4 F
Vapor fraction: 0.994
Material of construction: Carbon steel

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section

Equipment base f.o.b. cost: $3300
Bare Module Factor: 1.0
Bare Module Cost: $3699

MIXER

Identification:	**Item**	*Mixer*		
	Item No.	M-102	Date:	30-Mar-11
	No. required	1	By:	KMH

Function: Combine crude glycerol, fresh water, and recycled water streams.

Operation: Continuous

Materials handled:	***Feed 1*** ***S-101***	***Feed 2*** ***S-102***	***Feed 3*** ***S-112***	***Outlet 1*** ***S-103***
Quantity (lb/hr):	19392	5384	9230	34007
Composition: (mass fraction)				
Glycerol	0.800	0	trace	0.456
Water	0.150	1.000	0.960	0.504
Methanol	0.010	0	0.040	0.017
NaCl	0.040	0	0	0.023

Design Data: Pressure: 25 psia
Outlet temperature: 54.8 F
Vapor fraction: 0
Material of construction: Carbon steel

Utilities:

Controls:

Tolerances:

Comments and drawings: See process flow sheet, pretreatment section

Equipment base f.o.b. cost: $3300

Bare Module Factor: 1.0

Bare Module Cost: $3699

MIXER

Identification:	**Item**	*Mixer*			
	Item No.	M-103		Date:	30-Mar-11
	No. required		1	By:	KMH

Function: Combine propylene glycol product streams from three separators for purification.

Operation: Continuous

Materials handled:	***Feed 1*** ***S-122***	***Feed 2*** ***S-129***	***Feed 3*** ***S-125***	***Outlet 1*** ***S-132***
Quantity (lb/hr):	4317	10398	4876	19591
Composition: (mass fraction)				
Glycerol	0	0	0	0
Water	0.114	0.535	0.156	0.348
Methanol	trace	0.005	0.003	0.004
Hydrogen	trace	trace	trace	trace
Propylene glycol	0.881	0.455	0.838	0.644
N-propanol	0.002	0.004	0.002	0.004
Isopropanol	0.003	0.005	0.003	0.004

Design Data: Pressure: 548 psia
Outlet temperature: 317 F
Vapor fraction: 0
Material of construction: Carbon steel

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, separation section

Equipment base f.o.b. cost: $3300
Bare Module Factor: 1
Bare Module Cost: $3699

PUMP

Identification:	**Item**	*Pump*			
	Item No.	P-101		Date:	4-Apr-11
	No. required		1	By:	KMH

Function: To increase the pressure of the glycerol/water stream exiting EDI prior to HX.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-105	***S-106***
Quantity (lb/hr):	33231	33231
Composition: (mass fraction)		
Glycerol	0.467	0.467
Water	0.516	0.516
Methanol	0.017	0.017

Design Data: Discharge pressure: 42 psia
Pressure change: 22 psi
Volumetric flow rate: 472 cuft/hr
Material of construction: Stainless steel
Pump speed: 3600 RPM
Pump efficiency: 0.463
Net work required: 1.629 hp

Utilities: Electricity requirement: 0.283 kW
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section

Equipment base f.o.b. cost: $3133
Bare Module Factor: 3.3
Bare Module Cost: $15,097

PUMP

Identification:	**Item**	*Pump*		
	Item No.	P-102	Date:	30-Mar-11
	No. required	1	By:	KMH

Function: To increase the pressure of the water/methanol stream for feed to the EDI process.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-111	***S-112***
Quantity (lb/hr):	9230	9230
Composition: (mass fraction)		
Glycerol	trace	trace
Water	0.960	0.960
Methanol	0.040	0.040

Design Data:
Discharge pressure: 30 psia
Pressure change: 10.3 psi
Volumetric flow rate: 151 cuft/hr
Material of construction: Stainless steel
Pump efficiency: 0.296
Net work required: 0.380 hp

Utilities: Electricity requirement: 0.283 kW
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section

Equipment base f.o.b. cost: $3081
Bare Module Factor: 3.3
Bare Module Cost: $14848

PUMP

Identification:	**Item**	*Pump*			
	Item No.	P-103		Date:	4-Apr-11
	No. required		1	By:	KMH

Function: To increase the pressure of the glycerol/water stream for feed to the reactor.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-111	***S-112***
Quantity (lb/hr):	19245	9230
Composition: (mass fraction)		
Glycerol	0.806	0.806
Water	0.194	0.194
Methanol	trace	trace

Design Data: Discharge pressure: 587 psia
Pressure change: 567 psi
Volumetric flow rate: 267 cuft/hr
Material of construction: Stainless steel
Pump efficiency: 0.378
Net work required: 29.1 hp

Utilities: Electricity requirement: 21.7 kW
Controls:
Tolerances:
Comments and drawings: See process flow sheet, reactor section

Equipment base f.o.b. cost: $3100
Bare Module Factor: 3.3
Bare Module Cost: $14,969

TURBINE

Identification:	**Item**	*Isentropic Turbine*		
	Item No.	T-101	Date:	11-Apr-11
	No. required	1	By:	KMH

Function: To decrease the pressure of the inlet hydrogen to acceptable process pressure.

Operation: Continuous

Materials handled:	***Inlet***	***Outlet***
	S-117	***S-118***
Quantity (lb/hr):	346	346
Composition: (mass fraction)		
Hydrogen	1	1

Design Data: Net work required: -27.7 hp
Efficiency: 0.80
Discharge pressure: 600 psia
Outlet temperature: 11.7 F
Isentropic outlet temperature: -3.1 F
Vapor fraction: 1.0

Utilities:
Controls:
Tolerances:
Comments and drawings: See process flow sheet, pretreatment section.

Equipment base f.o.b. cost: $7810
Bare Module Factor: 1
Bare Module Cost: $8754

Section 15

FIXED CAPITAL INVESTMENT SUMMARY

Discussion of Total Permanent Investment (C_{TPI})

The total permanent investment for this project was calculated by summing a number of costs, including the bare-module investment, direct permanent investment and total depreciable capital. The bare-module cost was found to be approximately $15.3 million, and it accounts for all on-site fabricated equipment and process machinery. The purchase cost for each piece of equipment was calculated using correlations provided in the text Product and Process Design Principals while the installed cost was determined using the factor-cost method. The cost of the catalyst was also included accounting for catalyst replacement over the course of the plant's projected life. It was found to be $1.97 million.

The total permanent investment accounts for site preparation and service facilities like installing utility lines, building plant facilities and other similar tasks. In total, direct permanent investment was assumed to be 10% of the bare-module cost for equipment. After adding funds to account for the cost of contingencies and contractor fees (assumed to be 18% of the direct permanent investment), the total depreciable capital was found. This value is used in the financial analysis section to determine tax reductions for the company.

Finally, the cost of land and plant start-up are added to determine the unadjusted total permanent investment. Start-up costs were assumed to be 20% of the total depreciable capital. Since the plant will be located in the Gulf Coast, a site factor of 1.00 was used to determine the final total permanent investment, $24.2 million.

Investment Summary

Bare Module Costs				
Fabricated Equipment	$	10,412,750		
Process Machinery	$	1,019,119		
Spares	$	311,696		
Storage	$	1,583,445		
Other Equipment	$	-		
Catalysts	$	1,972,383		
Computers, Software, Etc.	$	-		
Total Bare Module Costs:			$	15,299,392
Direct Permanent Investment				
Cost of Site Preparations:	$	764,970		
Cost of Service Facilities:	$	764,970		
Allocated Costs for utility plants and related facilities:	$	-		
Direct Permanent Investment			$	16,829,331
Total Depreciable Capital				
Cost of Contingencies & Contractor Fees	$	3,029,280		
Total Depreciable Capital			$	19,858,611
Total Permanent Investment				
Cost of Land:	$	397,172		
Cost of Royalties:	$	-		
Cost of Plant Start-Up:	$	3,971,722		
Total Permanent Investment - Unadjusted			$	24,227,505
Site Factor				1.00
Total Permanent Investment			$	24,227,505

Section 16

ENVIRONMENTAL CONSIDERATIONS

Environmental Considerations

The use of glycerol in propylene glycol manufacture will drastically decrease the negative environmental impact that is currently associated with the conventional methods of propylene glycol production. These conventional methods require propylene oxide as a feedstock. Propylene oxide is manufactured during the process of petroleum refinement; the manufacture of propylene oxide from crude oil reduces the availability of crude oil for refinement into gasoline and depletes natural resources, such as crude oil wells, that are already scarce. In contrast, glycerol is abundantly available as a byproduct from biodiesel manufacture. The amount of crude glycerol available is growing with the expansion of the biodiesel industry. By switching to this new method of propylene glycol production, the world's crude oil reserves will be conserved, and waste associated with biodiesel manufacture will be reduced.

According to their material safety data sheets, neither pure glycerol nor propylene glycol has significant environmental or health hazards, and both have a very low risk of flammability. As such, there are essentially no regulations on the transport and storage of industrial grade propylene glycol products. The large volume of hydrogen in the process is also essentially harmless to the environment, unless ignited.

The main environmental concerns in the glycerol to propylene glycol manufacturing process involve the disposal of the wastewater streams and the use of electricity for equipment operations. The entire plant will be drawing between 250 and 300 kW of power from the grid in operation. On the Gulf Coast, power is mainly supplied by oil power plants, which cause significant pollution and waste valuable resources. This negative impact could be offset by building and using a local power source such as solar panels on the roof of the plant. Government grants can be acquired to fund this endeavor. For example, Ford Motor Company recently built a 500 kW solar plant on the roof of one of its manufacturing facilities in Michigan. This cost Ford less than $3 million due to the government subsidies that it received.

The wastewater from the electrodeionization machine contains over 13% by mass of salt, which is approximately 4 times the salinity of the Gulf of Mexico. While not considered to be a pollutant, its disposal is non-negligible. The coastland on the Gulf of Mexico is mainly marshland, which is very sensitive to salinity changes. Disposing of such a highly concentrated saline solution in such an environment may have an enormous negative impact on the plant and animal species native to the area. The existing sewage treatment facilities are not equipped to remove these inorganic salts in large concentrations. Thus, this waste stream must be piped into the ocean far offshore, which is essentially a salt sink. As such, it is recommended that the construction of a pipeline to move the waste stream a safe distance from shore to dispose of the salt water should be strongly considered.

Two additional wastewater streams containing methanol and propanol must be considered. The methanol and propanol in these streams cause them to be toxic to the environment. These streams will be sent to the sewer authority for digestion. Since this is a commercial facility, sewage fees will be assessed by the sewer authority based on the quantities of water and organic compounds.

Finally, considerations must be made for the small pilot flame that will be used to burn excess hydrogen and propanol dissolved in the feed to the refinement column. Since propanol is easily combusted, the only expected products are water and carbon dioxide. With routine monitoring by plant personnel, it is not expected to pose significant environmental risks.

Section 17

HEALTH AND SAFETY CONSIDERATIONS

Health and Safety Considerations

The main safety issue in the plant's operation is the presence of hydrogen gas at high pressures. Hydrogen gas, a very small molecule, diffuses rapidly through many materials, so extreme caution must be exercised to avoid leakage into the plant. Hydrogen gas has an explosion limit between 4% and 47%. This is relatively low, and there is a risk of combustion in the presence of atmospheric air as the pressurized hydrogen gas escapes from the vessel.

Hydrogen embrittlement occurs when hydrogen adsorbs on certain metals and alloys causing a loss of ductility in the metal, making the equipment more brittle. This increases the likelihood of hydrogen leakage or large-scale breaks in the system, which could be catastrophic. To minimize the possibility of leakage and prevent embrittlement, process equipment that contains pressurized hydrogen uses stainless steel alloy, which is not susceptible to embrittlement.

To ensure that no dangerous buildup of hydrogen gas occurs, sensors will be installed in critical areas of the plant to monitor the presence of hydrogen in the air and alert operators of significant leaks. One target area for hydrogen leakage control is directly around the reactor vessel, which houses a large amount of pressurized hydrogen along with the liquid feed and products. Tight hydraulic fittings will be used throughout the process to minimize hydrogen leaks from the pipelines.

The heat of reaction of glycerol to propylene glycol varies slightly with temperature. It has a negligible effect due to the large volume of hydrogen gas that absorbs heat generated. The reactor is therefore assumed to operate adiabatically.

The large amount of electricity that will be drawn by the EDI machine requires appropriate insulation and warning systems to avoid the risk of electric shock, short circuiting, or fire. Sufficient insulation on all electric cables is required and close monitoring of electrical systems is required to swiftly detect any anomilies and possible short circuits. Any electric cable that is used must be checked periodically to prevent fraying or wire exposure, and in the event of damage, the cable must be replaced immediately. Smoke alarms must be installed throughout the plant to ensure rapid detection of and emergency response to any fires, which could arise from the electrical connectivity, hydrogen leakage or other accidental combustion. Fire extinguishers must be easily accessible by personnel as mandated by the municipality's fire safety inspector.

To ensure that there are no interruptions in the EDI function, a generator that can provide the power required for 12 hours of plant operation should be available in case of power outage. Such an interruption could cause immense damage to the propylene glycol product's purity and quality, imposing a large financial cost and potentially endangering consumers.

Product safety is a major concern with regard to USP grade propylene glycol, which is used widely in pharmaceutical and food products. The propylene glycol from this plant will be 99.99% pure, which must be guaranteed to avoid the risk of poisoning consumers. There is a chance that trace amounts of ethylene glycol could be produced in a side reaction during production. Consumption of ethylene glycol is hazardous to the kidneys, liver, and central nervous system of humans and is potentially fatal, according to its Material Safety Data Sheet. It also has mutagenic effects on some types of mammalian cells and is a known carcinogen. Therefore, it is very important that the product not be sold containing any ethylene glycol. Samples will be analyzed every 30 minutes with a gas chromatograph to ensure that trace quantities of ethylene glycol are not present in the USP grade product. This is especially important during startup (and in the early stages of the process).

Section 18

STARTUP CONSIDERATIONS

Startup Considerations

The majority of the analysis done on this process considers only steady state operation of the plant. However, certain considerations must be made for the startup period prior to reaching steady state. Specific startup considerations must be considered for the major equipment units, including both distillation columns, the reactor, and the EDI machine, as well as the hydrogen recycle loop and its integration into the system.

Initially, process-clean water will be run through all of the major process units, including the EDI machine, in order to clean out the system. Once all process units except for the EDI machine have been emptied of water, crude glycerol will be slowly introduced into the process and the EDI machine will begin to desalt the glycerol. Once the glycerol attains an acceptable level of salt content to remove the risk of corrosion, it will be sent to column D-101, which will operate at total reflux and use excess steam utility in the reboiler until the column temperature profile is achieved. The reflux ratio will then be adjusted to reach the process specification of a molar reflux ratio of 0.2, and the distillate will then start to heat the column feed in HX-101. This will reduce utility usage in the reboiler until the steady state value of 15700000 Btu/hr is achieved. The bottoms product of refined glycerol will be collected and analyzed until it meets the required specifications of 10 ppm salt content and 15% water by mass. Once these specifications are reached, this stream will be connected to the reactor section.

To avoid combustion when the pressurized hydrogen is introduced to the process, pipelines that will contain hydrogen must be flushed with nitrogen gas to remove oxygen. Once the hydrogen has been introduced and begins circulating through the reactor, the refined glycerol will slowly be introduced. Additionally, due to the extensive heat integration, startup heaters will be required to raise the temperature of the hydrogen and glycerol streams that enter the reactor to the reactor inlet temperature of 410 F. Additional cooling will be provided by C-102 until the heat exchanger network begins to operate.

Once the liquid reactor effluent is collected, it will be sent to column D-102, which will initially operate at total reflux in a manner similar to D-101. Once the temperature profile is achieved, product will start to be collected and analyzed until it meets specifications.

Section 19

PLANT LAYOUT

Plant Layout

Because the process requires only one tanker truck per hour of both product and feed, the plant does not necessarily need to have a rail connection, although it would increase efficiency. The only requirement for plant layout is that D-102 needs to not be covered by the factory roof since there will be a hydrogen flame coming off the condenser. Additionally, the EDI machine must be protected from the elements due to the sensitive nature of the electrodes. Aside from that, this layout was chosen to reduce pipeline length and to ensure that utilities are in proximity of process equipment that requires them (i.e. electricity connection near EDI, hydrogen near the reactor, and heating and cooling utilities near the distillation columns).

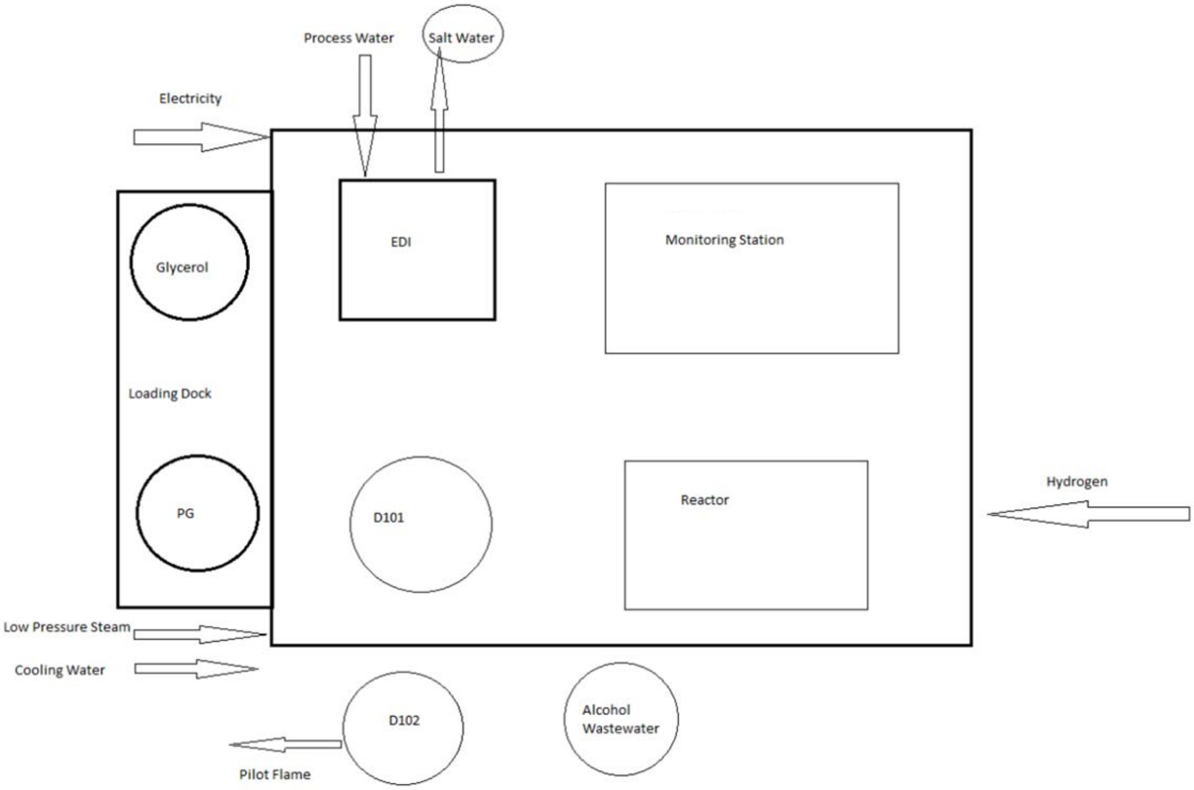


Figure 8 Plant layout diagram

Section 20

OPERATING COSTS AND ECONOMIC ANALYSIS

Operating Costs and Economic Analysis

A number of assumptions were made during the financial analysis process that led to the values presented above. The plant will be located in the Gulf Coast and will operate 330 days per year resulting in an overall operating factor of 0.9041. Two years are allocated for design and construction of the plant (2012, 2013) and operation is expected to begin in 2014. To account for a typical efficiency lag, production will begin at 50% efficiency and ultimately reach 90% efficiency in the third year of production (2016). A 5 year MACRS depreciation schedule was chosen for this project to remain consistent with financial analysis of projects of a similar scale.

A number of utilities will be required to run the plant, including medium pressure steam, process water, cooling water, electricity and treatment of waste streams. Of these utilities, electricity and organic waste water treatment are the most significant costs at $0.06/kWh and $0.048/lb respectively. In addition to the crude glycerol feed, the hydrogen feed will also be purchased at $0.50/lb. Although n-propanol and isopropanol are being created as byproducts of the reaction of glycerol to propylene glycol, they are produced in such small quantities that it is more profitable to simply dispose of them as waste instead of investing in additional purification equipment. Summing the raw material costs and utilities with the general expenses yields a total variable cost of $45.1 million.

Based on the proposed design, the process requires 4 operators per shift, while assuming each operator will have 5 shifts per week. The EDI pretreatment section, reactor section and separation section will each need one dedicated operator while a fourth operator will be charged with managing the hydrogen recycle system and storage systems for the waste and product steams. The EDI equipment is expected to be licensed from Dow, formerly Rohm and Haas, for $2.00 million per year. In total, the fixed costs for per year will equal $7.16 million.

The total bare module cost is projected to be $15.3 million, which includes the process equipment, catalyst, storage equipment and spares. Accounting for multiple recycle streams EDI integration, 20% of total depreciable capital was allocated to plant start-up costs. The total permanent investment is found to be $22.2 million and will be completely accounted for in the cash flow during the year of construction, 2013. Working capital is projected based on 14 days in inventory for the raw materials and final product as well as 30 days of accounts receivable and cash reserves. When summed with the $11.8 million in working capital, the total capital investment was found to be $34.0 million.

Analysis of the resulting cash flows shows that the first year of cumulative positive net present value occurs in 2016. Variable costs for the year total $40.5 million while fix costs total $6.60 million. Clearly, the calculated NPV value is heavily weighted by variable costs such as raw material prices and utilities. Thus, a sensitivity analysis will focus on these factors to understand the overall volatility of the process profitability.

As discussed in the Market Analysis section of the report, the production of propylene glycol from renewable biodiesel represents a rapidly growing market that has the potential for high profitability. Using techniques and correlations presented in Product and Process Design Principles (Seider *et al.* 2009), the proposed process was found to be highly profitable, as expected. The base case scenario projected a net present value (NPV) of $88.4 million in 2012 with an investor's rate of return (IRR) of 58.54%. These high values are primarily driven by the large margin between the selling price of propylene glycol and the cost of the crude glycerol feed, $1.00/lb and $0.22/lb respectively.

Sensitivity Analysis

As previously mentioned, a number of key factors were identified that could have a significant impact on the overall profitability. The factors include commodity costs such as the price of propylene glycol, glycerol and hydrogen feed prices and electricity costs in addition to variable costs such as organic waste water treatment and EDI licensing fees. The sensitivity-plot shown in Figure 9 is a graphical representation of the sensitivity analysis on these variables. This graph plots the percent change in a given factor against the change in IRR relative to the base case, 58.5%. Thus, a ten unit increase on the y-axis corresponds to an IRR of 68.5%.

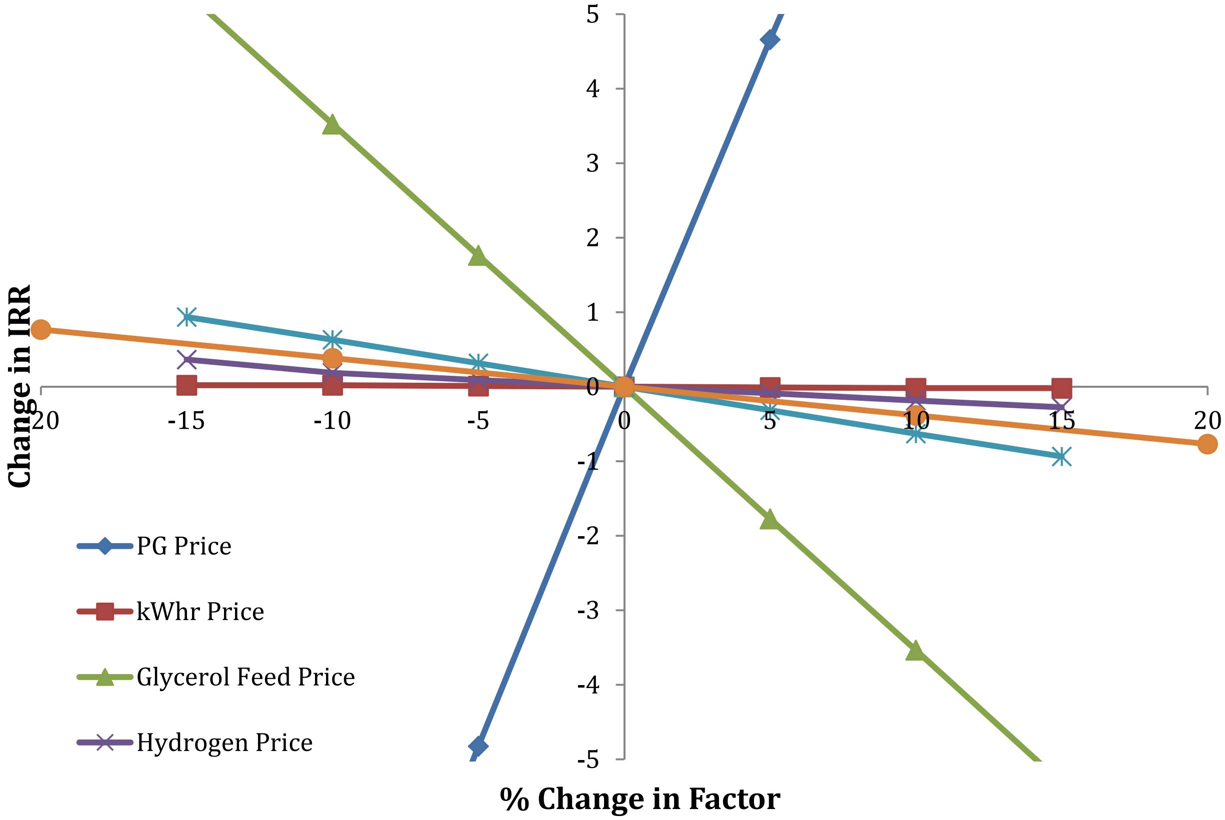


Figure 9 Sensitivity Graph

The commodity costs were varied by plus and minus 15% to understand the profitability relationship to tangential markets. In spite of our best efforts, we were not able to confidently estimate the EDI licensing costs; therefore, this factor was varies by plus or minus 30% to account for the increased uncertainty.

Propylene Glycol (PG) Price Sensitivity

The plus or minus 15% uncertainly in spot propylene glycol prices appears to be an accurate representation of the uncertainty in the market. According to a recent ICIS, a subsidiary of Reed Business Information and trusted information provider for the chemical and oil industry, propylene glycol prices in the US were \$0.93-\$1.05/lb in January 2011, up from \$0.88-\$0.96/lb in November 2010. The unusually harsh winters of the past 3 years has increased the demand for antifreeze and plane de-icing fluid, and as global mean temperatures continue to rise, the increased moisture in the atmosphere will result in greater snowfall. Prices are projected to potential increase another \$0.15/lb in the first half of 2011 due to a seasonal spike in demand (ICIS 2011) Furthermore, an increase in natural gas prices increased the price of the percent of propylene glycol market derived propylene, a product of natural gas. However, these price points could easily relax as the artificial boost due to seasonal volatility will not continue into the later spring and early summer months.

In general, the demand for propylene glycol has been steady at 2%, with a yearly growth of about 1.5% in the unsaturated polyester resins (UPRs) and about 2.5% in the cosmetics and consumer products industry. In Asia, demand for propylene glycol has been estimated as growing about 6% per year (ICIC 2011). Coupled with the expected increase in supply of crude glycerol in the coming years, and thus lower feed prices, it is reasonable to expect that the increased demand for propylene glycol will be offset by increased supply of feed. Thus, the price of propylene glycol likely will remain relatively stable within a plus or minus 15% swing.

As shown in Figure 9, the IRR is the most sensitive to volatility in PG prices relative to the other six factors studied. Figure 10 shows that a 15% decrease in PG prices to $0.85/lb could decrease the IRR as much as 15% to 43.5%. However, the current process is still exceedingly profitable and is able to absorb a commodity price shock of this magnitude. In fact, assuming constant variable costs and working capital, the price of propylene glycol would have to fall to $0.68/lb to make the project just barely viable at 20.67% IRR. With the expected increase it PG production in the coming years as well as a potential decrease in price due to competition in a number of the chemical's largest markets, this could be a very possible scenario in the coming decade; however, it is unlikely to happen in the short-term five year horizon.

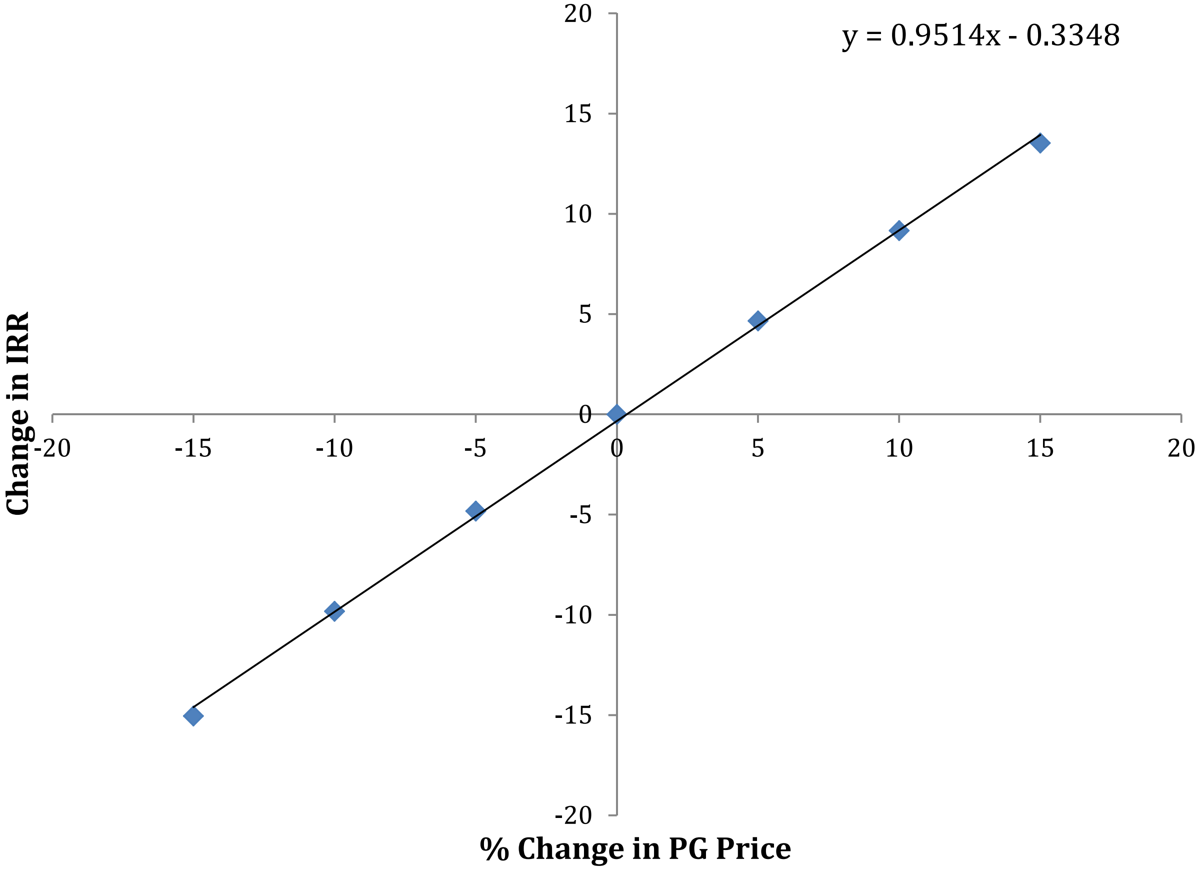


Figure 10 Sensitivity of PG price.

Glycerol (feed) Price Sensitivity

As previously mentioned, crude glycerol is a natural by-product of biodiesel production. For every 9 kg of biodiesel produced, about 1 kg of glycerol is formed (Suppes 2006). With US production of glycerol exclusively from biodiesel projected to be 1.92 billion pounds in 2012, up from 281 million lbs in 2007, the price of crude glycerol is expected to be significantly depressed from the estimate of $0.22/lb used in this financial assessment (Gobina 2007). Gobina goes on to project crude glycerol prices to fall as low as $0.05/lb, citing the fact that some biodiesel producers find it more profitable to burn it as waste than attempt to sell it on the open market.

However, recent technologies have open up alternative markets for excess glycerol that may help curb over-supply. Solvay Chemicals commercialized a process to reverse the conventional route of making synthetic glycerol from epichlorohydrin. After the success of their pilot plant in 2007, a full scale commercial plant is scheduled to be built in Map Tha Phut, Thailand. Alkylene carbonate (reactive intermediate or solvent), biomethanol, and acrylic acid are additional examples of potential products produced from glycerol feed material. (Chemical Business 2010). Furthermore, new purification systems, such as EDI, offer alternatives to cost and labor intensive vacuum distillation, which could further equalize glycerol supply and demand.

The price of glycerol feed, being one of the two primary inputs to the process, obviously has a significant effect on the overall profitability. Using a very conservative estimate of a 15% decrease in the price of crude glycerol to \$0.187/lb, the IRR increases 5.3% to 63.8% as shown in Figure 11. If the current spot price of glycerol, \$0.10/lb, is used, the IRR increases to 76.5%. The greater the drop in crude glycerol price, the larger the margin for propylene glycol and thus the greater the overall profitability for the process.

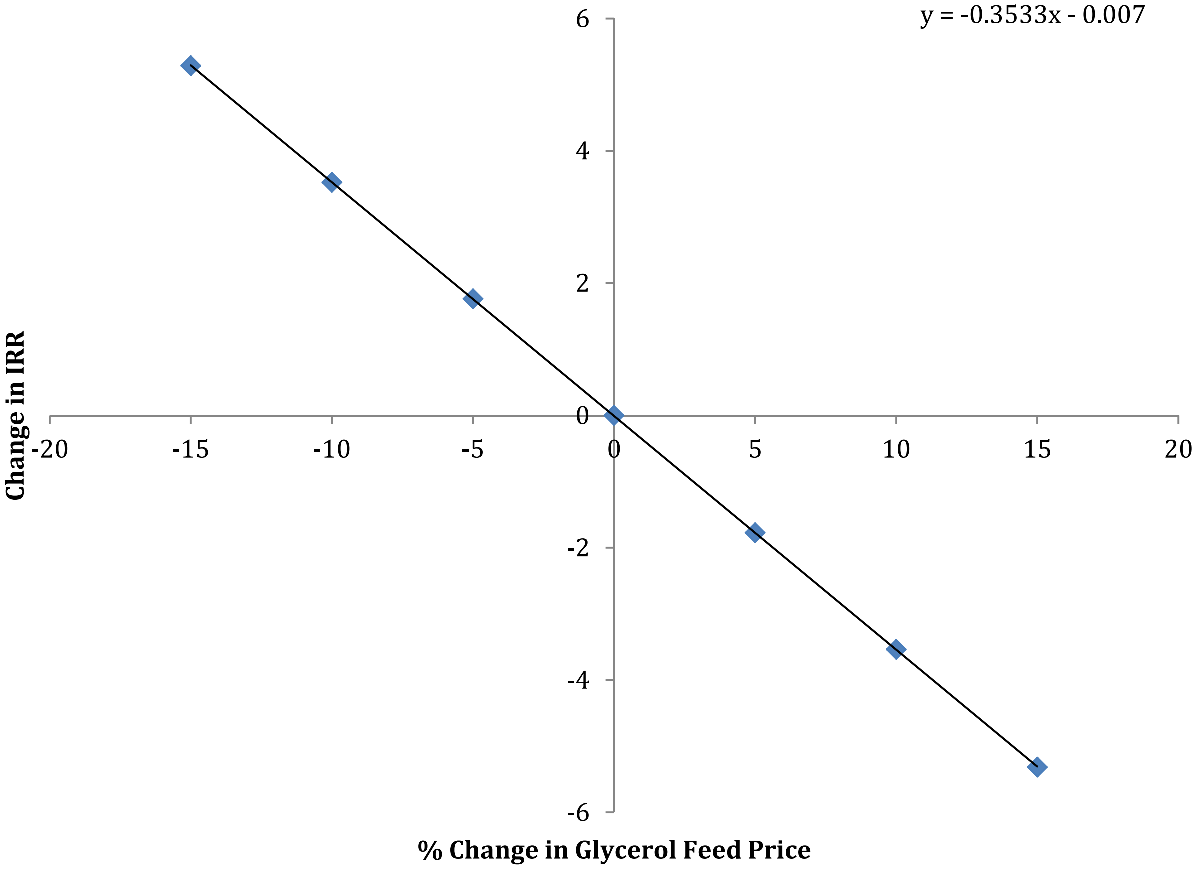


Figure 11 Sensitivity of glycerol feed price.

Organic Waste Water Treatment Sensitivity

Waste water from this process will contain methanol, n-propanol and iso-propanol. The cost of water treatment was calculated using a correlation provided by Bruce Vrana from DuPont:

$$Cost\left[\frac{\$}{lb}\right] = 0.044 + 0.048 * (\%\ organic\ impurities\ by\ weight)$$

It is understood that this correlation is an estimate that can be used to quantify this cost; however, the actual value could vary based on geography, market conditions and quantity of wastewater. A 10% increase in waste water treatment costs corresponds to a 0.64% increase in IRR.

However, this variable represents a moderate contribution to variable costs and thus is not a critical concern based on the economic analysis.

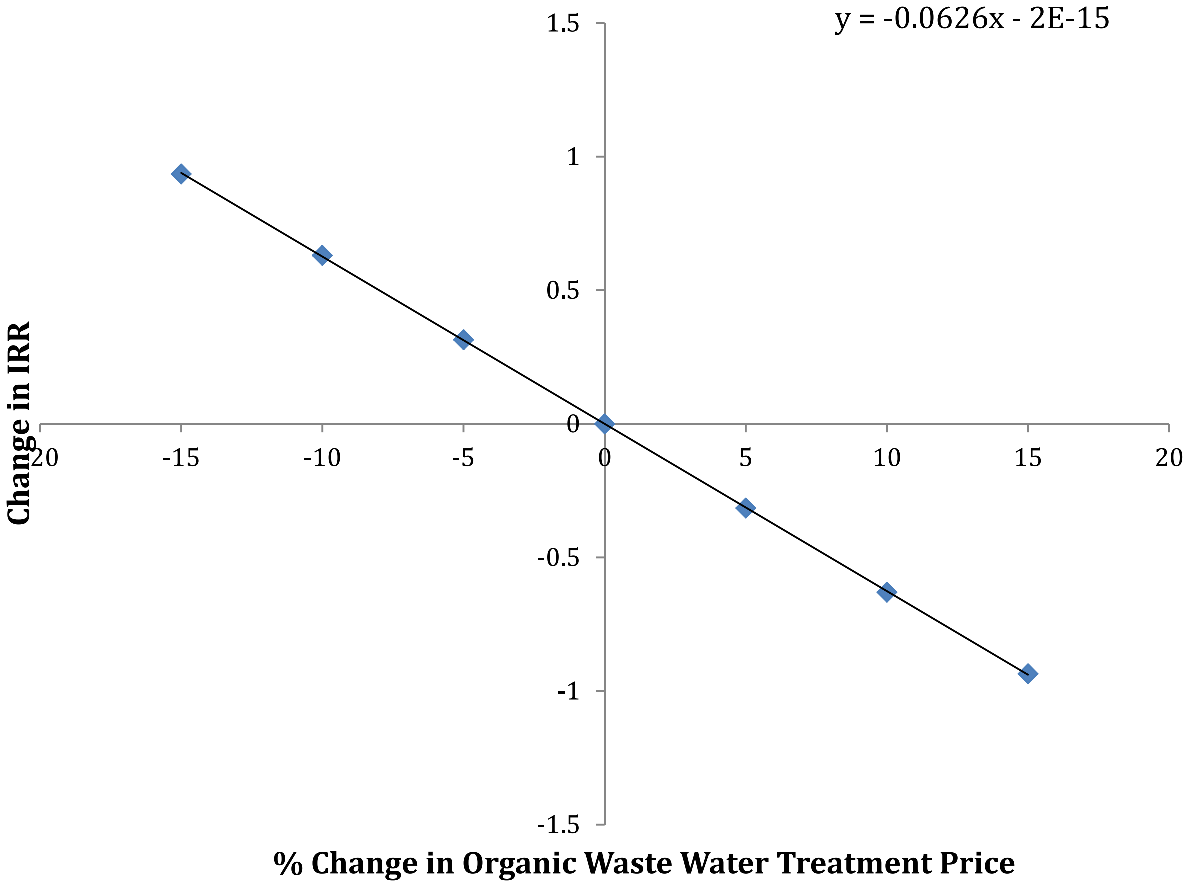


Figure 12 Sensitivity of waste water treatment price.

EDI Licensing

EDI Licensing is assumed to be $2.00 million per year. This estimate has significant uncertainty as we were unable to obtain an exact quote for a process of this scale. As a result, a larger sensitivity analysis was performed, varying the licensing fee by 30% in both directions. Relative to the commodity costs of PG and glycerol, the licensing fee does not have as critical of an impact on the overall profitability, providing confidence that this is an economically viable technology to incorporate into the process. A 30% increase in licensing fees for a total of $2.6 million per year would decrease the IRR by 1.17% to 56.9%.

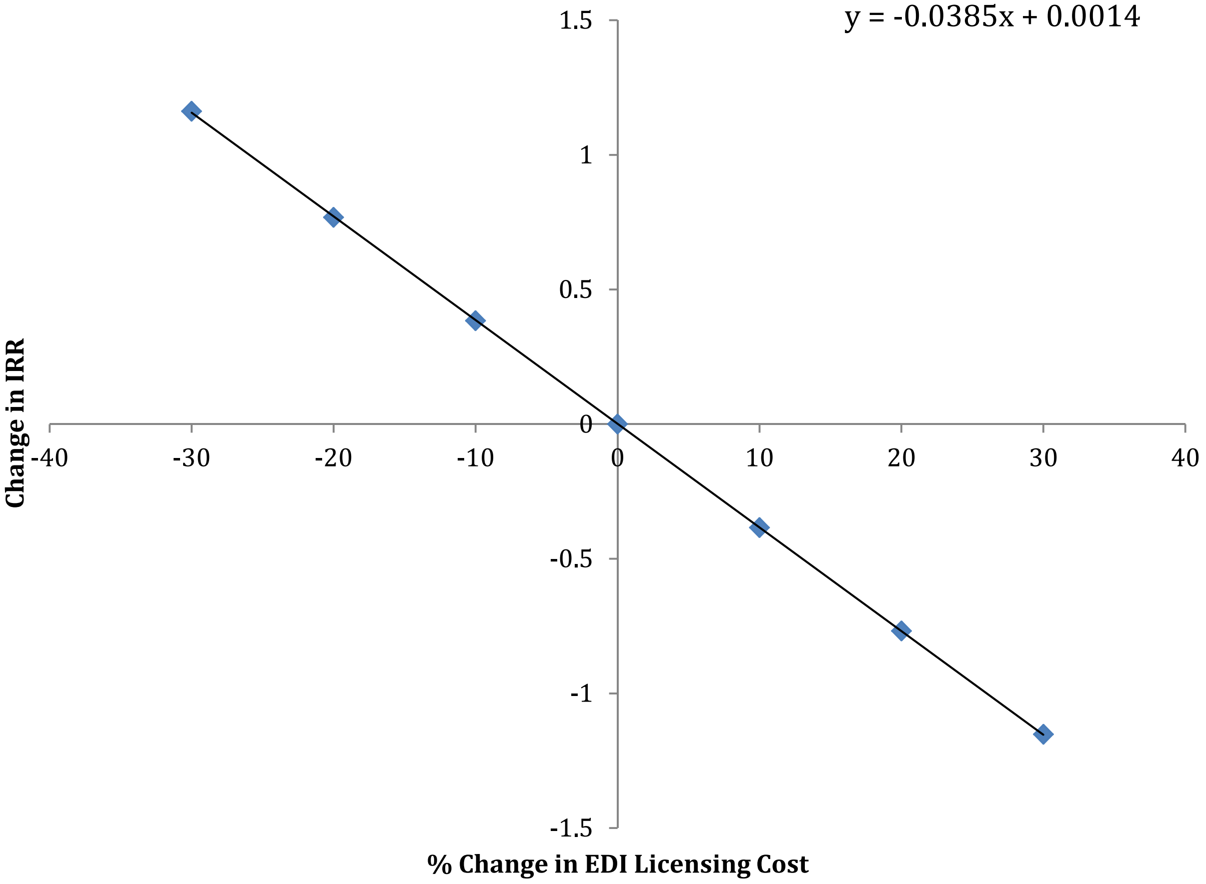


Figure 13 Sensitivity of EDI licensing cost.

Hydrogen Sensitivity

Hydrogen will be supplied to the plant via direct pipeline from the supplier at a cost of $0.50/lb. Although hydrogen will be conserved via recycle streams to reduce utility usage, a significant amount will be needed during the start-up process to fill the system. The price of hydrogen is historically constant, and our analysis shows that a plus or minus 15% fluctuation would minimally affect IRR.

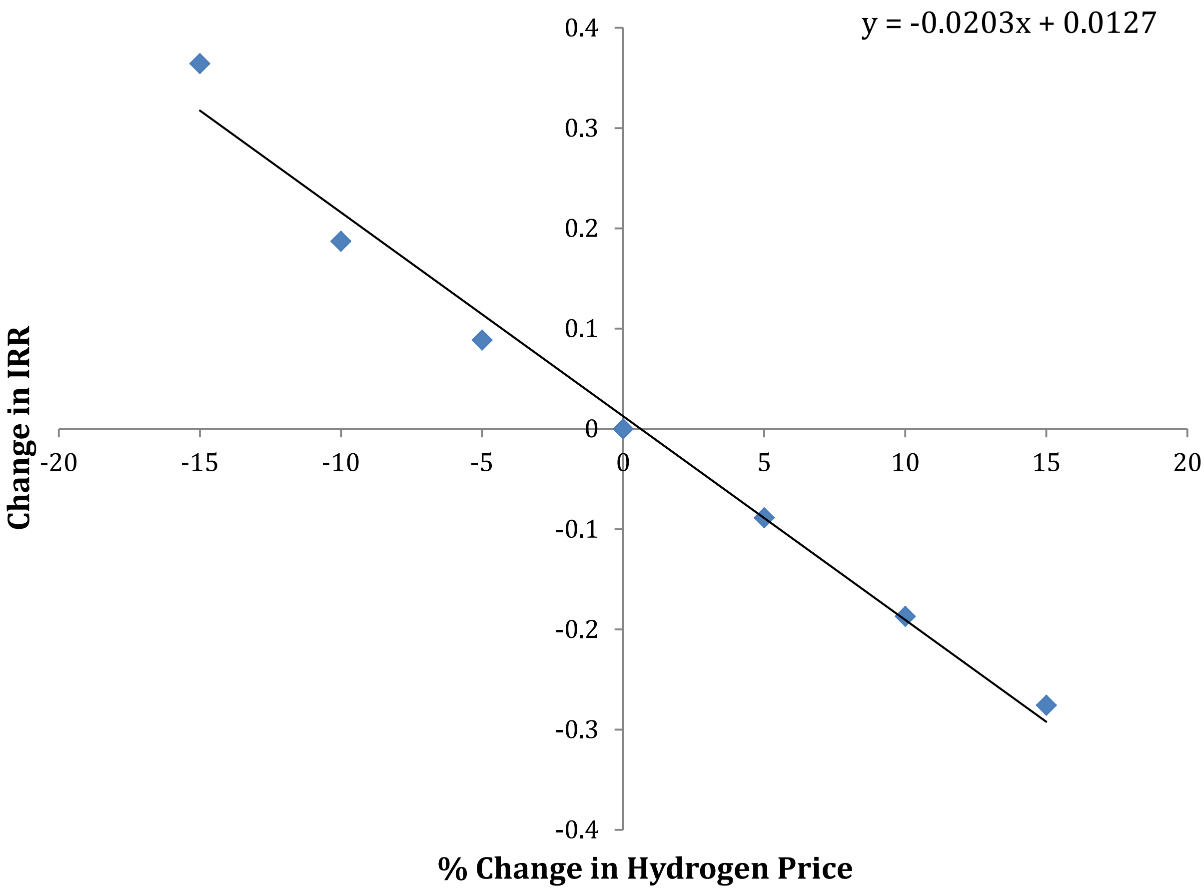


Figure 14 Sensitivity of hydrogen price.

Electricity Sensitivity

Electricity was projected to cost $0.06/kWh, based on information provided in Process Design Principles. The EDI pre-treatment section adds a significant demand for electricity for the process, approximately 200kW, resulting in an overall electricity need of 241kW. Since the plant is designed to be environmentally friendly with a minimal carbon footprint, it is possible that electricity will be sought from renewable sources for a higher fee. There already exists a significant network of wind energy generation facilities in the local area, and the recent British Petroleum Oil spill will likely encourage further development of renewable energy sources in the region. (Save Energy 2004) Assuming a potential surcharge of up to 15% would cause a decrease in IRR by 0.28%. The high profitability of the current process would justify a marginal surcharge in sourcing electricity from green sources.

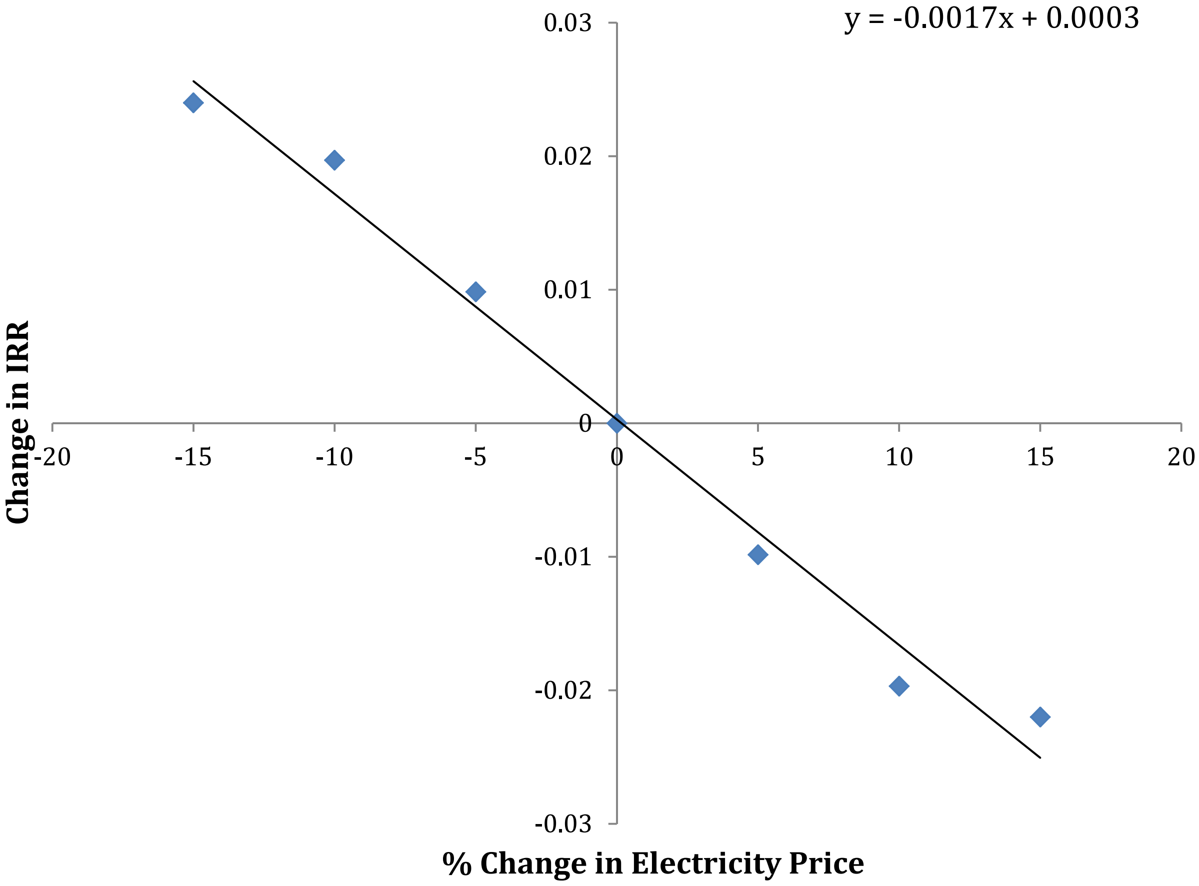
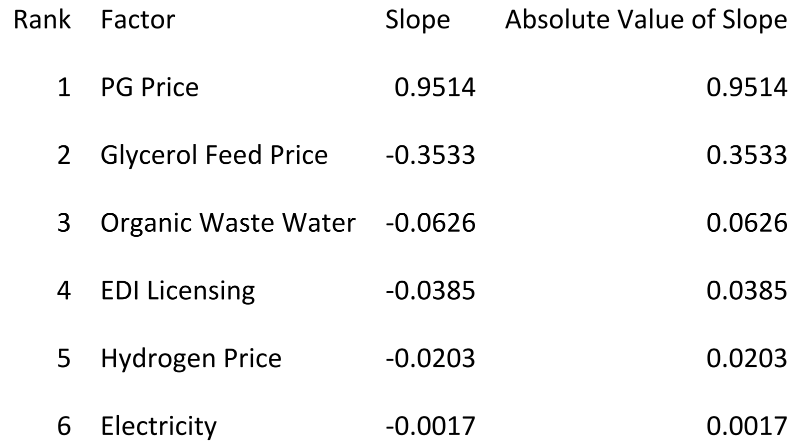


Figure 15 Sensitivity of Electricity price.

Summary of Sensitivity Analysis

The slope of the linear regressions found for each line indicates the relative influence on the IRR of the project. As shown in Figure 9, the price of PG and glycerol are by far the most significant levers that determine the overall profitability. Based on market analysis, the price of PG is expected to seasonally fluctuate but trend downward over the next decade. However, the price of crude glycerol is also expected to decrease significantly ensuring the next margin will remain. From a financial point of view, this process warrants serious consideration for implementation.



Rank	Factor	Slope	Absolute Value of Slope
1	PG Price	0.9514	0.9514
2	Glycerol Feed Price	-0.3533	0.3533
3	Organic Waste Water	-0.0626	0.0626
4	EDI Licensing	-0.0385	0.0385
5	Hydrogen Price	-0.0203	0.0203
6	Electricity	-0.0017	0.0017

Figure 16 Ranked factors based on sensitivity.

General Information

Process Title: **Glycerol to Propylene Glycol**
Product: **Propylene Glycol**
Plant Site Location: **Gulf Coast**
Site Factor: 1.00
Operating Hours per Year: 7920
Operating Days Per Year: 330
Operating Factor: 0.9041

Product Information

This Process will Yield

12,379 lb of Propylene Glycol per hour
297,096 lb of Propylene Glycol per day
98,041,680 lb of Propylene Glycol per year

Price $1.00/lb

Chronology

Year	Action	Distribution of Permanent Investment	Production Capacity	Depreciation 5 year MACRS	Product Price
2012	Design		0.0%		
2013	Construction	100%	0.0%		
2014	Production	0%	45.0%	20.00%	$1.00
2015	Production	0%	67.5%	32.00%	$1.00
2016	Production	0%	90.0%	19.20%	$1.00
2017	Production		90.0%	11.52%	$1.00
2018	Production		90.0%	11.52%	$1.00
2019	Production		90.0%	5.76%	$1.00
2020	Production		90.0%		$1.00
2021	Production		90.0%		$1.00
2022	Production		90.0%		$1.00
2023	Production		90.0%		$1.00
2024	Production		90.0%		$1.00
2025	Production		90.0%		$1.00
2026	Production		90.0%		$1.00
2027	Production		90.0%		$1.00
2028	Production		90.0%		$1.00

Equipment Costs

Equipment Description		Bare Module Cost
M-102	Process Machinery	$3,699
S-101	Fabricated Equipment	$4,483,200
P-101	Process Machinery	$13,993
HX-101	Fabricated Equipment	$77,519
H-101	Fabricated Equipment	$222,840
D-101	Fabricated Equipment	$1,166,781
D-101a	Process Machinery	$81,770
D-101b	Process Machinery	$37,593
D-101c	Process Machinery	$37,003
D-101d	Process Machinery	$141,198
P-103	Process Machinery	$15,097
Catalyst	Catalysts	$1,972,383
P-102	Process Machinery	$14,847
R-101a	Fabricated Equipment	$796,642
R-101b	Fabricated Equipment	$796,642
F-101	Process Machinery	$111,058
HX-102	Fabricated Equipment	$67,135
F-102	Process Machinery	$89,031
HX-103	Fabricated Equipment	$67,421
C-102	Fabricated Equipment	$85,504
F-103	Process Machinery	$31,808
CP-101	Process Machinery	$258,602
TR-100	Process Machinery	$57,089
M-101	Process Machinery	$20,233
M-103	Process Machinery	$3,699
V-101	Process Machinery	$11,208
D-102	Fabricated Equipment	$2,477,126
D-102a	Fabricated Equipment	$23,458
D-102b	Process Machinery	$37,258
D-102c	Process Machinery	$45,179
D-102d	Fabricated Equipment	$72,944
C-103	Fabricated Equipment	$75,539
T-101	Storage	$542,691
T-102	Storage	$313,824
T-103	Storage	$100,029
T-103	Storage	$56,322
T-104/T-105	Storage	$125,967
T-106	Storage	$444,611
Additional Equipment		$320,449
Total		*$15,299,392*

Raw Materials

Raw Material:	Unit:	Required Ratio:	Cost of Raw Material:
Crude Glycerol	lb	1.2287lb per lb of PG	$0.220per lb
Water	lb	0.052407lb per lb of PG	$0.00per lb
Hydrogen	lb	0.027948lb per lb of PG	$0.50per lb
Total Weighted Average:			$0.284per lb of PG

Utilities

Utility:	Unit:	Required Ratio	Utility Cost
Med Pressure Steam	lb	2.515464lb per lb of PG	$3.000E-03per lb
Process Water	gal	0.049633gal per lb of PG	$7.500E-04per gal
Cooling Water	lb	71.1lb per lb of PG	$7.500E-05per lb
Electricity	kWh	0.0194743kWh per lb of PG	$0.060per kWh
Organic Waste Water	lb	0.9556lb per lb of PG	$0.048per lb
Salt Waste Water	lb	0.474637lb per lb of PG	$0.00per lb
Total Weighted Average:			$0.060per lb of PG

Variable Costs

General Expenses:

Selling / Transfer Expenses:	3.00%of Sales
Direct Research:	4.80%of Sales
Allocated Research:	0.50%of Sales
Administrative Expense:	2.00%of Sales
Management Incentive Compensation:	1.25%of Sales

Working Capital

Accounts Receivable	⇨	30	Days
Cash Reserves (excluding Raw Materials)	⇨	30	Days
Accounts Payable	⇨	0	Days
Propylene Glycol Inventory	⇨	14	Days
Raw Materials	⇨	14	Days

Total Permanent Investment

Cost of Site Preparations: 5.00% of Total Bare Module Costs
Cost of Service Facilities: 5.00% of Total Bare Module Costs
Allocated Costs for utility plants and related facilities: $0
Cost of Contingencies and Contractor Fees: 18.00% of Direct Permanent Investment
Cost of Land: 2.00% of Total Depreciable Capital
Cost of Royalties: $0
Cost of Plant Start-Up: 20.00% of Total Depreciable Capital

Fixed Costs

Operations

Operators per Shift: 4 (assuming 5 shifts)
Direct Wages and Benefits: $40/operator hour
Direct Salaries and Benefits: 15% of Direct Wages and Benefits
Operating Supplies and Services: 6% of Direct Wages and Benefits
Technical Assistance to Manufacturing: $0.00 per year
Control Laboratory: $0.00 per year

Maintenance

Wages and Benefits: 4.50% of Total Depreciable Capital
Salaries and Benefits: 25% of Maint. Wages + Benefits
Materials and Services: 100% of Maint. Wages + Benefits
Maintenance Overhead: 5% of Maint. Wages + Benefits

Operating Overhead

General Plant Overhead: 7.10% of Maint and Ops Wages and Benefits
Mechanical Department Services: 2.40% of Maint and Ops Wages and Benefits
Employee Relations Department: 5.90% of Maint and Ops Wages and Benefits
Business Services: 7.40% of Maint and Ops Wages and Benefits

Property Taxes and Insurance

Property Taxes and Insurance: 2% of Total Depreciable Capital

Straight Line Depreciation

Direct Plant: 8.00% of Total Depreciable Capital, less 1.18 times the Allocated Costs for Utility Plants and Related Facilities
Allocated Plant: 6.00% of 1.18 times the Allocated Costs for Utility Plants and Related Facilities

Other Annual Expenses

Rental Fees (Office and Laboratory Space): $0
Licensing Fees: $2,000,000
Miscellaneous: $0

Depletion Allowance

Annual Depletion Allowance: $0

Variable Cost Summary

Variable Costs at 100% Capacity:

General Expenses

Selling / Transfer Expenses:	$	2,941,250
Direct Research:	$	4,706,001
Allocated Research:	$	490,208
Administrative Expense:	$	1,960,834
Management Incentive Compensation:	$	1,225,521

Total General Expenses		$	11,323,814
Raw Materials	$0.284293per lb of Propylene Glycol		$27,872,536
Byproducts	$0.000000per lb of Propylene Glycol		$0
Utilities	$0.060025per lb of Propylene Glycol		$5,884,956
Total Variable Costs		$	45,081,306

Fixed Cost Summary

Operations

Direct Wages and Benefits	$	1,664,000
Direct Salaries and Benefits	$	249,600
Operating Supplies and Services	$	99,840
Technical Assistance to Manufacturing	$	-
Control Laboratory	$	-
Total Operations	$	2,013,440

Maintenance

Wages and Benefits	$	893,637
Salaries and Benefits	$	223,409
Materials and Services	$	893,637
Maintenance Overhead	$	44,682
Total Maintenance	$	2,055,366

Operating Overhead

General Plant Overhead:	$	215,176
Mechanical Department Services:	$	72,736
Employee Relations Department:	$	178,808
Business Services:	$	224,268
Total Operating Overhead	$	690,987

Property Taxes and Insurance

Property Taxes and Insurance:	$	397,172

Other Annual Expenses

Rental Fees (Office and Laboratory Space):	$	-
Licensing Fees:	$	2,000,000
Miscellaneous:	$	-
Total Other Annual Expenses	$	2,000,000

Total Fixed Costs	$	7,156,966

Investment Summary

Bare Module Costs

Fabricated Equipment	$	10,412,750		
Process Machinery	$	1,019,119		
Spares	$	311,696		
Storage	$	1,583,445		
Other Equipment	$	-		
Catalysts	$	1,972,383		
Computers, Software, Etc.	$	-		
Total Bare Module Costs:			$	15,299,392

Direct Permanent Investment

Cost of Site Preparations:	$	764,970		
Cost of Service Facilities:	$	764,970		
Allocated Costs for utility plants and related facilities:	$	-		
Direct Permanent Investment			$	16,829,331

Total Depreciable Capital

Cost of Contingencies & Contractor Fees	$	3,029,280		
Total Depreciable Capital			$	19,858,611

Total Permanent Investment

Cost of Land:	$	397,172		
Cost of Royalties:	$	-		
Cost of Plant Start-Up:	$	3,971,722		
Total Permanent Investment - Unadjusted			$	24,227,505
Site Factor				1.00
Total Permanent Investment			$	24,227,505

Working Capital

	2013	2014	2015
Accounts Receivable	$ 3,626,199	$ 1,813,100	$ 1,813,100
Cash Reserves	$ 408,400	$ 204,200	$ 204,200
Accounts Payable	$ -	$ -	$ -
Propylene Glycol Inventory	$ 1,692,226	$ 846,113	$ 846,113
Raw Materials	$ 481,088	$ 240,544	$ 240,544
Total	$ 6,207,913	$ 3,103,956	$ 3,103,956
Present Value at 15%	*$ 5,398,185*	*$ 2,347,037*	*$ 2,040,902*

Total Capital Investment	$ 34,013,629

Cash Flow Summary

Year	Percentage of Design Capacity	Product Unit Price	Sales	Capital Costs	Working Capital	Var Costs	Fixed Costs	Depreciation	Depletion Allowance	Taxible Income	Taxes	Net Earnings	Cash Flow	Cumulative Net Present Value at 15%
2012	0%		-	-	-	-	-	-	-	-	-	-	-	-
2013	0%		-	(24,227,500)	(6,207,900)	-	-	-	-	-	-	-	(30,435,400)	(26,465,600)
2014	45%	$1.00	44,118,800	-	(3,104,000)	(20,286,600)	(7,157,000)	(3,971,700)	-	12,703,500	(4,700,300)	8,003,200	8,871,000	(19,757,900)
2015	68%	$1.00	66,178,100	-	(3,104,000)	(30,429,900)	(7,157,000)	(6,354,800)	-	22,236,500	(8,227,500)	14,009,000	17,259,800	(8,409,300)
2016	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	(3,812,900)	-	36,694,500	(13,577,000)	23,117,500	26,930,400	6,988,300
2017	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	(2,287,700)	-	38,219,700	(14,141,300)	24,078,400	26,366,100	20,096,900
2018	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	(2,287,700)	-	38,219,700	(14,141,300)	24,078,400	26,366,100	31,495,700
2019	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	(1,143,900)	-	39,363,500	(14,564,500)	24,799,000	25,942,900	41,248,600
2020	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	49,591,000
2021	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	56,845,300
2022	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	63,153,300
2023	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	68,638,600
2024	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	73,408,400
2025	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	77,556,100
2026	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	81,162,700
2027	90%	$1.00	88,237,500	-	-	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	25,519,600	84,298,900
2028	90%	$1.00	88,237,500	-	12,415,800	(40,573,200)	(7,157,000)	-	-	40,507,400	(14,987,700)	25,519,600	37,935,500	88,352,900

Profitability Measures

The Internal Rate of Return (IRR) for this project is 58.45%

The Net Present Value (NPV) of this project in 2012 is $ 88,352,900

ROI Analysis (Third Production Year)

Annual Sales	88,237,512	
Annual Costs	(47,730,141)	
Depreciation	(1,938,200)	
Income Tax	(14,270,593)	
Net Earnings	24,298,577	
Total Capital Investment		36,643,331
ROI	66.31%	

Sensitivity Analyses

Note: The Sensitivity Analyses section below takes quite a bit of memory to update each time a cell is changed; therefore, automatic calculations are turned off. After making your axis selections, press "F9" to recalculate the IRR values. (These two lines may be deleted before printing.)

	Vary Initial Value by +/-
x-axis	50%
y-axis	80%

		Variable Costs										
		$22,540,653	$27,048,784	$31,556,914	$36,065,045	$40,573,175	*$45,081,306*	$49,589,436	$54,097,567	$58,605,698	$63,113,828	$67,621,959
Product Price	$0.20	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
	$0.36	5.67%	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
	$0.52	31.45%	24.93%	17.86%	9.85%	-0.13%	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR	Negative IRR
	$0.68	50.71%	45.15%	39.43%	33.51%	27.30%	20.67%	13.36%	4.80%	Negative IRR	Negative IRR	Negative IRR
	$0.84	67.63%	62.52%	57.33%	52.04%	46.65%	41.12%	35.42%	29.48%	23.21%	16.43%	8.78%
	$1.00	83.12%	78.29%	73.42%	68.49%	63.50%	58.45%	53.31%	48.07%	42.72%	37.22%	31.51%
	$1.16	97.54%	92.93%	88.28%	83.60%	78.88%	74.12%	69.31%	64.44%	59.51%	54.51%	49.42%
	$1.32	111.12%	106.67%	102.20%	97.71%	93.19%	88.64%	84.06%	79.44%	74.79%	70.09%	65.33%
	$1.48	123.97%	119.67%	115.35%	111.01%	106.65%	102.27%	97.87%	93.44%	88.99%	84.50%	79.98%
	$1.64	136.21%	132.03%	127.83%	123.62%	119.40%	115.16%	110.90%	106.63%	102.34%	98.02%	93.68%
	$1.80	147.89%	143.81%	139.73%	135.64%	131.53%	127.42%	123.29%	119.14%	114.98%	110.81%	106.61%

Section 21

CONCLUSION AND RECOMMENDATIONS

Conclusion and Recommendations

The extremely high profitability metrics calculated and presented in this report show that this process is very profitable and should be implemented immediately. However, this analysis is likely optimistic. The equipment costing estimation methods used produced cost values for some of the process units that appear to be lower than the typical cost for such equipment. Discussions with industrial design consultants revealed that the distillation towers particularly should cost approximately 2-3 times more than the calculated prices. Additionally, the annual cost of the electrodeionization equipment leasing was rougly estimated. Due to the proprietary nature of the process, detailed information is not currently available to the public regarding its price or operation; however, conservative estimates were made to account for this uncertainty.

The reaction mechanism remains yet unverified on an industrial scale of our magnitude. The construction of a pilot plant would be an excellent indication of whether such large scale up is feasible. It is expected that the reaction will not reach 100% conversion, but as similar reactions are used in methanol production and hydrodesulfurization, the scale up is expected to be successful. If the large scale reaction produces measurable quantities of ethylene glycol, although this was unobserved in the work of Zhou et.al. (2010), another distillation tower would be required in order to remove this heavier impurity.

Despite these challenges, the difference in purchase price between propylene glycol and crude glycerol is very high at approximately $0.78/lb, and so there inheriently is potential for profitability. The price of glycerol is inversely correlated with the production of biodiesel, as glycerol is a byproduct of this process. As biodiesel production is predicted to increase over the allotted time period for the project, the price of crude glycerol should decrease. The invention and implementation of new methods such as electrodeionization for refining crude glycerol that are currently being developed will make glycerol refinement increasingly profitable, which may cause an increase in the price of the raw material. While the price of propylene glycol varies seasonally with highest demand in the winter, its overall usefulness and superiority over ethylene glycol in almost every specification will ensure that the price of propylene glycol remains high. Additionally, propylene glycol is traditionally manufactured from petroleum products, so there will continue to be a large opportunity cost involved in using propylene oxide, since the propylene oxide could be transformed instead into other useful products if it was not being used for propylene glycol production. EDI is an increasingly more attractive method of purifying glycerol, since the operating costs are extremely low. In the future, it will be increasingly hard for companies like Dow to maintain as much proprietary control over this process.

Overall, the method presented in this report is expected to be profitable and successful. It is recommended that this project be further investigated with the construction of a pilot plant, and then cautiously implemented industrially.

Section 22

ACKNOWLEDGEMENTS

Acknowledgements

This work could not have been completed without the guidance and advice of a number of faculty members, industrial consultants, librarians, current students and alumni of the University of Pennsylvania's Chemical Biomolecular Engineering department.

We would especially like to extend the utmost gratitude to our faculty advisor, Dr. Warren Seider, and Professor Leonard Fabiano for their assistance on this project, and Mr. Bruce Vrana of DuPont Engineering Technology for proposing this problem statement.

We would also like to especially thank Mr. John Wismer of Arkema, Inc, for his guidance regarding the choice of our reactor, Mr. Gary Sawyer of Lyondell Chemical Company, and Mr. Steven Tieri of DuPont Engineering Research and Technology.

Section 23

BIBLIOGRAPHY

Chiu, Chuang-Wei. "Dehydration of Glycerol and Acetol via Catalytic Reactive Distillation." American Institute of Chemical Engineering. J.52:3543-3543, 2006.

Datta, Rathin, YuPo Lin, Dennis Burke, and Shih-Perng Tsai. 2002. Electrodeionization substrate, and device for electrodeionization treatment. US Patent 6495014 B1. Filed Aug 17, 2000. Issued Jul 12, 2001.

Dudukovic, Milorad P., and Patrick L. Mills. "A Comparison of Current Models for Isothermal Trickle-Bed Reactors: Application to a Model Reaction System." *Chemical and Catalytic Reactor Modeling*. Washington, D.C.: American Chemical Society, 1984. Print.

Economic Indicators. *Chemical Engineering*. March 2011. 118, 3; ABI/INFORM Global. http://www.che.com

EET Corp. Electrodialysis Efficiency Graph.
http://www.eetcorp.com/lts/graph_HEED1.htm

Gates, Bruce C., James R. Katzer, and George C. A. Schuit. *Chemistry of Catalytic Processes*. New York: McGraw-Hill, 1979. Print.

Green Car Congress 500 kW Solar PV System Goes Online at Ford's Michigan Assembly 11 March 2011 http://www.greencarcongress.com/2011/03/ford-20110311.html

Gobina, Edward. Biorefinery Technologies and Products. Volume I. BCC Research. Wellesley, MA. July 2007

Johnson, Duane T. and Katherine A. Tacomi. "Glycerine and Environmental Progress." Vol. 26, No. 4. 95388. 2007

Propylene Glycol Manufacturers of the European Union.
http://www.propylene-glycol.com/index.html

Propylene Glycol Prices and Pricing Information.
http://www.icis.com/v2/chemicals/9076442/propylene-glycol/pricing.html

Propylene Glycol Uses and Usage Information.
http://www.icis.com/v2/chemicals/9076443/propylene-glycol/uses.html

Seider, Warren D., J.D. Seader, Daniel R. Lewin, and Soemantri Widago. Product and Process Design Principles. John Wiley & Sons, Inc. 2004.

Seider, Warren D.
http://www.seas.upenn.edu/~dlewin/CACHE_Workshop/Batch%20Manufacture%20of%20Propylene%20Glycol.pdf

Shaffer, L., and Mintz, M., "Electrodialysis." In Principles of Desalination. Spiegler, K., and Laird, A., eds., 2nd Ed., Academic Press, New York (1980)

Suppes, G.J., C.W. Chiu, A. Tekeei, J.M. Ronco, M.L. Banks. “Reducing Byproduct Formation during Conversion of Glycerol to Propylene Glycol.” Ind. Eng. Chem. Res. 2008, 47, (18), 6878-6892

Section 25

APPENDIX

Detailed Equipment Pricing Sample Calculations

The following examples are rigorous calculations examples for every type of unit used during this process. Correlations, calculations and heuristics were taken from the text Product & Process Design Principles by Seader, Seider and Lewin (2009). The accuracy of this method is plus or minus 20%.

The price index for all calculations were based on the CE Index = 560.4 for December 2010, which is the most recent CE Index value posted on www.CHE.com (2011).

Mixer M-102

The mixer uses a turbine, which is the preferred type of agitator for mixing miscible and immiscible liquids. To find the horsepower requirement for mixing miscible liquids, the following correlation was used:

$$\frac{HP}{1000\ Gallons} = 0.5$$

ASPEN Reports:
Q = 3520.33 gal/hr

At a residence time of 10 minutes,

Q = 586.7 gallons

$$HP = 586.7 gallons \times \frac{0.5HP}{1000\ gallons} = 0.29HP$$

For an efficiency of $\eta = 0.3$, HP = 1

The cost of a closed vessel mixer is given by:

$$C_p = 3300S^{0.17}$$
$$C_p = 3300(1)^{0.17} = \$3{,}000$$

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (1)(3{,}300)$
$C_{BM\text{-}2006} = \$3{,}300$

2006 CE Index = 500
2011 CE Index = 560.4

$C_{BM\text{-}2011} = \$3{,}300 \text{ x } 560.4/500$
$C_{BM\text{-}2011} = \$3{,}699$

Distillation Column D-101

The total free on board (f.o.b) purchase cost for the unit is calculated using the following relationship:

$C_P = F_M C_V + C_{PL} + C_T$

Where
F_M = the material cost factor
C_V = the cost of an empty vessel
C_{PL}= the cost for the platforms and ladders
C_T = the cost of the trays

Length Calculation

ASPEN Report:
After accounting for the condenser and reboiler,
Theoretical trays = 4

O'Connell Efficiency = 0.093

$$N(actual) = \frac{4}{0.093} = 43\ trays$$

$$L = (43)(2) + (14) = 100\ feet$$

Thickness Calculation

The thickness for the column was estimated using the following equation:

$$t_s = \frac{P_d D_i}{2SE - 1.2P_d}$$

Where
P_d = Design pressure
S = Maximum allowable stress
E = Weld efficiency

ASPEN Report:
D_i = 3.9 ft

P_d = 10 psig.
This assumption is made because the column operates at 20 psia (5 psig)
S = 13,750 psi
Commonly used for carbon steel over a design temperature range of -20F to 650F
E=1.0

$$t_s = \frac{(10)(3.9)}{2(13750)(1) - 1.2(10)} = 0.001415\ inches$$

The theoretically determined thickness is too small for the required rigidity; therefore, a minimum wall thickness of 0.25 inches was used with a corrosion allowance of 0.125 inches.

$$t_s = 0.375\ inches = 0.0313\ feet$$

Weight Calculation

The weight of the column was calculated using the following equation:

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho$$

Where
D_i = diameter of the column (ft)
L = the length (ft)
t_s = the wall thickness (ft)
ρ = the density of carbon steel (490 lb/ft^3)

$$W = \pi(3.9 + 0.0313)(100 + 0.8 * 3.9) * 0.0313 * 490$$

$$W = 25{,}315\ lbs$$

Cost of Empty Vessel

The f.o.b cost of the empty vessel was calculated using the following equation:

$$C_V = e^{[7.037+0.18255(\ln(W)+0.02297(\ln(W)^2)]}$$

$$\boldsymbol{C_V = 165794.26}$$

Cost of Platforms and Ladders

The f.o.b cost of the platforms and ladders was calculated using the following equation:

$$C_{PL} = 361.8(D_i)^{0.7960}(L)^{0.70684}$$

$$\boldsymbol{C_{PL} = 28517.01}$$

Cost of Trays

The f.o.b cost of the empty vessel was calculated using the following equation:
$C_T = N_tF_{nt}F_{tt}F_{tm}C_{bt}$

N_t = number of trays = 43
$F_{nt} > 1$ therefore = 1
F_{tt} = 1.0 since sieve trays are used
F_{tm} = 1.413 since stainless steel is used

$$C_{bt} = 468e^{(0.1739*D_i)}$$

C_{bt} = base cost = 922.1

$C_T = (43)(1)(1)(1)(1)(922.1)$

$\boldsymbol{C_T = 55935.83}$

Cost of Vertical Tower

$C_P = F_M C_V + C_{PL} + C_T$

$C_P = (1)(165794.26) + (28517.01) + (39650.3)$

C_P = \$250,244

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (4.16)(250244)$
$C_{BM\text{-}2006}$ = \$1,041,027

2006 CE Index = 500
2011 CE Index = 560.4

$C_{BM\text{-}2011}$ = \$1,041,027 x 560.4/500
$C_{BM\text{-}2011}$ = \$1,166,781

Cost of Reflux Accumulator D-101b

The total free on board (f.o.b) purchase cost for the unit is calculated using the following relationship:

$C_P = F_M C_V + C_{PL}$

Where
F_M = the material cost factor
C_V = the cost of an empty horizontal vessel
C_{PL}= the cost for the platforms and ladders

Cost of Horizontal Vessel

ASPEN Report:
Distillate Rate = 248.65 cuft/hr
Reflux Ration = 0.2

$$Volumetric\ Flow\ Rate = 248.65 + 0.2 * 248.65 = 297.6 \frac{cuft}{hr}$$

For a residence time of $\tau = 0.08\ hrs$,
$Volume = \tau * 297.6 = 47.6\ cuft$

$$D = \frac{4 * V * \tau}{\pi}^{0.33}$$

$$D = \frac{4 * 47.6 * (.08)}{\pi}^{0.33} = 1.61\ feet$$

$$L = 2(D) = 3.21\ feet$$

Using the equations for vessel thickness presented before, the thickness is found to be 0.375 inches. The weight is then found to equal 355 lbs.

The f.o.b cost of the empty vessel was calculated using the following equation:

$$C_V = e^{\left(8.717 - 0.2330 * \ln(W) + 0.04333 * \ln(\mathrm{W})^2\right)}$$

$$\boldsymbol{C_V = 8,788.46}$$

Cost of Platforms and Ladders

The f.o.b cost of the platforms and ladders was calculated using the following equation:

$C_{PL} = 2005(D_i)^{0.79600.20294}$

$\boldsymbol{C_{PL} = 2208.45}$

Cost of Reflux Accumulator

$C_P = F_M C_V + C_{PL}$

$C_P = (1)(8788.46) + 2208.45$

C_p = $10,996.91

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (3.05)(10996.91)$
$C_{BM\text{-}2006} = \$33,540$

2006 CE Index = 500
2011 CE Index = 560.4

$C_{BM\text{-}2011} = \$33,540 \times 560.4/500$
$C_{BM\text{-}2011}$ = $37,593

Cost of Centrifugal Pump D-101c

The cost of a centrifugal pump is given by the equation:

$C_P=(F_t)(F_m)(C_b)$

Where
F_t = pump-type factor
F_m = material factor
C_b = base cost

The size factor for the centrifugal pump is calculated using the following equation:

$$S = QH^{0.5}$$

$$Q = 31 * 0.2 + 31 = 37.2 \text{ gpm}$$

$$H = \frac{P}{\rho} = \frac{\rho g h}{\rho} = 2085.5 \text{ ft}$$

ρ = 56.25 lb/cuft
g = 32.0 ft/s^2
g_c = 3.28 ft/s^2
h = 100 ft

$$S = (37.2)(2085.2)^{0.5} = 1698.7$$

$$C_B = \exp[9.7171 - 0.6019[\ln(S)] + 0.519[\ln(S)]^2]$$

$$C_B = 3332.25$$

$C_P = (F_t)(F_m)(C_b)$
$C_P = (1.35)(1)(3332.25) = \$4498.54$

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (3.3)(4498.54)$
$C_{BM\text{-}2006} = \$12,162.7$

Electric Motor:

The size parameter of the motor, P_c, can be found using the following equation:

$$P_c = \frac{QH\rho}{(33000\eta_p\eta_m)}$$

Where:

Q = flow rate through the pump (gpm)
H = Pump Head
ρ = density (lb/gal)
η_p = fractional efficiency
η_m = fractional efficiency of the electric motor

ASPEN Report:

Q = 37.2 gpm
H = 2085.5 ft
ρ = 7.52 lb/gal

$$\eta_P = -0.316 + 0.24015\ln(Q) - 0.01199\ln(Q)^2$$
$$\eta_P = 0.396$$

$$\eta_m = 0.8 + 0.0319\ln(P_b) - 0.00182\ln(P_b)^2$$
$$\eta_m = 0.895$$

Where:

$$P_b = \frac{QH\rho}{(33000\eta_p)} = 44.64$$

Plugging into the equation for P_c above, it was found to equal 373.2 HP.

The cost of the motor was then calculated using the following equation:

$$C_b = \exp[5.8259 + 0.1314\ln(P_C) + 0.053255\ln\ln(P_C)^2 + 0.02865\ln(P_C)^3$$
$$C_b = \$22,852$$

$C_P=(F_t)(C_b)$
$C_P = (1)(22,852) = \$22,852$

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (1.0)(22852)$
$C_{BM\text{-}2006} = \$22,852$

Adding the cost of the electric motor,

$C_{BM\text{-}2006} = 12162.7 + 22852.3$
$C_{BM\text{-}2006} = \$35,015$

2006 CE Index = 500
2011 CE Index = 560.4

$C_{BM\text{-}2011} = \$35,015 \times 560.4/500$
$C_{BM\text{-}2011} = \$37,003$

Cost of the Fired Heater H-101

The cost of a fired heater is given by the equation:

$C_P=(F_t)(F_m)(C_b)$

Where

$$C_b = \exp[0.32325 + 0.766 * \ln(Q)]$$

ASPEN Report:
Q = 106,893 Btu/hr

C_p = (1.7)(0.986)(106893) = 179,162

$C_{BM\text{-}2006}$ = $(F_{BM})(C_p)$
$C_{BM\text{-}2006}$ = (1.86)(117162)
$C_{BM\text{-}2006}$ = $333,241

Cost of Turbine TR-100

The cost of a turbine is given by the equation:

$$C_p = 3620S^{0.57}$$

ASPEN Report:
S = 27 HP

$$C_p = 3620(27)^{0.57} = \$23{,}391$$

$C_{BM\text{-}2006}$ = $(F_{BM})(C_p)$
$C_{BM\text{-}2006}$ = (2.15)(23391)
$C_{BM\text{-}2006}$ = $50,936

Cost of Storage Tank T-101

The cost of the storage tank T-101 is given by the equation:

$$C_P = 475V^{0.51}$$

ASPEN Report
Q = 1181.02 gal/hr

For two weeks of storage, the required volume is:

$$1811.02\frac{gal}{hr} \times \frac{24hr}{day} \times 14days = 608503\ gal$$

$$C_P = 475(608503)^{0.51}$$

$$C_P = \$423,319$$

$C_{BM\text{-}2006} = (F_{BM})(C_p)$
$C_{BM\text{-}2006} = (1.0)(423319)$
$C_{BM\text{-}2006}$ = $423,319

Electricity Requirement of EDI Machine

$$\xi = \frac{zFQ_f(C^d_{inlet} - C^d_{outlet})}{NI}$$

Efficiency is about 0.8 for USP applications. (EETCorp, 2011)

Charge magnitude (z) = 1 for NaCl

Faraday's Constant = 96485 Amp-s/mol

Diluent volumetric flow rate (Q_f) = 1.63 L/s

Salt inlet concentration = 0.82 mol/L for each sodium and chloride ions. (assuming sulfate and nitrates are negligible).

Salt outlet concentration is 10ppm = 2.05 x 10^-5 for both ions\

N = 800 (Datta, 2002)

So I = 400 Amps

Assume 0.5 V/cell (Ibid.)

With 400 V (.5 V/cell * 800 cells), power requirements are 160 kW. Actual power draw requirements should be 200 kW to account for scale buildup on the membranes. (Ibid.)

Calculation for Mass of Catalyst in Reactor

	lb/hr	MW	lbmol/hr	gram-mol/hr	gram-mol/s
Glycerol In	20075.16	92.09	217.995	98902.15155	27.47281988
H2 In (7:1 Mole ratio w/ Glycerol)	3051.93	2	1525.965	692315.0609	192.3097391
H2O In	3764.092	18	209.1162	94873.94934	26.35387482
Glycerol Out	3713.905	92.09	40.32908	18296.89804	5.082471677
PG Out	12626.26	76.09	165.9385	75284.65095	20.91240304
H2 Consumed by Rxn	355.3319	2	177.6659	80605.25351	22.3903482
H2O Produced by Rxn	24480.48	18	1360.026	617030.4099	171.3973361
H2 Out	2696.598	2	1348.299	611709.8073	169.9193909
H2O Out	28244.57	18	1569.143	711904.3592	197.7512109
Acetol Out	157.9415	74.08	2.13204	967.2852276	0.268690341
Ethylene Glycol Out	297.7604	62.07	4.797171	2176.428511	0.604563475
Other Out			4.797171	2176.428511	0.604563475

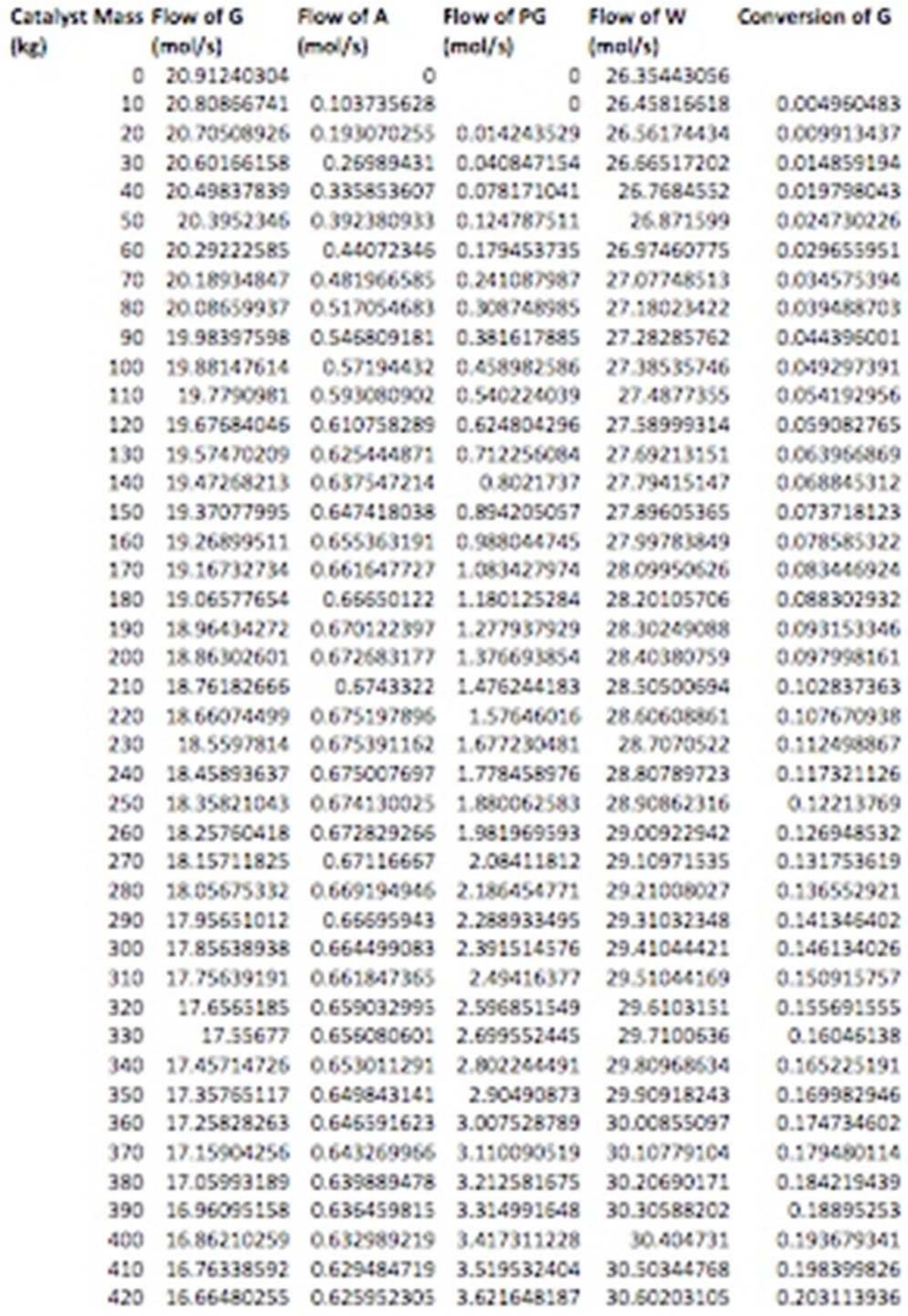
After scaling up to find 100% Conversion

	lb/hr	MW	lbmol/hr	gram-mol/hr	gram-mol/s
Glycerol In	15281.28	92.09	165.9385	75284.65095	20.91240304
H2 In (7:1 Mole ratio w/ Glycerol)	2323.139	2	1161.57	526992.5567	146.3868213
H2O In	2865.24	18	159.18	72218.36986	20.06065829
Glycerol Out	2827.037	92.09	30.69863	13927.66043	3.868794563
PG Out	12626.26	76.09	165.9385	75284.65095	20.91240304
H2 Consumed by Rxn	270.4798	2	135.2399	61356.99053	17.04360848
H2O Produced by Rxn	17921.36	18	995.6312	451707.9057	125.4744183
H2 Out	2052.66	2	1026.33	465635.5661	129.3432128
H2O Out	20786.6	18	1154.811	523926.2756	145.5350765
Acetol Out	157.9415	74.08	2.13204	967.2852276	0.268690341
Ethylene Glycol Out	297.7604	62.07	4.797171	2176.428511	0.604563475
Other Out			4.797171	2176.428511	0.604563475

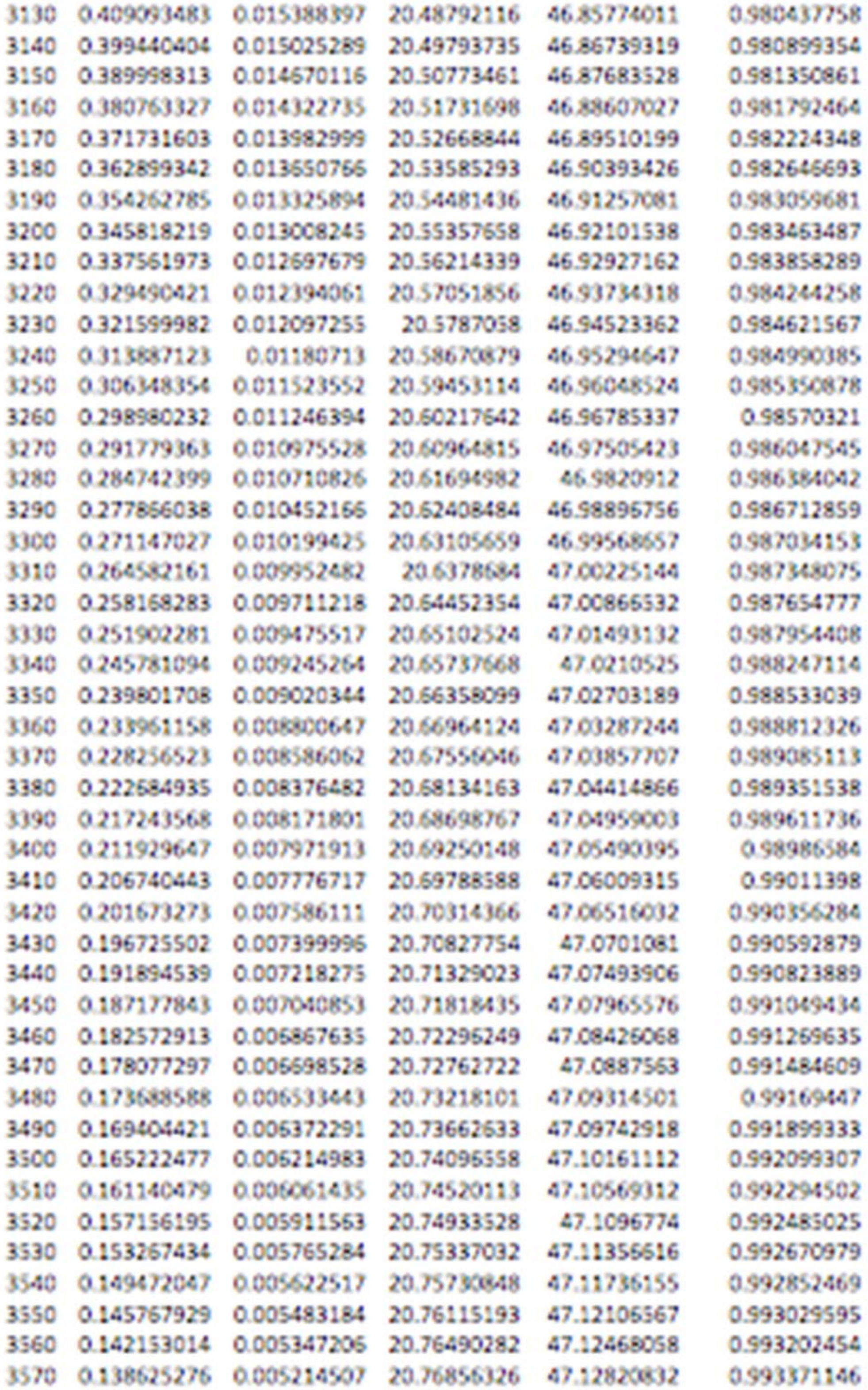
Using Conversion and Selectivity data from ZHOU et al

		Selectivity %			
Catalyst (3.0g Loading)	Glycerol C(	PG	Acetol	EG	Other*
40% CuO; 40% ZnO; 20% Al2O3	81.5	93.4	1.2	2.7	2.7

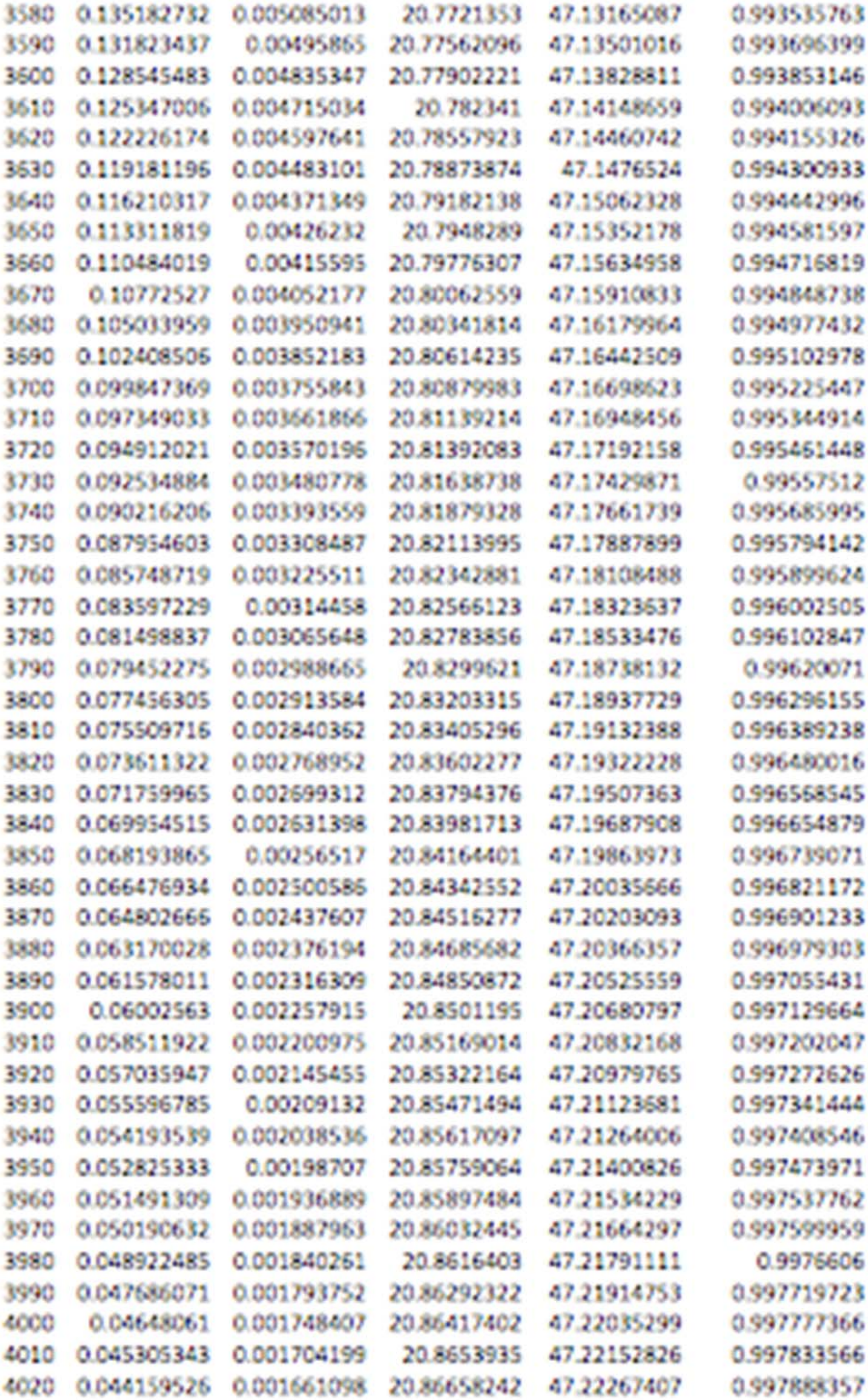
LHSV = 4.6 h-1



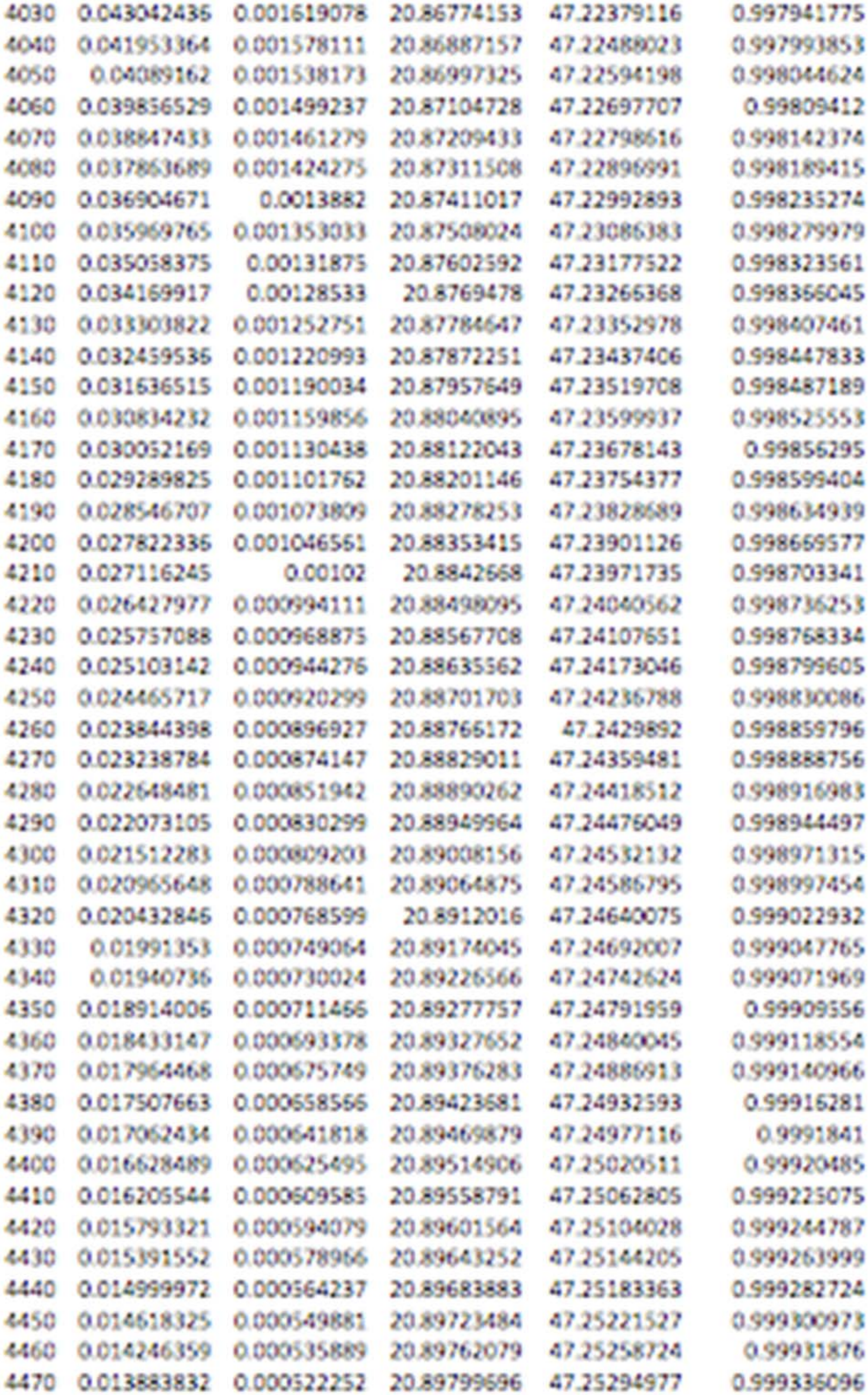
Catalyst Mass (kg)	Flow of G (mol/s)	Flow of A (mol/s)	Flow of PG (mol/s)	Flow of W (mol/s)	Conversion of G
0	20.91240304	0	0	26.35443056	
10	20.80866741	0.103735628	0	26.45816618	0.004960483
20	20.70508926	0.193070255	0.014243529	26.56174434	0.009913437
30	20.60166158	0.26989431	0.040847154	26.66517202	0.014859194
40	20.49837839	0.335853607	0.078171041	26.7684552	0.019798043
50	20.3952346	0.392380933	0.124787511	26.871599	0.024730226
60	20.29222585	0.44072346	0.179453735	26.97460775	0.029655951
70	20.18934847	0.481966585	0.241087987	27.07748513	0.034575394
80	20.08659937	0.517054683	0.308748985	27.18023422	0.039488703
90	19.98397598	0.546809181	0.381617885	27.28285762	0.044396001
100	19.88147614	0.57194432	0.458982586	27.38535746	0.049297391
110	19.7790981	0.593080902	0.540224039	27.4877355	0.054192956
120	19.67684046	0.610758289	0.624804296	27.58999314	0.059082765
130	19.57470209	0.625444871	0.712256084	27.69213151	0.063966869
140	19.47268213	0.637547214	0.8021737	27.79415147	0.068845312
150	19.37077995	0.647418038	0.894205057	27.89605365	0.073718123
160	19.26899511	0.655363191	0.988044745	27.99783849	0.078585322
170	19.16732734	0.661647727	1.083427974	28.09950626	0.083446924
180	19.06577654	0.66650122	1.180125284	28.20105706	0.088302932
190	18.96434272	0.670122397	1.277937929	28.30249088	0.093153346
200	18.86302601	0.672683177	1.376693854	28.40380759	0.097998161
210	18.76182666	0.6743322	1.476244183	28.50500694	0.102837363
220	18.66074499	0.675197896	1.57646016	28.60608861	0.107670938
230	18.5597814	0.675391162	1.677230481	28.7070522	0.112498867
240	18.45893637	0.675007697	1.778458976	28.80789723	0.117321126
250	18.35821043	0.674130025	1.880062583	28.90862316	0.12213769
260	18.25760418	0.672829266	1.981969593	29.00922942	0.126948532
270	18.15711825	0.67116667	2.08411812	29.10971535	0.131753619
280	18.05675332	0.669194946	2.186454771	29.21008027	0.136552921
290	17.95651012	0.66695943	2.288933495	29.31032348	0.141346402
300	17.85638938	0.664499083	2.391514576	29.41044421	0.146134026
310	17.75639191	0.661847365	2.49416377	29.51044169	0.150915757
320	17.6565185	0.659032995	2.596851549	29.6103151	0.155691555
330	17.55677	0.656080601	2.699552445	29.7100636	0.16046138
340	17.45714726	0.653011291	2.802244491	29.80968634	0.165225191
350	17.35765117	0.649843141	2.90490873	29.90918243	0.169982946
360	17.25828263	0.646591623	3.007528789	30.00855097	0.174734602
370	17.15904256	0.643269966	3.110090519	30.10779104	0.179480114
380	17.05993189	0.639889478	3.212581675	30.20690171	0.184219439
390	16.96095158	0.636459815	3.314991648	30.30588202	0.18895253
400	16.86210259	0.632989219	3.417311228	30.404731	0.193679341
410	16.76338592	0.629484719	3.519532404	30.50344768	0.198399826
420	16.66480255	0.625952305	3.621648187	30.60203105	0.203113936



3130	0.409093483	0.015388397	20.48792116	46.85774011	0.980437758
3140	0.399440404	0.015025289	20.49793735	46.86739319	0.980899354
3150	0.389998313	0.014670116	20.50773461	46.87683528	0.981350861
3160	0.380763327	0.014322735	20.51731698	46.88607027	0.981792464
3170	0.371731603	0.013982999	20.52668844	46.89510199	0.982224348
3180	0.362899342	0.013650766	20.53585293	46.90393426	0.982646693
3190	0.354262785	0.013325894	20.54481436	46.91257081	0.983059681
3200	0.345818219	0.013008245	20.55357658	46.92101538	0.983463487
3210	0.337561973	0.012697679	20.56214339	46.92927162	0.983858289
3220	0.329490421	0.012394061	20.57051856	46.93734318	0.984244258
3230	0.321599982	0.012097255	20.5787058	46.94523362	0.984621567
3240	0.313887123	0.01180713	20.58670879	46.95294647	0.984990385
3250	0.306348354	0.011523552	20.59453114	46.96048524	0.985350878
3260	0.298980232	0.011246394	20.60217642	46.96785337	0.98570321
3270	0.291779363	0.010975528	20.60964815	46.97505423	0.986047545
3280	0.284742399	0.010710826	20.61694982	46.9820912	0.986384042
3290	0.277866038	0.010452166	20.62408484	46.98896756	0.986712859
3300	0.271147027	0.010199425	20.63105659	46.99568657	0.987034153
3310	0.264582161	0.009952482	20.6378684	47.00225144	0.987348075
3320	0.258168283	0.009711218	20.64452354	47.00866532	0.987654777
3330	0.251902281	0.009475517	20.65102524	47.01493132	0.987954408
3340	0.245781094	0.009245264	20.65737668	47.0210525	0.988247114
3350	0.239801708	0.009020344	20.66358099	47.02703189	0.988533039
3360	0.233961158	0.008800647	20.66964124	47.03287244	0.988812326
3370	0.228256523	0.008586062	20.67556046	47.03857707	0.989085113
3380	0.222684935	0.008376482	20.68134163	47.04414866	0.989351538
3390	0.217243568	0.008171801	20.68698767	47.04959003	0.989611736
3400	0.211929647	0.007971913	20.69250148	47.05490395	0.98986584
3410	0.206740443	0.007776717	20.69788588	47.06009315	0.99011398
3420	0.201673273	0.007586111	20.70314366	47.06516032	0.990356284
3430	0.196725502	0.007399996	20.70827754	47.0701081	0.990592879
3440	0.191894539	0.007218275	20.71329023	47.07493906	0.990823889
3450	0.187177843	0.007040853	20.71818435	47.07965576	0.991049434
3460	0.182572913	0.006867635	20.72296249	47.08426068	0.991269635
3470	0.178077297	0.006698528	20.72762722	47.0887563	0.991484609
3480	0.173688588	0.006533443	20.73218101	47.09314501	0.99169447
3490	0.169404421	0.006372291	20.73662633	47.09742918	0.991899333
3500	0.165222477	0.006214983	20.74096558	47.10161112	0.992099307
3510	0.161140479	0.006061435	20.74520113	47.10569312	0.992294502
3520	0.157156195	0.005911563	20.74933528	47.1096774	0.992485025
3530	0.153267434	0.005765284	20.75337032	47.11356616	0.992670979
3540	0.149472047	0.005622517	20.75730848	47.11736155	0.992852469
3550	0.145767929	0.005483184	20.76115193	47.12106567	0.993029595
3560	0.142153014	0.005347206	20.76490282	47.12468058	0.993202454
3570	0.138625276	0.005214507	20.76856326	47.12820832	0.993371146



3580	0.135182732	0.005085013	20.7721353	47.13165087	0.993535763
3590	0.131823437	0.00495865	20.77562096	47.13501016	0.993696399
3600	0.128545483	0.004835347	20.77902221	47.13828811	0.993853146
3610	0.125347006	0.004715034	20.782341	47.14148659	0.994006093
3620	0.122226174	0.004597641	20.78557923	47.14460742	0.994155326
3630	0.119181196	0.004483101	20.78873874	47.1476524	0.994300933
3640	0.116210317	0.004371349	20.79182138	47.15062328	0.994442996
3650	0.113311819	0.00426232	20.7948289	47.15352178	0.994581597
3660	0.110484019	0.00415595	20.79776307	47.15634958	0.994716819
3670	0.10772527	0.004052177	20.80062559	47.15910833	0.994848738
3680	0.105033959	0.003950941	20.80341814	47.16179964	0.994977432
3690	0.102408506	0.003852183	20.80614235	47.16442509	0.995102978
3700	0.099847369	0.003755843	20.80879983	47.16698623	0.995225447
3710	0.097349033	0.003661866	20.81139214	47.16948456	0.995344914
3720	0.094912021	0.003570196	20.81392083	47.17192158	0.995461448
3730	0.092534884	0.003480778	20.81638738	47.17429871	0.99557512
3740	0.090216206	0.003393559	20.81879328	47.17661739	0.995685995
3750	0.087954603	0.003308487	20.82113995	47.17887899	0.995794142
3760	0.085748719	0.003225511	20.82342881	47.18108488	0.995899624
3770	0.083597229	0.00314458	20.82566123	47.18323637	0.996002505
3780	0.081498837	0.003065648	20.82783856	47.18533476	0.996102847
3790	0.079452275	0.002988665	20.8299621	47.18738132	0.99620071
3800	0.077456305	0.002913584	20.83203315	47.18937729	0.996296155
3810	0.075509716	0.002840362	20.83405296	47.19132388	0.996389238
3820	0.073611322	0.002768952	20.83602277	47.19322228	0.996480016
3830	0.071759965	0.002699312	20.83794376	47.19507363	0.996568545
3840	0.069954515	0.002631398	20.83981713	47.19687908	0.996654879
3850	0.068193865	0.00256517	20.84164401	47.19863973	0.996739071
3860	0.066476934	0.002500586	20.84342552	47.20035666	0.996821172
3870	0.064802666	0.002437607	20.84516277	47.20203093	0.996901233
3880	0.063170028	0.002376194	20.84685682	47.20366357	0.996979303
3890	0.061578011	0.002316309	20.84850872	47.20525559	0.997055431
3900	0.06002563	0.002257915	20.8501195	47.20680797	0.997129664
3910	0.058511922	0.002200975	20.85169014	47.20832168	0.997202047
3920	0.057035947	0.002145455	20.85322164	47.20979765	0.997272626
3930	0.055596785	0.00209132	20.85471494	47.21123681	0.997341444
3940	0.054193539	0.002038536	20.85617097	47.21264006	0.997408546
3950	0.052825333	0.00198707	20.85759064	47.21400826	0.997473971
3960	0.051491309	0.001936889	20.85897484	47.21534229	0.997537762
3970	0.050190632	0.001887963	20.86032445	47.21664297	0.997599959
3980	0.048922485	0.001840261	20.8616403	47.21791111	0.9976606
3990	0.047686071	0.001793752	20.86292322	47.21914753	0.997719723
4000	0.04648061	0.001748407	20.86417402	47.22035299	0.997777366
4010	0.045305343	0.001704199	20.8653935	47.22152826	0.997833566
4020	0.044159526	0.001661098	20.86658242	47.22267407	0.997888357



4030	0.043042436	0.001619078	20.86774153	47.22379116	0.997941775
4040	0.041953364	0.001578111	20.86887157	47.22488023	0.997993853
4050	0.04089162	0.001538173	20.86997325	47.22594198	0.998044624
4060	0.039856529	0.001499237	20.87104728	47.22697707	0.99809412
4070	0.038847433	0.001461279	20.87209433	47.22798616	0.998142374
4080	0.037863689	0.001424275	20.87311508	47.22896991	0.998189415
4090	0.036904671	0.0013882	20.87411017	47.22992893	0.998235274
4100	0.035969765	0.001353033	20.87508024	47.23086383	0.998279979
4110	0.035058375	0.00131875	20.87602592	47.23177522	0.998323561
4120	0.034169917	0.00128533	20.8769478	47.23266368	0.998366045
4130	0.033303822	0.001252751	20.87784647	47.23352978	0.998407461
4140	0.032459536	0.001220993	20.87872251	47.23437406	0.998447833
4150	0.031636515	0.001190034	20.87957649	47.23519708	0.998487189
4160	0.030834232	0.001159856	20.88040895	47.23599937	0.998525553
4170	0.030052169	0.001130438	20.88122043	47.23678143	0.99856295
4180	0.029289825	0.001101762	20.88201146	47.23754377	0.998599404
4190	0.028546707	0.001073809	20.88278253	47.23828689	0.998634939
4200	0.027822336	0.001046561	20.88353415	47.23901126	0.998669577
4210	0.027116245	0.00102	20.8842668	47.23971735	0.998703341
4220	0.026427977	0.000994111	20.88498095	47.24040562	0.998736253
4230	0.025757088	0.000968875	20.88567708	47.24107651	0.998768334
4240	0.025103142	0.000944276	20.88635562	47.24173046	0.998799605
4250	0.024465717	0.000920299	20.88701703	47.24236788	0.998830086
4260	0.023844398	0.000896927	20.88766172	47.2429892	0.998859796
4270	0.023238784	0.000874147	20.88829011	47.24359481	0.998888756
4280	0.022648481	0.000851942	20.88890262	47.24418512	0.998916983
4290	0.022073105	0.000830299	20.88949964	47.24476049	0.998944497
4300	0.021512283	0.000809203	20.89008156	47.24532132	0.998971315
4310	0.020965648	0.000788641	20.89064875	47.24586795	0.998997454
4320	0.020432846	0.000768599	20.8912016	47.24640075	0.999022932
4330	0.01991353	0.000749064	20.89174045	47.24692007	0.999047765
4340	0.01940736	0.000730024	20.89226566	47.24742624	0.999071969
4350	0.018914006	0.000711466	20.89277757	47.24791959	0.99909556
4360	0.018433147	0.000693378	20.89327652	47.24840045	0.999118554
4370	0.017964468	0.000675749	20.89376283	47.24886913	0.999140966
4380	0.017507663	0.000658566	20.89423681	47.24932593	0.99916281
4390	0.017062434	0.000641818	20.89469879	47.24977116	0.9991841
4400	0.016628489	0.000625495	20.89514906	47.25020511	0.99920485
4410	0.016205544	0.000609585	20.89558791	47.25062805	0.999225075
4420	0.015793321	0.000594079	20.89601564	47.25104028	0.999244787
4430	0.015391552	0.000578966	20.89643252	47.25144205	0.999263999
4440	0.014999972	0.000564237	20.89683883	47.25183363	0.999282724
4450	0.014618325	0.000549881	20.89723484	47.25221527	0.999300973
4460	0.014246359	0.000535889	20.89762079	47.25258724	0.99931876
4470	0.013883832	0.000522252	20.89799696	47.25294977	0.999336096

Section 25

PROBLEM STATEMENT

Glycerol to Renewable Propylene Glycol
(recommended by Bruce M. Vrana, DuPont)

Propylene glycol (PG), is used to make unsaturated polyester resins, cosmetics, aircraft deicer, environmentally-friendly (and pet-friendly) automotive antifreezes, etc. PG is conventionally made from propylene. Propylene is itself a byproduct of ethylene manufacture. Since demand for polypropylene is growing faster than ethylene, propylene is in short supply and prices are rising. Demand and prices for PG are expected to increase. And there will likely be a price premium and plenty of demand for PG made from renewable resources.

Glycerol is a byproduct of biodiesel manufacture, with relatively few industrial uses. As the production of biodiesel increases, particularly in Europe due to government regulations but also in the U.S. due to public demand for renewable fuels, the price of glycerol is expected to continue to decrease.

BASF has patented a catalyst to convert glycerol to propylene glycol in very high yield – up to 100% glycerol conversion and 98.5% selectivity. The patent does not disclose quantitatively what the byproducts are, but you can assume the 1.5% of glycerol that does not form propylene glycol goes to equal amounts of n-propanol and isopropanol.

$$CH_2OH\text{-}CH_2OH\text{-}CH_2OH + H_2 \rightarrow \quad CH_2OH\text{-}CH_2OH\text{-}CH_3 + H_2O$$

Crude glycerol from biodiesel manufacture contains 15% water, 4% NaCl, 1% methanol. It also contains trace amounts of organic sulfur and chlorine compounds, which must be removed, as described in the patent.

Design a process to make 100MM lb/yr of propylene glycol from crude glycerol. Your plant is on the U.S. Gulf Coast. Crude glycerol delivered to you costs \$0.22/lb (for the crude stream at 80% concentration). Hydrogen is available on your plant site for \$0.50/lb.
Renewable propylene glycol can be sold for \$1.00/lb. Byproduct renewable n-propanol and isopropanol can be sold for \$0.80/lb. All products will need to meet normal specs for that product. All prices are forecasts by your marketing organization for long-term average prices, expressed in 2011 dollars on the Gulf Coast.

The plant design should be as environmentally friendly as possible. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that you will be there for the plant start-up and will have to live with whatever design decisions you have made.

Reference
U.S. Patent 7.790,937, September 7, 2010, assigned to BASF

Section 25

PATENT AND ASPEN SIMULATION

US007790937B2

(12) **United States Patent**
Henkelmann et al.

(10) **Patent No.: US 7,790,937 B2**
(45) **Date of Patent: Sep. 7, 2010**

(54) **PROCESS FOR THE PREPARATION OF 1,2-PROPANEDIOL**

(75) Inventors: **Jochem Henkelmann**, Mannheim (DE); **Michael Becker**, Offenburg (DE); **Jochen Buerkle**, Mannheim (DE); **Peter Wahl**, Heidelberg (DE); **Gerhard Theis**, Maxdorf (DE); **Stephen Maurer**, Neustadt-Gimmeldingen (DE)

(73) Assignee: **BASF SE**, Ludwigshafen (DE)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/281,406**

(22) PCT Filed: **Mar. 2, 2007**

(86) PCT No.: **PCT/EP2007/051983**

§ 371 (c)(1),
(2), (4) Date: **Sep. 2, 2008**

(87) PCT Pub. No.: **WO2007/099161**

PCT Pub. Date: **Sep. 7, 2007**

(65) **Prior Publication Data**

US 2009/0216050 A1 Aug. 27, 2009

Related U.S. Application Data

(60) Provisional application No. 60/778,371, filed on Mar. 3, 2006.

(30) **Foreign Application Priority Data**

Mar. 3, 2006 (EP) 06004414

(51) **Int. Cl.**
C07C 29/132 (2006.01)

(52) **U.S. Cl.** **568/861**

(58) **Field of Classification Search** 568/861
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,360,844	A	10/1944	Bradshaw et al.
4,297,247	A	10/1981	Krabetz et al.
5,354,878	A	10/1994	Connemann et al.
5,403,962	A	4/1995	Schneider et al.
5,536,694	A	7/1996	Schuetz et al.
5,616,817	A	4/1997	Schuster et al.
5,677,261	A	10/1997	Tenten et al.
6,121,188	A	9/2000	Breitscheidel et al.
2005/0204612	A1	9/2005	Connemann et al.

FOREIGN PATENT DOCUMENTS

CA	2208720	C	7/1996
CA	2570915	A1	1/2006
DE	524101		5/1931
DE	541362		1/1932
DE	2628987	A1	1/1978
DE	2909671	A1	10/1980
DE	4021230	A1	1/1991
DE	4028295	A1	3/1992
DE	4302464	A1	8/1994
DE	4335360	A1	4/1995
DE	4345265	A1	9/1995
DE	4446907	A1	7/1996
DE	10243700	A1	4/2004
EP	0434062	A1	6/1991
EP	0523015	A2	1/1993
EP	0552463	A1	7/1993
EP	0714700	A2	6/1996
EP	0842699	A2	5/1998
GB	1579159		11/1980
WO	WO-2005/095536	A2	10/2005
WO	WO-2006/005505	A1	1/2006

OTHER PUBLICATIONS

Dasari, M.A., et al., “Low-pressure hydrogenolysis of glycerol to propylene glycol,” Applied Catalysis A: General, 2005, vol. 281, pp. 225-231.

Connor, R., et al., “Hydrogenolysis of oxygenated organic compounds,” J. Am. Chem. Soc., 1932, vol. 54, pp. 4678-4690.

Chaminand, J., et al., “Glycerol hydrogenolysis on heterogeneous catalysts,” Green Chem., 2004, vol. 6, pp. 359-361.

Montassier, C., et al., “Transformation de polyols par catalyse hétérogène en phase liquide sur les métauxe,” Bulletin de la Societe Chimique de France, 1989, No. 2, pp. 148-155.

Primary Examiner—Sikarl A Witherspoon
(74) *Attorney, Agent, or Firm*—Connolly Bove Lodge & Hutz LLP

(57) **ABSTRACT**

The present invention relates to a process for the preparation of 1,2-propanediol, in which a glycerol-containing stream, in particular a stream obtained on an industrial scale in the production of biodiesel, is subjected to a hydrogenation.

16 Claims, No Drawings

PROCESS FOR THE PREPARATION OF 1,2-PROPANEDIOL

RELATED APPLICATIONS

This application is a national stage application (under 35 U.S.C. §371) of PCT/EP2007/051983, filed Mar. 2, 2007, which claims benefit of European Application No. 06004414.6, filed Mar. 3, 2006, and U.S. Provisional Application Ser. No. 60/778,371, filed Mar. 3, 2006.

The present invention relates to a process for the preparation of 1,2-propanediol, in which a glycerol-containing stream, in particular a stream obtained on an industrial scale in the preparation of biodiesel, is subjected to a hydrogenation.

Diminishing mineral oil reserves and increasing fuel prices are leading to a growing interest in the replacement of fuels produced on the basis of mineral oil by economical and environmentally friendly alternatives. Processes for the production of fuels from biogenic fat- or oil-containing starting mixtures and used oils obtained, for example, in restaurants and animal fats have long been known, rapeseed oil currently predominantly being used in Central Europe as a starting material in the production of biogenic fuels. Biogenic oils and fats themselves are less suitable as engine fuel since they have to be purified beforehand by generally complicated methods. These include the removal of lecithins, carbohydrates and proteins, the removal of the so-called oil sludge and the removal of the free fatty acids present in relatively large amounts, for example, in rapeseed oil. Vegetable oils treated in this manner nevertheless differ from the technical properties of conventional diesel fuels in several respects. Thus, they have as a rule a higher density than diesel fuel, the cetane number of rapeseed oil is lower than that of diesel fuel and the viscosity is several times higher compared with that of diesel fuel. This leads to an unacceptable deterioration in the fuel properties, such as to nonuniform running behavior of the engine, to substantially increased noise emission and, owing to the higher viscosity, to poorer atomization and combustion in the combustion chamber. In conventional engines, the use of pure vegetable oils therefore leads to coking, associated with increased particle emission. It is known that these problems can be solved by converting the triglycerides (fatty acid esters of glycerol) present in the biogenic oil and fat starting mixtures into monoalkyl esters of fatty acids, in particular methyl or ethyl esters. These esters, also referred to as "biodiesel", can as a rule be used in diesel engines without major retrofits, it often even being possible to reduce the emission of uncombusted hydrocarbons and soot particles in comparison with normal diesel fuel. The transesterification of the triglycerides for biodiesel production also results in glycerol (≈10%), which, for reasons of both cost-efficiency and sustainability, should be utilized. There is therefore a need for effective and economical processes which also permit utilization of the glycerol obtained in biodiesel production. These processes should in particular also be suitable for the utilization of further glycerol streams available on an industrial scale.

U.S. Pat. No. 2,360,844 describes a process for the preparation of soaps, in which a crude glyceride is transesterified with C_1-C_4-alkanols and the glycerol liberated is separated from the monoalkyl esters. The utilization of the glycerol obtained is not described.

U.S. Pat. No. 5,354,878 describes a process for the preparation of lower alkyl esters of higher fatty acids having a low residual glycerol content by transesterification of fatty acid triglycerides and the use of these esters as diesel fuel.

DE 102 43 700 A1 describes a pressureless process for the preparation of alkyl esters of higher fatty acids, in particular biodiesel, from fatty acid triglyceride starting mixtures comprising free fatty acids by a combination of acidic esterification and basic transesterification. The glycerol obtained in the transesterification is partly used as an entraining agent in the esterification of the free fatty acids.

It is known that alcohols having a relatively high hydricity can be converted into alcohols having a lower hydricity by catalytic hydrogenation. Thus, German Patent 524 101 describes such a process in which, inter alia, glycerol is subjected to a gas-phase hydrogenation in the presence of a hydrogenation catalyst with hydrogen in considerable excess. Specifically, copper or cobalt catalysts activated with Cr are used for the hydrogenation of glycerol.

German patent 541 362 describes a process for the hydrogenation of polyoxy compounds such as, for example, glycerol, in the presence of catalysts at elevated temperatures above 150° C. and under superatmospheric pressure. Specifically, the hydrogenation of glycerol using a nickel catalyst at a temperature from 200 to 240° C. and a hydrogen pressure of 100 atm is described.

R. Connor and H. Adkins, in J. Am. Chem. Soc. 54, 1932, pages 4678-4690, describe the hydrogenolysis of oxygen-containing organic compounds, inter alia of 98% strength glycerol, to 1,2-propanediol in the presence of a copper-chromium-barium oxide catalyst.

C. Montassier et al., in Bulletin de la Société Chimique de France 1989, No. 2, pages 148-155, describe investigations of the reaction mechanism of the catalytic hydrogenation of polyols in the presence of various metallic catalysts, such as, for example, of glycerol in the presence of Raney copper.

J. Chaminand et al., in Green Chem. 6, 2004, pages 359-361, describe the hydrogenation of aqueous glycerol solutions at 180° C. and 80 bar hydrogen pressure in the presence of supported metal catalysts based on Cu, Pd and Rh.

DE 43 02 464 A1 describes a process for the preparation of 1,2-propanediol by hydrogenation of glycerol in the presence of a heterogeneous catalyst at pressures of from 20 to 300 bar, in particular at from 100 to 250 bar, and temperatures of from 150° C. to 320° C., glycerol in vapor or liquid form being passed over a catalyst bed. Inter alia, copper chromite, copper zinc oxide, copper aluminum oxide and copper silicon dioxide are mentioned as catalysts. The use of glycerol-containing streams from biodiesel production and measures for the pretreatment of such streams before their use for the hydrogenation are not described in this document.

EP 0 523 015 describes a process for the catalytic hydrogenation of glycerol for the preparation of 1,2-propanediol and 1,2-ethanediol in the presence of a Cu/Zn catalyst at a temperature of at least 200° C. In this process, the glycerol is used as an aqueous solution having a glycerol content of from 20 to 60% by weight, the maximum glycerol content in the working examples being 40% by weight.

WO 2005/095536 describes a low-pressure process for converting glycerol into propylene glycol, in which a glycerol-containing stream having a water content of not more than 50% by weight is subjected to a catalytic hydrogenation at a temperature in the range of from 150 to 250° C. and a pressure in the range of from 1 to 25 bar.

M. A. Dasari et al., in Appl. Chem. A: General 281, 2005, pages 225-231, describe a process for the low-pressure hydrogenation of glycerol to propylene glycol at a temperature of 200° C. and a hydrogen pressure of 200 psi (13.79 bar) in the presence of a nickel, palladium, platinum, copper or copper chromite catalyst. Different reaction parameters were tested, such as, inter alia, the water content of the glycerol used. It was found that, although the conversion increased with decreasing water content, the highest selectivity was achieved in this low-pressure process at a water content of 20% by weight.

U.S. Pat. No. 5,616,817 describes a process for the preparation of 1,2-propanediol by catalytic hydrogenation of glycerol at elevated temperature and superatmospheric pressure, in which glycerol having a water content of not more than 20% by weight is reacted in the presence of a catalyst which comprises from 40 to 70% by weight of cobalt, if appropriate, manganese and/or molybdenum and a low copper content of from 10 to 20% by weight. The temperature is in the range of from about 180 to 270° C. and the pressure in a range of from 100 to 700 bar, preferably from 200 to 325 bar.

It is the object of the present invention to provide a process for the preparation of 1,2-propanediol which permits the hydrogenation of glycerol-containing streams with high selectivity and/or low energy consumption, as required, for example, for separating off water. The process should be suitable in particular for the further processing of glycerol streams obtained on an industrial scale, such as those obtained in the transesterification of fatty acid triglycerides for the preparation of alkyl esters of higher fatty acids.

The invention therefore relates to a process for the preparation of 1,2-propanediol, in which

a) a glycerol-containing stream is provided and

b) the glycerol-containing stream is subjected to a hydrogenation in the presence of a copper-containing, heterogeneous catalyst at a temperature of from 100 to 320° C. and a pressure of from 100 to 325 bar.

The hydrogenation product obtained in step b) can, if appropriate, be subjected to at least one working-up step (step c)).

In principle, all glycerol-containing streams, including those from processes carried out industrially and having the purities resulting there, are suitable for use in the process according to the invention. These include in particular glycerol-containing streams from the processing of oil- and/or fat-containing starting materials, for example from soap production, fatty acid and fatty acid ester production, etc. The glycerol-containing stream provided in step a) is preferably a glycerol-containing stream obtained in the preparation of alkyl esters of higher fatty acids by transesterification of fatty acid triglycerides, as obtained in particular in the production of “biodiesel”. This embodiment of the process according to the invention is described in more detail below.

The glycerol-containing stream used in step a) preferably has a water content of not more than 30% by weight, preferably of not more than 20% by weight. A water content corresponding to glyceryl monohydrate (water content 16.3% by weight) or less is particularly preferred. In a special embodiment, a glycerol-containing stream which is substantially anhydrous is used. In the context of the present invention, “substantially anhydrous” is understood as meaning a water content of not more than 3% by weight, particularly preferably of not more than 1% by weight. The use of glycerol-containing streams having a water content in the range of up to 30% by weight, in particular up to 20% by weight, permits the preparation of 1,2-propanediol in high yields and with high selectivity in the temperature and pressure range used for the hydrogenation. The hydrogenation of glycerol-containing streams which are not substantially anhydrous and in particular of streams which have a higher water content than glyceryl monohydrate, is likewise possible in high yields and with high selectivities but, owing to the reduced space-time yield, is less economical. Nevertheless, a water content in the range of from 3 to 30% by weight may be advantageous for the rheological properties during the hydrogenation. A special embodiment of the process according to the invention therefore relates to the use of glycerol-containing streams having a water content in the range of from 3 to 30% by weight, preferably from 5 to 20% by weight, for reducing the viscosity during the hydrogenation.

The glycerol-containing streams may have at least one further, preferably glycerol-miscible (and hence as a rule also water-miscible), organic solvent instead of or in addition to water. The glycerol-containing streams provided in step a) preferably have a total solvent content of not more than 20% by weight, particularly preferably not more than 15% by weight, in particular not more than 10% by weight and especially not more than 5% by weight. If solvent mixtures which comprise water and at least one glycerol- or water-miscible organic solvent are used, the proportion of the organic solvent is preferably not more than 50% by weight, particularly preferably not more than 20% by weight, based on the total weight of the solvent. Suitable glycerol-miscible organic solvents are C_1-C_4-alkanols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, tert-butanol, polyols and mono- and dialkyl ethers thereof, cyclic ethers, such as dioxane and tetrahydrofuran, etc. Other suitable solvents are aromatic hydrocarbons, such as benzene, toluene or the xylenes. Preferred organic solvents are C_1-C_4-alkanols, in particular methanol and/or ethanol, and mixtures thereof with water. However, the glycerol-containing streams used in step a) preferably have no organic solvents.

The glycerol-containing streams provided in step a) may be subjected to at least one working-up step. This includes, for example, at least one purification step for removing undesired components. This furthermore includes a reduction of the content of water and/or, if present, organic solvents.

Depending on the origin, the glycerol-containing streams may also comprise inorganic salts as undesired components. These can be removed from the crude glycerol by the working-up processes described below. Thermal working-up (for example with the use of a Sambay evaporator) is particularly suitable for this purpose.

Depending on the origin, the glycerol-containing streams may also comprise catalyst poisons, i.e. components which adversely affect the hydrogenation by deactivating the hydrogenation catalyst. These include, for example, nitrogen-containing compounds, such as amines, and sulfur-containing compounds, such as sulfuric acid, hydrogen-sulfide, thioalcohols, thioethers, e.g. dimethyl sulfide and dimethyl disulfide, carbon oxide sulfide, amino acids, e.g. amino acids comprising sulfur and additional nitrogen groups, fatty acids and salts thereof etc. The catalyst poisons furthermore include halogen compounds, traces of conventional extracting agents, e.g. acetonitrile or N-methylpyrrolidone, etc. and, if appropriate, organic phosphorus and arsenic compounds. A catalyst poison frequently present in glycerol-containing streams from oil and fat refining is sulfuric acid, which is used as a catalyst in the esterification or transesterification.

For example, thermal working-up, preferably distillation, adsorption, ion exchange, a membrane separation method, crystallization or extraction or a combination of two or more of these methods can be used for working up the glycerol-containing streams in step a). Membrane separation methods with the use of membranes of defined pore sizes are especially suitable for reducing the water content and/or for salt removal. Crystallization is also understood as meaning the partial freezing of the glycerol-containing streams on cooled surfaces. Thus, it is possible to remove impurities which accumulate in the solid phase.

In a first embodiment, the glycerol-containing stream in step a) is subjected to a distillation for reducing the water content and/or for removing components which adversely affect the catalytic hydrogenation. This can in principle be effected by conventional distillation methods known to the person skilled in the art. Suitable apparatuses for the distillative working-up comprise distillation columns, such as tray columns, which may be equipped with caps, sieve plates, sieve trays, stacked packings, dumped packings, valves, side take-offs, etc., evaporators, such as thin-film evaporators, falling-film evaporators, forced-circulation evaporators, Sambay evaporators, etc., and combinations thereof. The removal of sulfuric acid takes place even as a result of a simple distillation, in particular a short path distillation.

Suitable separation processes are described in the following documents: Sattler, Klaus: Thermische Trennverfahren, 3rd edition, Wiley VCH, 2001; Schlünder E. U., Thurner F.: Destillation, Absorption, Extraktion, Springer Verlag, 1995; Mersmann, Alfons: Thermische Verfahrenstechnik, Springer Verlag, 1980; Grassmann P., Widmer F.: Einführung in die thermische Verfahrenstechnik, de Gruyter, 1997; Weiβ S., Militzer K.-E., Gramlich K.: Thermische Verfahrenstechnik, Dt. Verlag für Grundstoffindustrie, Leipzig, Stuttgart, 1993. Reference is made here to these documents.

In a further embodiment, the glycerol-containing stream in step a) is subjected to a catalytic desulfurization, if appropriate in the presence of hydrogen, for reducing the contents of sulfur-containing compounds, especially sulfur-containing aromatic compounds. Suitable desulfurization agents comprise a metal component, wherein the metals are preferably selected from metals of groups 6, 7, 8, 9, 10, 11 and 12 of the periodic table of the elements. The metals are selected in particular from Mo, Ni, Cu, Ag, Zn and combinations thereof. Further suitable components of the desulfurization agents are doping agents. The metal component can be employed in oxidized form, reduced form and in form of a mixture that comprises oxidized and reduced constituents. The active components of the desulfurization agents (metal component(s) and optionally doping agent(s)) can be applied on a supporting material. Suitable supports are in principal the adsorbents and the catalyst supports mentioned in the following. Preferably, the supporting material is selected from active carbons, graphites, carbon black, Al_2O_3, SiO_2, TiO_2, ZrO_2, SiC, silicates, zeolithes, argillaceous earth (e.g. bentonite) and combinations thereof. The application of at least one metal component and optionally further components to a supporting material can be carried out by methods known to a person skilled in the art, e.g. by (co)-precipitation or impregnation. The desulfurization agents may be present in form of a geometric body, e.g. in form of spheres, rings, cylinders, cubes, cuboids or other geometric bodies. Unsupported desulfurization agents can be shaped by customary shaping processes, e.g. by extruding, tabletting, etc. The form of supported desulfurization agents is determined by the shape of the support. The desulfurization agents can be employed e.g. in the form of pressed cylinders, tablets, lozenges, wagon wheels, rings, stars or extrudates, such as solid extrudates, polylobal extrudates (e.g. trilobal), hollow extrudates and honeycomb bodies. A preferred desulfurization agent which comprises copper and zinc in an atomic ratio of from 1:0.3 to 1:10, preferably from 1:0.5 to 1:3, in particular from 1:0.7 to 1:1.5, is preferably used for the catalytic desulfurization. A desulfurization agent which comprises from 35 to 45% by weight of copper oxide, from 35 to 45% by weight of zinc oxide and from 10 to 30% by weight of alumina is preferably used. In a special embodiment, the desulfurization agent is a component capable of use as a hydrogenation catalyst in step b). In this respect, reference is made to the following disclosure of hydrogenation catalysts of the above mentioned composition and processes for their preparation.

In one configuration of this process variant, the glycerol-containing streams are brought into contact in at least one desulfurization zone with the desulfurization agent and then hydrogenated in at least one reaction zone.

It is self-evident to the person skilled in the art that the specific configuration and arrangement of the desulfurization and reaction zone(s) can be effected in any known manner. It is possible to arrange the desulfurization and reaction zone(s) spatially separate from one another, i.e. to separate them structurally from one another by the configuration of the apparatus or to realize them in one or more common desulfurization/hydrogenation zone(s).

The copper-zinc desulfurization agent can be obtained, for example, by a conventional precipitation or coprecipitation method and used in oxidized as well as in reduced form.

In a particular embodiment, the copper-zinc desulfurization agent comprises at least copper, zinc and aluminum, the copper:zinc:aluminum atomic ratio being in the range of from 1:0.3:0.05 to 1:10:2, preferably from 1:0.6:0.3 to 1:3:1 and in particular from 1:0.7:0.5 to 1:1.5:0.9.

For conversion into the reduced form, it is possible to subject the desulfurization agent to a hydrogen reduction. This is carried out at from about 150 to 350° C., preferably from about 150 to 250° C., in the presence of hydrogen, the hydrogen being diluted by an inert gas, such as, for example, nitrogen, argon, or methane, in particular nitrogen, so that the hydrogen content is 10% by volume or less, preferably 6% by volume or less, in particular from 0.5 to 4% by volume. The copper-zinc desulfurization agent thus obtained ("reduced form") can be used in this form in the desulfurization.

In an embodiment, the desulfurization of the glycerol-containing stream is carried out over the copper-zinc desulfurization agent in oxidized form without addition of hydrogen.

In a further embodiment, the desulfurization of the glycerol-containing stream is carried out over the copper-zinc desulfurization agent in oxidized form in the presence of hydrogen.

In a further embodiment, the desulfurization of the glycerol-containing stream is carried out over the copper-zinc desulfurization agent in reduced form without addition of hydrogen.

In a further embodiment, the desulfurization of the glycerol-containing stream is carried out over the copper-zinc desulfurization agent in reduced form in the presence of hydrogen.

Usually, the desulfurization is carried out in a temperature range of from 40 to 200° C., in particular at from 50 to 180° C., especially at from 60 to 160° C., preferably at from 70 to 120° C., at a pressure of from 1 to 40 bar, in particular at from 1 to 32 bar, preferably at from 1.5 to 5 bar, especially at from 2.0 to 4.5 bar. The desulfurization can be carried out in the presence of inert gases, such as, for example, nitrogen, argon or methane. As a rule, however, the desulfurization is carried out without addition of inert gases.

Usually—if desired—hydrogen having a purity of $\geqq$99.8% by volume, in particular of $\geqq$99.9% by volume, preferably of $\geqq$99.95% by volume, is used here. These purities apply analogously to the hydrogen which is used in the catalyst activations carried out if appropriate.

Usually, the weight ratio of glycerol-containing stream to hydrogen is in the range of from 40 000:1 to 1000:1, particularly in the range of from 38 000:1 to 5000:1, in particular in the range of from 37 000:1 to 15 000:1, preferably in the range of from 36 000:1 to 25 000:1, especially in the range of from 35 000:1 to 30 000:1.

The glycerol-containing stream thus desulfurized generally has a content of sulfur-containing impurities, especially of aromatic sulfur compounds of not more than 70 ppb, preferably of not more than 50 ppb and the total sulfur content is ≦200 ppb, preferably ≦150 ppb, in particular ≦100 ppb altogether.

The desulfurization agents described above also make it possible to reduce or to remove chlorine, arsenic and/or phosphorus or corresponding chlorine, arsenic- and/or phosphorus-containing compounds from the aromatic hydrocarbon or from the mixture of aromatic hydrocarbons.

In a further embodiment, the glycerol-containing stream in step a) is brought into contact with at least one adsorbent for removing components which adversely affect the catalytic hydrogenation.

The adsorbents generally have a specific surface area, determined according to BET, in the range of from about 10 to 2000 m^2/g, preferably in the range of from 10 to 1500 m^2/g, more preferably in the range of from 10 to 400 m^2/g, especially in the range of from 60 to 250 m^2/g.

Suitable adsorbents are, for example, active aluminas. They are prepared, for example, starting from aluminum hydroxide, which is obtainable from aluminum salt solutions by conventional precipitation methods. Active aluminas suitable for the process according to the invention are also obtainable starting from aluminum hydroxide gels. For the preparation of such gels, for example, precipitated aluminum hydroxide can be activated by conventional working-up steps, such as filtration, washing and drying, and then, if appropriate, milled or agglomerated. If desired, the resulting alumina can then also be subjected to a shaping method, such as extrusion, granulation, tabletting, etc. Suitable adsorbents are preferably the Selexsorb™ types from Alcoa.

Suitable adsorbents are furthermore alumina-containing solids. These include, for example, the so-called clays, which likewise have aluminas as the main constituent.

Other suitable adsorbents are aluminum phosphates.

Other suitable adsorbents are silicas, which are obtainable, for example, by dehydration and activation of silica gels. A further process for the preparation of silica is the flame hydrolysis of silicon tetrachloride, it being possible to vary the desired surface properties of the resulting silica in wide ranges by suitable variations of the reaction parameters, such as, for example, of the stoichiometric composition of the starting mixture and of the temperature.

Other suitable adsorbents are kieselguhrs, which likewise have silicas as the main constituent. These include, for example, the diatomaceous earth obtained from silicic sediments.

Other suitable adsorbents are titanium dioxides and zirconium dioxides, as described, for example, in Römpp, Chemie-Lexikon, 9th edition (paperback), vol. 6, page 4629 et seq. and page 5156 et seq. and the literature cited there. Reference is made here to these in their entirety.

Other suitable adsorbents are phosphates, in particular condensed phosphates, such as, for example, fused or calcined phosphates, which have a large active surface area. Suitable phosphates are described, for example, in Römpp, Chemie-Lexikon, 9th edition (paperback) vol. 4, page 3376 et seq. and the literature cited there. Reference is made here to this in its entirety.

Other suitable adsorbents are carbon-containing adsorbents, preferably active carbon. Active carbon is understood here in general as meaning carbon having a porous structure and large internal surface area. For the preparation of active carbon, vegetable, animal and/or mineral carbon-containing raw materials are heated, for example, with dehydrating agents, such as zinc chloride or phosphoric acid, or are carbonized by dry distillation and then oxidatively activated. For this purpose, for example, the carbonized material can be treated at elevated temperatures of from about 700 to 1000° C. with steam, carbon dioxide and/or mixtures thereof.

Use of ion exchangers and/or adsorber resins is also possible.

The adsorbents are preferably selected from titanium dioxides, zirconium dioxides, silicas, kieselguhr, aluminas, alumina-containing solids, aluminum phosphates, natural and synthetic aluminum silicates, phosphates, carbon-containing adsorbents and mixtures thereof.

The adsorbents generally have a specific surface area, determined according to BET, in the range of from about 10 to 2000 m^2/g, in particular in the range of from 10 to 1500 m^2/g and especially in the range of from 20 to 600 m^2/g.

For the adsorptive removal of undesired components, in particular of components which adversely affect the catalytic hydrogenation, the glycerol-containing stream in step a) is brought into contact with at least one adsorbent in an adsorption zone.

In a special embodiment, an adsorbent which comprises at least one component also capable of use as a hydrogenation catalyst in step b) is used. The hydrogenation catalysts described in more detail below are referred to here in their entirety. Combinations of two or more than two adsorbents are also suitable for use as adsorbents. It is possible to use either exclusively components also capable of being hydrogenation catalysts, exclusively adsorbents not suitable as hydrogenation catalysts or combinations thereof.

In a preferred embodiment, the same component is used as adsorbent and as hydrogenation catalyst. If appropriate, one or more further, conventional adsorbents, as described above, differing from the hydrogenation catalyst, are additionally used here.

In a configuration of the process, glycerol-containing streams are brought into contact in at least one adsorption zone with the adsorbent and then hydrogenated in at least one reaction zone.

It is self-evident to the person skilled in the art that the specific configuration and arrangement of the adsorption and reaction zone(s) can be effected in any known manner. It is preferably to arrange the adsorption and reaction zone(s) spatially separate from one another, i.e. to separate them structurally from one another by the configuration of the apparatus.

If different adsorbents are used, for example, a first adsorption zone which comprises a first adsorbent can be provided in a first adsorption zone in a first reactor and separately, i.e. structurally separate therefrom, for example in a second reactor, a second adsorption zone which comprises a second adsorbent. Here, the first and/or the second adsorbent may comprise at least one component capable of use of a hydrogenation catalyst.

In a further embodiment, a conventional adsorbent is used together with an adsorbent capable of hydrogenation in a single adsorption zone, for example, in stratified form, mixed in the form of a random distribution or in the form of a gradient bed. The use in mixed form permits, if appropriate, better control of the temperature. In the case of a gradient bed, linear and non-linear gradients can be used. It may be advantageous here to implement the distribution within the bed in such a way that the glycerol-containing stream to be hydrogenated is first brought into contact with the conventional adsorbent before it is brought into contact with the adsorbent capable of hydrogenation.

Advantageously, at least two adsorption zones will be arranged in such a way that the glycerol-containing stream to be hydrogenated is brought into contact with a conventional adsorbent in the first adsorption zone and is brought into contact, in the second adsorption zone, with an adsorbent which comprises at least one component capable of use as a hydrogenation catalyst.

The glycerol-containing streams provided in step a) of the process according to the invention preferably originate from the production of biodiesel. In the context of the present invention, "biodiesel" is understood as meaning a mixture of fatty acid monoalkyl esters which can be obtained from biogenic oil- and/or fat-containing starting mixtures and can be used as fuel in diesel engines.

In principle, all available biogenic oil- and/or fat-containing starting mixtures are suitable for providing the glycerol-containing stream. Oils and fats are generally solid, semisolid or liquid fatty acid triglycerides, in particular from vegetable and animal sources, which chemically substantially comprise glyceryl esters of higher fatty acids. Suitable higher fatty acids are saturated or mono- or polyunsaturated fatty acids having preferably 8 to 40, particularly preferably 12 to 30, carbon atoms. These include, for example, n-nonanoic acid, n-decanoic acid, n-undecanoic acid, n-tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, nonadecanoic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, stearic acid, elaostearic acid, etc.

Vegetable fats and oils are substantially based on fatty acids having an even number of carbon atoms, whereas animal fats and oils may also comprise fatty acids having an odd number of carbon atoms, in free form or bound as triglyceride esters. The unsaturated fatty acids occurring in vegetable fats and oils are present in the cis form, while animal fatty acids frequently have a trans configuration.

In principle, used or unused, unpurified or purified vegetable, animal or industrial oils or fats or mixtures thereof can be used for providing the glycerol-containing stream in step a). These may comprise proportions of further ingredients, for example free fatty acids. The proportion of free fatty acids is in general from 0% to 50%, e.g. from 0.1 to 20%, of the starting mixture used for the transesterification of the fatty acid triglycerides. Free fatty acids can, if desired, be removed before or after the transesterification of the fatty acid triglycerides. Salts of these fatty acids (for example the alkali metal salts) can be converted into the free acid beforehand by acidification with a strong acid, e.g. HCl. The isolation of the free fatty acids is effected, for example, by centrifuging. Preferably, the free fatty acids present in the starting mixture are likewise converted into the alkyl esters. This can be effected before, during or after the transesterification of the fatty acid triglycerides.

Used fats and oils suitable for providing the glycerol-containing stream in step a) are fat- and/or oil-containing components which, after their recovery from appropriate biogenic starting materials were first used for other purposes, for example for technical purposes or purposes for food production, and may be chemically modified or unmodified as a result of this use or may have additional ingredients which in particular are associated with this use. These can, if desired, be at least partly removed by transesterification before the use for providing the glycerol-containing stream. Unused fats and oils suitable for providing the glycerol-containing stream in step a) are fat- or oil-containing components which still have not been used for any other purpose after their recovery from the appropriate vegetable or animal starting materials and which therefore have only ingredients which originate from the starting materials or are associated with the recovery from the starting materials. Ingredients other than fatty acid triglycerides (and, if appropriate, free fatty acids) can, if desired, also be at least partially removed from these starting materials by transesterification before the use for providing the glycerol-containing stream.

For the purification and/or enrichment, the unused or used fats or oils can be subjected to removal of undesired ingredients, such as lecithins, carbohydrates, proteins, oil sludge, water, etc.

Vegetable oils and fats are those which originate predominantly from vegetable starting materials, such as seeds, roots, leaves or other suitable plant parts. Animal fats or oils originate predominantly from animal starting materials, such as animal organs, tissues or other body parts or body fluids, such as milk. Industrial oils and fats are those which were obtained in particular from animal or vegetable starting materials and treated for technical purposes. The used or unused, unpurified or purified oils and/or fats used according to the invention are selected in particular from the group consisting of soapstock, brown grease, yellow grease, industrial tallow, industrial lard, frying oils, animal fat, edible tallow, crude vegetable oils, crude animal oils or fats or mixtures thereof.

"Soapstock" is understood as meaning a byproduct obtained in the processing of vegetable oils, in particular a byproduct of edible oil refineries which is based on soybean, colza or sunflower oil. Soapstock has a proportion of from about 50% to 80% of free fatty acids.

"Brown grease" is understood as meaning an animal fat-containing waste product which has a proportion of from more than 15% to 40% of free fatty acids. "Yellow grease" comprises from about 5% to 15% of free fatty acids.

"Industrial tallow" and "industrial lard" are understood as meaning animal fats which are produced for industrial purposes and are obtained after the drying or wet melting process, for example from slaughter wastes. Industrial tallows are rated and handled according to their acid number, the content of free fatty acids being, for example, between 1 and 15 to 20% by weight and in some cases even higher, depending on origin.

The "animal fats" include in particular fat-containing waste products obtained in the utilization of poultry, cattle, pig, fish and marine mammal bodies, for example solar stearin, a solid residue which remains after lard oil has been forced out of pork lard.

The glycerol-containing stream in step a) is preferably provided from crude vegetable oils as starting material. It is possible to start from unpurified crude vegetable oils, i.e. from liquid or solid compositions which are obtained from vegetable starting materials, for example by pressing, these having undergone no other treatment than settling in generally customary periods and centrifuging or filtering, in which only mechanical forces, such as gravitational force, centrifugal force or pressure, are used for separating the oil from solid constituents. Such unpurified crude vegetable oils may also be vegetable oils obtained by extraction if the properties thereof do not differ, or differ only insignificantly, from the corresponding vegetable oils obtained by means of pressing. The proportion of free fatty acids in unpurified vegetable fats and oil differs and is, for example, from about 0 to 20%, such as, for example from 0.1 to 15%.

Before they are used for the transesterification, the vegetable oils can of course be subjected to one or more working-up steps, as described in more detail below. Thus, purified vegetable oils, for example raffinates or semiraffinates, of the abovementioned vegetable oils may also be used as starting materials.

A vegetable oil or fat which is preferably selected from rapeseed oil, palm oil, colza oil, soybean oil, sunflower oil, corn oil, cottonseed oil, palm kernel and coconut fat and mixtures thereof is preferably used for providing the glycerol-containing stream in step a). Particularly preferably used are rapeseed oil or a mixture containing rapeseed-oil.

Animal oil or fat which is preferably selected from milk fat, wool fat, beef tallow, pork lard, fish oils, blubber, etc. and mixtures thereof is also suitable for providing the glycerol-containing stream in step a). Before they are used for the transesterification, these animal fats or oils, too can be subjected to one or more working-up steps, as described in more detail below.

Preferably, the provision of the glycerol-containing stream in step a) comprises the following steps:

a1) provision of a biogenic fat- and/or oil-containing starting mixture,

a2) transesterification of the fatty acid triglycerides present in the starting mixture with at least one C_1-C_9-monoalcohol and, if appropriate, esterification of the free fatty acids present in the starting mixture with formation of an esterification mixture,

a3) separation of the esterification mixture to obtain at least one fraction enriched with biodiesel and at least one fraction enriched with glycerol liberated in the esterification,

a4) if appropriate, purification of the fraction enriched with glycerol.

Step a1)

In a preferred embodiment, the provision of the biogenic fat- and/or oil-containing starting mixture in step a1) comprises at least one purification step. For the purification, the fat- and/or oil-containing starting mixture can be subjected to at least one purification process usually used for fats and oils, such as clarification, filtration, treatment with bleaching earths or treatment with acids or alkali for separating off troublesome impurities, such as proteins, phosphatides and slimes, and a combination of at least two of these purification steps.

Step a2)

At least one C_1-C_9-monoalcohol, in particular at least one C_1-C_4-monoalcohol is preferably used for the transesterification of the fatty acid triglycerides. The use of methanol or ethanol is preferred.

The transesterification of the fatty acid triglyceride can be effected by acidic or preferably basic catalysis. Suitable acids are, for example, mineral acids, such as HCl, H_2SO_4 or H_3PO_4.

At least one base is preferably used as the catalyst. Said base is preferably selected from alkali metal hydroxides, such as NaOH and KOH, alkaline earth metal hydroxides, such as $Ca(OH)_2$, alkali and alkaline earth metal C_1-C_6-alkanolates, such as $NaOCH_3$, $KOCH_3$, $Na(OCH_2CH_2)$ and $Ca(OCH_2CH_2)_2$ and mixtures thereof. NaOH, KOH or $NaOCH_3$ is particularly preferably used, very particularly preferably $NaOCH_3$.

The amount of base used is usually in the range of from 0.1 to 10% by weight, in particular from 0.2 to 5% by weight, based on the amount of fatty acid triglycerides used.

The base is preferably used in the form of an aqueous or alcoholic, particularly preferably alcoholic, solution. The solvent already used for the alcoholysis of the triglycerides is advantageously used as a solvent for the base. $NaOCH_3$ solution in methanol is preferably used for the transesterification.

The transesterification is preferably effected at a temperature from about 20 to 150° C., in particular from 30 to 95° C.

The transesterification is effected in apparatuses customary for this purpose and known to the person skilled in the art. In a suitable embodiment, the transesterification is effected continuously. The transesterification is preferably effected in at least one column, the transesterification mixture obtained simultaneously being subjected to a separation. In general, a higher-boiling phase which with enriched with the basic catalyst, with unconverted monoalcohol and with the glycerol formed in the transesterification is obtained and a lower-boiling phase which is enriched with the transesterification product is obtained. If the transesterification product still contains triglycerides which have not undergone transesterification, these can also be separated off and subjected to a further transesterification in the first or a further transesterification stage.

The last transesterification mixture is then transferred to a drying unit, residual amounts of water again being removed. After the drying in the drying apparatus, the desired end product biodiesel is present in purified form and can be used directly as fuel.

If the fat- and/or oil-containing starting mixture used for providing the glycerol-containing stream in step a) comprises free fatty acids, these can preferably be subjected to an esterification for conversion into esters suitable for biodiesel.

The free fatty acids are preferably transesterified with the same C_1-C_9-monoalcohol which was used for the transesterification of the fatty acid triglycerides. The esterification of free fatty acids can be effected before, during or after the transesterification of the fatty acid triglycerides. In a preferred embodiment the esterification of free fatty acids is effected before the transesterification of the fatty acid triglycerides.

The esterification of the free fatty acids can be effected by basic or preferably acidic catalysis. Suitable acids are the abovementioned mineral acids, such as HCl, H_2SO_4 or H_3PO_4, p-toluene sulfonic acid, etc. The esterification is preferably effected at a temperature of from about 20 to 95° C., in particular from 40 to 80° C.

The esterification is effected in apparatuses customary for this purpose and known to the person skilled in the art. These include stirred vessels and/or columns which, if desired, are connected to form cascades. The esterification of the free fatty acids is preferably effected in at least one esterification apparatus designed as a column, the esterification mixture obtained simultaneously being subjected to a separation. In a suitable embodiment, the esterification is effected in the presence of an entraining agent for facilitating the separation.

Step a3)

During or after the transesterification and/or esterification, the esterification mixture is subjected to a separation to obtain at least one fraction enriched with C_1-C_9-monoalcohol esters and at least one fraction enriched with glycerol liberated in the transesterification. The separation is preferably effected by conventional distillation methods known to the person skilled in the art. Suitable distillation apparatuses are those mentioned above.

Step a4)

The fraction obtained after separation of the esterification mixture in step a3) and enriched with glycerol can, if appropriate, be subjected to at least one working-up step. This includes, for example, the removal of undesired components, such as salts, and of components which adversely affect the catalytic hydrogenation or the removal of water and, if present, organic solvent. Reference is made to the above statements on these working-up steps, in their entirety.

The catalysts used in the process according to the invention may be unsupported catalysts or supported catalysts. They can be used in form of uniform-composition catalysts, impregnated catalysts, coated catalyst and precipitated catalysts.

In principle, a large number of copper-containing catalysts which may additionally comprise at least one further element of main group I, II or III, IV, V, or sub group I, II, IV, V, VI, VII, or VIII and of the lanthanides (IUPAC: groups 1 to 15 and the lanthanides) are suitable, in particular Ca, Mg, Al, La, Ti, Zr, Cr, Mo, W, Mn, Ni, Co, Zn and combinations thereof.

A special embodiment of catalysts which are particularly advantageous for use in the process according to the invention comprises skeletal or metal sponge catalysts, such as those referred to as "Raney catalysts". These include in particular Raney copper and copper-containing metal alloys in the form of a Raney catalyst. Raney catalysts whose metal component comprises at least 95%, in particular at least 99%, of copper are preferred. Processes for the preparation of Raney catalysts are known to the person skilled in the art and are described, for example, in DE-A-43 35 360, DE-A-43 45 265, DE-A-44 46 907 and EP-A-842 699. Raney copper can be prepared in a manner known per se by treating copper-aluminum alloys with alkali metal hydroxides. A Raney catalyst suitable for use in the process according to the invention is obtainable, for example, by preparation of a mixture of at least one copper-containing catalyst alloy and at least one binder, the catalyst alloy comprising copper and, if appropriate, at least one further catalytically active catalyst metal and a leachable alloy component, if appropriate with addition of moistening agents and/or additives, such as molding assistants, lubricants, plasticizers and/or pore formers, homogenization of this mixture and molding to give the desired molding, calcination of the molding and activation of the catalyst precursor thus obtained, by partial or complete leaching out of the leachable alloy component and, if appropriate, final washing of the prepared catalyst.

A further special embodiment of catalysts which are particularly advantageously used in the process according to the invention comprises catalysts which comprise copper in oxidic form and, if appropriate, additionally in elemental form. The hydrogenation catalyst used in step b) then preferably comprises at least 23% by weight, particularly preferably at least 35% by weight, of copper in oxidic and/or elemental form, based on the total weight of the catalyst.

A frequently used process for the preparation of such catalysts comprises the impregnation of support materials with solutions of the catalyst components, which are then converted into the catalytically active state by thermal treatment, decomposition or reduction.

A further suitable process for the preparation of catalysts comprises the precipitation of a catalyst component or the coprecipitation of two or more catalyst components. Thus, a copper compound, optionally at least one further metal compound and/or an additive are precipitated and subjected to subsequent drying, calcination and shaping to produce a shaped catalyst body. The precipitation can be performed in the presence of a support material. Suitable starting materials for the precipitation are metal salts and metal complexes. As copper compound for the precipitation it is in principle known to use all Cu(I) and/or Cu(II) salts which are soluble in the solvents used for application to the support, for example nitrates, carbonates, acetates, oxalates or ammonium complexes. Particular preference is given to using copper nitrate. The catalytically active component of the catalyst may further comprise, apart from a copper compound, other elements as additive components, e.g. metals, nonmetals and their compounds. These preferably include a metal of groups 4 to 15 and the lanthanides. These preferably include metals as La, Ti, Zr, Cu, Mo, W, Mn, Re, Co, Ni, Cu, Ag, Au, Zn, Sn, Pb, As, Sb and Bi. Preferably, an aqueous medium is used for the precipitation.

Suitable aqueous media are substances or mixtures which are liquid under the process conditions and contain at least 10% by weight, preferably at least 30% by weight and in particular at least 50% by weight, of water. The part other than water is preferably selected from among inorganic or organic substances which are at least partially soluble in water or at least partially miscible with water. For example, the substances other than water are selected from among organic solvents, C_1-C_{22}-alkanols, in particular methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, pentanoles and hexanoles, C_4-C_8-cycloalkyl ethers, such as tetrahydrofurans, pyrans, dioxanes and trioxanes, C_1-C_{12}-dialkyl ethers, such as dimethyl ether, dibutyl ether and methyl butyl ether. The aqueous medium preferably contains less than 40%, in particular less than 30% and particularly preferably less than 20%, of organic solvent. In preferred embodiments of the process of the present invention, the aqueous medium is essentially free of organic solvents.

Precipitation can be induced by known methods, e.g. cooling a saturated solution, adding a precipitating agent, etc. Suitable precipitating agents are e.g. acids, bases, reducing agents, etc.

Precipitation can be induced by addition of an acid or a base to the aqueous medium containing the copper compound and optionally further compounds. Suitable acids are mineral acids, like HCl, H_2SO_4 and H_3PO_4. The base is preferably selected from among metal oxides, metal hydroxides, in particular alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide, metal carbonates, in particular alkali metal and alkaline earth metal carbonates, e.g. lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate and calcium carbonate, nitrogen bases, in particular ammonia, primary, secondary and tertiary amines.

Examples of suitable reducing agents are carboxylic acids, such as formic acid, citric acid, lactic acid, tartaric acid and in particular the salts of carboxylic acids, preferably the alkali metal, alkaline earth metal, ammonium and C_1-C_{10}-alkylammonium salts, phosphorus or hypophosphorus acid, the salts of phosphorus or hypophosphorus acid, in particular the alkali metal or alkaline earth metal salts, C_1C_{10}-alkanols, such as methanol, ethanol and isopropanol, sugars, such as aldoses and ketoses in the form of monosaccharides, disaccharides and oligosaccharides, in particular glucose, fructose and lactose, aldehydes, such as formaldehyde, boron-hydrogen compounds, such as boron hydrides, boranes, metal boranates and borane complexes, e.g. diborane, sodium borohydride and aminoboranes, in particular trimethylaminoborane, hydrazine and alkylhydrazines, such as methylhydrazine, hydrogendithionites and dithionites, in particular sodium and potassium hydrogendithionites, sodium, potassium and zinc dithionites, hydrogensulfites and sulfites, in particular sodium and potassium hydrogensulfites, sodium, potassium and calcium sulfites, hydroxylamine and urea, and also mixtures thereof.

For example, catalysts which comprise nickel and copper, in addition to other metals, as active constituents on a silica support are suitable for the hydrogenation. Such catalysts are described, for example, in DE-A 26 28 987. The active material of these catalysts comprises in particular from 40 to 80%

by weight of nickel, from 10 to 50% by weight of copper and from 2% to 10% by weight of manganese.

EP-A-0 434 062 describes hydrogenation catalysts which are obtainable by reduction of a precursor comprising oxides of copper, of aluminum and at least of one further metal selected from magnesium, zinc, titanium, zirconium, tin, nickel and cobalt.

The hydrogenation catalysts which are described in DE 102 18 849 and comprise from 0.1 to 10% by weight of chromium, calculated as Cr_2O_3, from 0.1 to 10% by weight of calcium, calculated as CaO_x and from 5 to 20% by weight of copper, calculated as CuO, deposited on a silica support material and based in each case on the total weight of the calcined catalyst, are also suitable.

DE-A-40 21 230 discloses copper/zirconium oxide catalysts, the ratio of copper atoms to zirconium atoms, expressed as a weight ratio, being from 1:9 to 9:1.

DE-A-4 028 295 describes copper/manganese hydrogenation catalysts.

EP-A-552463 describes hydrogenation catalysts in a first embodiment, the oxidic form substantially corresponding to the composition $Cu_aAl_bZr_cMn_dO_x$, the following relationships being applicable: a>0; b>0; c>/=0; d>0; a>b/2; b>a/4; a>c; a>d;

and x is the number of oxygen ions which is required for preserving the electroneutrality per formula unit. According to a further embodiment, the catalyst according to the invention comprises a smaller proportion of alumina. The catalyst according to this embodiment substantially corresponds to the composition $Cu_aAl_bZr_cMn_dO_x$, the following relationships being applicable: a>0; b=a/40 to a/4; c>/=0; d>0; a>c; a=0.5d to 0.95d and x is the number of oxygen ions which is required for preserving the electroneutrality per formula unit.

WO 2006/005505 discloses moulded catalyst bodies that are particularly advantageous for use in the process according to the invention. Those catalysts can be produced by a process in which

(i) an oxidic material comprising copper oxide, aluminum oxide and at least one of the oxides of lanthanum, tungsten, molybdenum, titanium or zirconium, with preference being given to the oxides of lanthanum and/or tungsten, is made available,

(ii) pulverulent metallic copper, copper flakes, pulverulent cement or a mixture thereof or a mixture thereof with graphite can be added to the oxidic material, and

(iii) the mixture resulting from (ii) is shaped to form a catalyst pellet or a catalyst extrudate having a diameter d and/or a height h of <2.5 mm, catalyst spheres having a diameter d of <2.5 mm or catalyst honeycombs having a cell diameter r_z of <2.5 mm.

Among the oxides of lanthanum, tungsten, molybdenum, titanium or zirconium, lanthanum oxide is preferred. The composition of the oxidic material is generally such that the proportion of copper oxide is in the range from 40 to 90% by weight, the proportion of oxides of lanthanum, tungsten, molybdenum, titanium or zirconium is in the range from 0 to 50% by weight and the proportion of aluminum oxide is up to 50% by weight, in each case based on the total weight of the abovementioned oxidic constituents, with these three oxides together making up at least 80% by weight of the oxidic material after calcination and cement not being included as part of the oxidic material in the above sense.

In a preferred embodiment, the oxidic material comprises

(a) copper oxide in a proportion in the range $50 \leqq x \leqq 80\%$ by weight, preferably $55 \leqq x \leqq 75\%$ by weight,

(b) aluminum oxide in a proportion in the range $15 \leqq y \leqq 35\%$ by weight, preferably $20 \leqq y \leqq 30\%$ by weight, and

(c) at least one of the oxides of lanthanum, tungsten, molybdenum, titanium or zirconium, preferably of lanthanum and/or tungsten, in a proportion in the range $2 \leqq z \leqq 20\%$ by weight, preferably $3 \leqq z \leqq 15\%$ by weight,

in each case based on the total weight of the oxidic material after calcination, where $80 \leqq x+y+z \leqq 100$, in particular $95 \leqq x+y+z \leqq 100$.

Preferred catalysts comprise the following metals in oxidic form, reduced form (elemental form) or a combination thereof. Metals that are stable in more than one oxidation state can be employed entirely in one of the oxidation states or a combination of different oxidation states:

Cu
Cu, Ti
Cu, Zr
Cu, Mn
Cu, Al
Cu, Ni, Mn
Cu, Al, at least one further metal selected from La, W, Mo, Mn, Zn, Ti, Zr, Sn, Ni, Co
Cu, Zn, Zr
Cu, Cr, Ca
Cu, Cr, C
Cu, Al, Mn, optionally Zr

Especially preferred catalysts comprise the following metals:

Cu
Cu, Ti
Cu, Al
Cu, Al, La
Cu, Al, Zn
Cu, Zn, Zr
Cu, Al, Mn
Cu, Cr, C

Virtually all support materials of the prior art, as advantageously used in the preparation of supported catalysts, for example, SiO_2 (quartz), porcelain, magnesium oxide, tin dioxide, silicon carbide, TiO_2 (rutile, anatas), ZrO_2, Al_2O_3 (alumina), aluminum silicate, steatite (magnesium silicate), zirconium silicate, cerium silicate or mixtures of these support materials, may be used as inert support material for the catalysts according to the invention. Preferred support materials are alumina and silica. Silica materials of different origin and preparation, for example pyrogenically produced silicas or silicas produced by a wet chemical method, such as silica gels, aero gels or precipitated silicas, can be used as silica support material for the catalyst preparation (for the preparation of various SiO_2 starting materials cf.: W. Büchner; R. Schliebs; G. Winter; K. H. Büchel: Industrielle Anorganische Chemie; 2nd edition, pages 532-533, VCH Verlagsgesellschaft, Weinheim 1986).

The catalysts may be present in the form of a geometric body, e.g. in form of spheres, rings, cylinders, cubes, cuboids or other geometric bodies. Unsupported catalysts can be shaped by customary processes, e.g. by extruding, tabletting, etc. The form of supported catalysts is usually determined by the shape of the support. In an alternative, the support can be subjected to a shaping process prior to or after application of the catalytically active compound(s) or a precursor thereof. The catalysts can be employed e.g. in the form of pressed cylinders, tablets, lozenges, wagon wheels, rings, stars or extrudates, such as solid extrudates, polylobal extrudates (e.g. trilobal), hollow extrudates and honeycomb bodies.

The catalyst particles generally have a mean value of the (largest) diameter of from 0.5 to 20 mm, preferably from 1 to 10 mm. These include, for example, catalysts in the form of tablets, for example having a diameter of from 1 to 7 mm, preferably 2 to 6 mm, and a height of from 3 to 5 mm, rings having, for example an external diameter of from 4 to 7 mm, preferably 5 to 7 mm, a height of from 4 to 7 mm, preferably 2 to 5 mm, and a hole diameter of from 2 to 3 mm, or strands of different lengths having a diameter of, for example, from 1.0 to 5 mm. Such shapes can be obtained in a manner known per se, by tabletting, extrusion molding or extrusion. For this purpose, conventional adjuvants, for example lubricants, such as graphite, polyethylene oxide, cellulose or fatty acids (such as stearic acid), and/or molding assistants and reinforcing agents, such as fibers of glass, asbestos or silicon carbide can be added to the catalyst material.

A special embodiment of supported catalysts comprises coated catalysts. Coated catalysts are also preferably suitable for the process according to the invention. Coated catalysts comprise a catalytic material applied in the form of a coat to a support. They may be present in the form of spheres, rings, cylinders, cubes, cuboids or other geometrical bodies. Regardless of the type and composition of the catalytically active material, coated catalyst particles can be provided in principle by bringing the support into contact with a liquid binder and the catalytically active material, applying a layer of the material to the support and then, if appropriate, partially removing the binder. In order to provide the catalyst particles, the catalytically active material is applied already in its prepared catalytically active form, for example as calcined mixed oxide. Suitable processes for the preparation of coated catalysts are described, for example, in DE-A-29 09 671 and in EP-A-714 700. According to the last-mentioned process, the support is first moistened with the liquid binder, a layer of active catalyst material is then bonded to the surface of the moistened support body by bringing into contact with dry, finely divided, active catalyst material, and, if appropriate, the liquid binder is then partly removed. In a special embodiment, the steps of moistening of the support, bringing into contact with the catalyst material and removal of the liquid binder are repeated once or several times until the desired layer thickness of the coated catalyst is reached.

A further special embodiment of supported catalysts comprises catalysts prepared by impregnation methods. For this purpose, the catalytically active catalyst components or precursor compounds thereof can be applied to the support material. In general, aqueous salt solutions of the components, for example aqueous solutions of their halides, sulfates, nitrates, etc. are applied for impregnating the support material. The copper component can also be applied, for example, in the form of an aqueous solution of its amine complex salts, for example as $[Cu(NH_3)_4]SO_4$ or as $[Cu(NH_3)_4](NO_3)_2$ solution, if appropriate in the presence of sodium carbonate, to the support material. Of course, copper-amine complexes other than those mentioned by way of example can also be used with the same success for the catalyst preparation.

The impregnation of the support material with the precursor compounds of the catalytically active components can be effected in principle in one stage or in a plurality of stages. The impregnation can be carried out in conventional impregnation apparatuses, for example impregnation drums. After drying and/or calcination, the prepared catalyst is then obtained. The drying of the impregnated catalyst moldings can be effected continuously or batchwise, for example in belt or tray furnaces. The drying can be effected at atmospheric pressure or reduced pressure. Furthermore the drying can be effected in a gas stream, for example in an air stream or a nitrogen stream. Depending on the pressure applied, the drying is generally carried out at temperatures of from 50 to 200° C., preferably from 80 to 150° C. The calcination of the catalyst, dried beforehand if appropriate is effected in general at temperatures of from 200 to 800° C., preferably from 500 to 700° C. The calcination, like the drying, can be carried out continuously or batchwise, for example in belt or tray furnaces. The calcination can be effected at atmospheric pressure or reduced pressure and/or in a gas stream, for example in an air stream or hydrogen stream. A pretreatment with hydrogen or gases comprising hydrogen, in general under conditions which correspond to the hydrogenation conditions, serves for preliminary reduction/activation of the hydrogenation catalyst. However, the catalyst can also be reduced in situ under the conditions specified in the case of the hydrogenation, preferably under pressure (for example at a hydrogen pressure of from about 100 to 325 bar).

In the hydrogenation, the glycerol and the resulting 1,2-propanediol are preferably present in the liquid phase.

The catalysts may be arranged, for example, in a fixed bed or may be used as a suspension. The hydrogenation can accordingly be carried out, for example, by the trickle-bed procedure or the liquid-phase procedure. For the liquid-phase hydrogenation, the catalysts are preferably used in finely divided form, for example as powder, in suspension. In the hydrogenation in the trickle phase, the catalysts are used as moldings, as described above, for example in the form of pressed cylinders, tablets, lozenges, wagon wheels, rings, stars or extrudates, such as solid extrudates, polylobal extrudates, hollow extrudates and honeycomb bodies. Excess hydrogen is preferably circulated, it being possible for a small part to be discharged as waste gas for removing inert materials. It is possible to use one reactor or a plurality of reactors which can be connected in series or parallel to one another.

The temperature in the hydrogenation in step b) is preferably from 150 to 300° C., in particular from 175 to 250° C.

The reaction pressure in step b) is preferably from 140 bar to 250 bar.

The molar ratio of hydrogen to glycerol is preferably from 2:1 to 500:1, preferably from 3:1 to 100:1.

The catalyst space velocity in the continuous procedure is preferably from 0.1 to 1, more preferably from 0.2 to 0.6, and in particular from 0.3 to 0.6, kg of glycerol to be hydrogenated per kg (catalyst) per h.

The conversion, based on glycerol, is preferably at least 90%, in particular at least 95%. The selectivity, based on 1,2-propanediol is preferably at least 85%, particularly preferably at least 90%, in the process according to the invention. Often, even higher selectivities of up to 95% or more can be achieved.

The hydrogenation is expediently carried out continuously. The hydrogenation discharge substantially comprises 1,2-propanediol. Further constituents are, inter alia, methanol, ethanol, n-propanol, isopropanol, 1,3-propanediol, glycerol, ethylene glycol and water. The hydrogenation discharge can then be worked up by conventional methods known to the person skilled in the art. For example, thermal working-up, preferably distillation, adsorption, ion exchange, a membrane separation method, crystallization or extraction or a combination of two or more of these methods can be used. Preferred is a working-up by distillation. This can in principle be effected by conventional distillation methods known to the person skilled in the art. Suitable apparatuses for the distillative working-up comprise distillation columns, such as tray columns, which may be equipped with caps, sieve plates, sieve trays, stacked packings, dumped packings, valves, side take-offs, etc. evaporators, such as thin-film evaporators, falling-film evaporators, forced-circulation evaporators, Sambay evaporators, etc., and combinations thereof. Glycerol still present in the hydrogenation discharge can be recycled to the hydrogenation stage, if appropriate after being separated off by distillation.

The invention is explained in more detail with reference to the following, non-limiting examples.

EXAMPLES

Glycerol of the pharmaceutical glycerol and pure glycerol qualities from Biodiesel Schwarzheide GmbH was used as feedstock for the experiments for catalyst screening. Table 1 shows the analytical data of the glycerol used.

TABLE 1

Glycerol quality	Water [%]	pH [pH]	chloride [ppm]	Glycerol content [%]
Pure	0.1	7	2	97-98
Pharmaceutical	0.141	7	1.4	99.8

The analysis of the feedstock glycerol and of the reaction discharge is effected by gas chromatography (data in GC % by area).

Apparatus:	HP 5890-2 with sampler
Range:	2
Column:	30 m DBWax; film thickness: 0.25 μm
Sample volume:	1 μl
Carrier gas:	Helium
Fluid rate:	100 ml/min
Injector temperature:	240° C.
Detector:	FID (Flame ionization detector)
Detector temperature:	250° C.
Temperature program:	5 min at 40° C., 10° C./min to 240° C., 15 min at 240° C. Total run time 45 min

Copper-containing catalysts of different compositions were tested (cf. table 2).

TABLE 2

Overview of the catalysts tested

Catalyst	Composition
A	67% CuO; 5% La_2O_3; Al_2O_3 (ad 100%) + 15% Cu
B	40% CuO; 40% ZnO; 20% Al_2O_3
C*	40% CuO; 40% ZnO; 20% Al_2O_3
D	61% CuO; 39% Al_2O_3
E	70% CuO; 24.5% ZnO; 5.5% Al_2O_3
F	55% CuO/Al_2O_3
G	16% CuO/64% Al_2O_3/20% ZnO
H	100% Cu (Raney-Cu**)
I	40% Cu/TiO_2
J	70% CuO/20% ZnO/10% ZrO_2
K	60% CuO/30% Al_2O_3/10% MnO_3
L	66-77% CuO/21-32% Cu-Chromit/2% Graphit

*as for B, but higher calcination temperature (from 400 to 500° C.)
**from Aldrich

The catalysts were activated for 10 h at a temperature of 200° C. and a hydrogen pressure of 50 bar before the reaction.

General Method for Carrying Out Catalyst Tests Batchwise.

Pharmaceutical glycerol having a water content of 20% was used. The catalyst was initially taken in a 0.3 l mini autoclave and the autoclave was closed and was tested for leaks with 200 bar N_2 at room temperature. Catalyst extrudates were used in the form of moldings, and the extrudates were comminuted beforehand for the preparation of catalyst suspensions.

Thereafter, the autoclave was depressurized and the activation of the catalyst carried out. For this purpose, 50 bar H_2 was forced in at room temperature, heating was then effected to an internal temperature of 200° C. and the temperature was maintained for about 10 h without stirring. After cooling to 30° C. and subsequent inertization with N_2 the autoclave was evacuated and the reaction solution was aspirated.

For the reaction of the glycerol, 50 bar H_2 was forced in at room temperature and the reaction mixture was heated to 215° C. with stirring (speed from 700 to 1000 rpm). The pressure resulting in the autoclave was supplemented with H_2 to the desired final pressure of 200 bar. Hydrogen consumed in the reaction was replenished. The run time of the experiments was 10 hours. After the end of the run time of the experiment, the autoclave was cooled to room temperature and depressurized. The analysis of the samples and discharges was effected by means of gas chromatography by integration of the areas of the peaks (% by area). The results are shown in table 3.

TABLE 3

Comparison of the catalyst in the fixed bed and suspension procedures

Ex. No.	Catalyst	Catalyst form	Amount of catalyst [g]	Conversion [%]	Selectivity [%]	Yield [%]
1	A	Suspension	20.0	97.6	95.3	93.0
2	B	Extrudates 5 × 3	10.0	91.5	91.2	83.5
3	C	Extrudates 5 × 3	18.3	100.0	87.8	87.8
4	D	Suspension	20.0	97.2	93.6	91.0
5	E	Extrudates 5 × 5	10.0	99.1	88.8	88.0
6	F	Suspension	20.0	96.8	94.4	91.3
7	G	Suspension	10.0	92.3	92.5	85.4
8	H	Suspension	10.0	99.6	96.1	95.8
9	J	tablets	18.0	92.7	96.6	89.6
10	K	tablets	18.0	79.6	94.5	75.2
11	L	tablets	18.0	74.5	96.8	72.1

General Method for the Continuous Hydrogenation Using Fixed-Bed Catalysts

Pharmaceutical glycerol having a water content of 10% was used. The experiments were carried out in a continuously operated laboratory apparatus at from 200 to 240 bar. The experimental series 9 to 11 were operated for simulating the main reactor with liquid circulation in the liquid-phase procedure. In each case 70 ml of the catalysts were used.

The structure of the unit and the process description are described below:

The unit consists of a 75 ml tubular reactor R1 (internal Ø=12 mm, L=800 mm) having three liquid-heated heating zones, which is operated by the liquid-phase procedure. If required a liquid circulation which is operated with flow control (Danfoss) via an HPLC pump can be connected. All parts of the unit are made from metal and designed for an operating pressure of up to 250 bar.

The glycerol solution (aqueous, 90% strength) is metered continuously, regulated by a balance, into the reactor R1 and is reacted under defined conditions (pressure, temperature, catalyst space velocity) with hydrogen to give the desired product. The hydrogen is supplied from 50 l steel cylinders which are compressed to the required pressure by means of a compressed air-operated compressor. The desired reaction pressure is established via pressure control (P2) in the waste gas stream, and the required amount of hydrogen is fed into the reactor R1 with flow control via a mass flow meter (Hi-Tec). The liquid reactor discharge is discharged with level control (container B2) via an HPLC pump and collected in the discharge container (B5). The gaseous reactor discharge is passed via a buffer vessel (B4) and depressurized by means of a pressure-controlled (P2) Recco valve.

In experimental series 15, the reactions were continued in a modified unit (main reactor with liquid circulation in the trickle-bed procedure, downstream reactor without liquid circulation in the liquid-phase procedure). In all experiments, the catalyst was stable, no catalyst loss occurred as a result of so-called “leaching”.

TABLE 4

Results of the continuous experiments (best setting from each experimental series)

Expt. No.	Catalyst	Run time [h]	Temp. [° C.]	Pressure [bar]	Feed [g/h]	Cat. space vel. [kg/l · h]	LR g/h	pH Discharge	Glycerol conversion	Yield	Selectivity
12	I	230	217	200	31.1	0.4	155	5.5	81	81	99
13	I	153	220	240	31.1	0.4	0	6	96	94	98
14	A	287	200	200	23.3	0.3	300	6	88	82	92
15	B	253	170-190	200	44.4	0.4	1800	6-7	100	98.5	98.5

LR = liquid recycling (circulation) from the reactor exit to the reactor entrance

We claim:

1. A process for preparing 1,2-propanediol, comprising

a) providing a glycerol-containing stream; and

b) hydrogenating said glycerol-containing stream in the presence of a heterogeneous catalyst which comprises copper at a temperature in the range of from 100° C. to 320° C. and at a pressure in the range of from 100 bar to 325 bar;

wherein said glycerol-containing stream has a water content of 30% by weight or less.

2. The process of claim **1**, wherein said glycerol-containing stream is obtained from the preparation of alkyl esters of higher fatty acids by transesterification of fatty acid triglycerides.

3. The process of claim **1**, wherein said glycerol-containing stream has a water content of 20% by weight or less.

4. The process of claim **1**, wherein said glycerol-containing stream is substantially anhydrous.

5. The process of claim **1**, wherein said glycerol-containing stream is worked-up via at least one work-up process selected from the group consisting of thermal working-up, adsorption, ion exchange, membrane separation, crystallization, extraction, and combinations thereof.

6. The process of claim **1**, wherein the water content of said glycerol-containing stream is reduced and/or components which adversely affect catalytic hydrogenation are removed from said glycerol-containing stream via distillation.

7. The process of claim **1**, wherein said glycerol-containing stream is subjected to catalytic desulfurization prior to step b).

8. The process of claim **7**, wherein said catalytic desulfurization is performed in the presence of hydrogen.

9. The process of claim **7**, wherein said sulfur-containing compounds comprise sulfur-containing aromatic compounds.

10. The process of claim **1**, wherein said glycerol-containing stream is contacted with at least one adsorbent for removing components which adversely affect catalytic hydrogenation.

11. The process according to claim **1**, wherein said adsorbent comprises at least one component capable of use as a hydrogenation catalyst.

12. The process according to claim **1**, wherein said glycerol-containing stream is provided by:

a1) providing a biogenic fat-and/or oil-containing starting mixture comprising fatty acid triglycerides and free fatty acids;

a2) transesterifying said fatty acid triglycerides with at least one C_1-C_9-monoalcohol and, optionally, esterifying said free fatty acids, to form an esterification mixture;

a3) separating said esterification mixture so as to obtain at least one fraction enriched with C_1-C_9-monoalkyl esters and at least one fraction enriched with glycerol liberated in the transesterification of a2),

a4) optionally, purifying said at least one fraction enriched with glycerol.

13. The process according to claim **1**, wherein said heterogenous catalyst comprises a Raney catalyst.

14. The process of claim **1**, wherein said heterogenous catalyst comprises at least 23% by weight of copper, in oxidic and/or elemental form, based on the total weight of the catalyst.

15. The process of claim **1**, wherein said heterogenous catalyst comprises at least 35% by weight of copper, in oxidic and/or elemental form, based on the total weight of the catalyst.

16. The process of claim **1**, wherein said heterogenous catalyst comprises metals or mixtures of metals selected from the group consisting of Cu; Cu and Ti; Cu and Zr; Cu and Mn; Cu and Al; Cu, Ni, and Mn; Cu, Al, and at least one further metal selected from the group consisting of La, W, Mo, Mn, Zn, Ti, Zr, Sn, Ni, and Co; Cu, Zn, and Zr; Cu, Cr, and Ca; Cu, Cr, and C; and Cu, Al, Mn, and optionally Zr; wherein each metal is present in oxidic form, elemental form, or a combination thereof.

* * * * *

ASPEN INPUT SUMMARY

```
;
;Input Summary created by Aspen Plus Rel. 24.0 at 18:36:42 Mon Apr 11, 2011
;Directory C:\temp  Filename c:\temp\~ap2e09.txt
;


DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

DATABANKS PURE22  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURE22  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    GLYCEROL C3H8O3 /
    ACETOL C3H6O2-D1 /
    WATER H2O /
    HYDROGEN H2 /
    PG C3H8O2-2 /
    N-PROP C3H8O-1 /
    ETHYL-01 C2H6O2 /
    ISO-PROP C3H8O-2 /
    SODIU-01 NACL /
    METHA-01 CH4O

HENRY-COMPS HC-1 HYDROGEN

FLOWSHEET
    BLOCK VALVE IN=S-132 OUT=S-133
    BLOCK D-102 IN=S-133 OUT=S-137 S-136 S-134
    BLOCK V-101 IN=S-128 OUT=S-130 S-129
    BLOCK P-100 IN=S-114 OUT=S-115
    BLOCK R-101 IN=S-116 S-120 OUT=S-121
    BLOCK CP-101 IN=S-130 OUT=S-131
    BLOCK M-101 IN=S-131 S-118 OUT=S-119
    BLOCK T-101 IN=S-117 OUT=S-118
    BLOCK HX-103 IN=S-126 S-119 OUT=S-127 S-120
    BLOCK C-102 IN=S-127 OUT=S-128
    BLOCK C-103 IN=S-134 OUT=S-135
    BLOCK M-102 IN=S-101 S-102 S-112 OUT=S-103
    BLOCK HX-101 IN=S-109 S-106 OUT=S-110 S-107
    BLOCK D-101 IN=S-108 OUT=S-109 S-114
    BLOCK H-101 IN=S-107 OUT=S-108
    BLOCK FSPLIT IN=S-110 OUT=S-113 S-111
    BLOCK F-101 IN=S-121 OUT=S-123 S-122
    BLOCK HX-102 IN=S-123 S-115 OUT=S-124 S-116
```

```
    BLOCK F-102 IN=S-124 OUT=S-126 S-125
    BLOCK M-103 IN=S-122 S-129 S-125 OUT=S-132
    BLOCK S-101 IN=S-103 OUT=S-104 S-105
    BLOCK P-101 IN=S-105 OUT=S-106
    BLOCK P-102 IN=S-111 OUT=S-112

PROPERTIES PENG-ROB TRUE-COMPS=YES
    PROPERTIES NRTL-RK / UNIQ-RK

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL HYDROGEN WATER 198.2062671 -12588.31790 -26.31190000  &
        8.35727785E-3 33.53000373 150.5300028 0.0
    BPVAL HYDROGEN N-PROP -71.55669085 3641.940059 13.38100000  &
        -.0153788890 -75.99999539 77.00000338 0.0

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL GLYCEROL WATER -.7026000000 283.4269177 .3000000000  &
        0.0 0.0 0.0 77.00000338 553.9999996
    BPVAL WATER GLYCEROL -1.093700000 407.9753967 .3000000000  &
        0.0 0.0 0.0 77.00000338 553.9999996
    BPVAL GLYCEROL PG -.6973000000 -65.90807947 .3000000000 0.0  &
        0.0 0.0 191.4800025 357.6200011
    BPVAL PG GLYCEROL .0663000000 454.1135364 .3000000000 0.0  &
        0.0 0.0 191.4800025 357.6200011
    BPVAL WATER PG 0.0 -543.0875357 .3000000000 0.0 0.0 0.0  &
        59.00000353 212.0000023
    BPVAL PG WATER 0.0 849.8359732 .3000000000 0.0 0.0 0.0  &
        59.00000353 212.0000023
    BPVAL WATER N-PROP 5.508500000 -1583.168747 .3000000000 0.0  &
        0.0 0.0 77.00000338 212.0000023
    BPVAL N-PROP WATER -1.809800000 1074.524751 .3000000000 0.0  &
        0.0 0.0 77.00000338 212.0000023
    BPVAL PG N-PROP 2.467600000 -2322.928601 .3000000000 0.0  &
        0.0 0.0 213.4400023 347.7200012
    BPVAL N-PROP PG -5.774100000 5454.272836 .3000000000 0.0  &
        0.0 0.0 213.4400023 347.7200012
    BPVAL GLYCEROL ETHYL-01 0.0 -621.3814150 .3000000000 0.0  &
        0.0 0.0 205.7000024 307.0400015
    BPVAL ETHYL-01 GLYCEROL 0.0 532.5047957 .3000000000 0.0  &
        0.0 0.0 205.7000024 307.0400015
    BPVAL WATER ETHYL-01 .3184000000 59.89895952 .3000000000  &
        0.0 0.0 0.0 86.72000331 386.0600009
    BPVAL ETHYL-01 WATER .0531000000 -314.0342975 .3000000000  &
        0.0 0.0 0.0 86.72000331 386.0600009
    BPVAL PG ETHYL-01 -1.262600000 1782.934906 .3000000000 0.0  &
        0.0 0.0 182.4800025 314.6900015
    BPVAL ETHYL-01 PG -.4391000000 -242.0443781 .3000000000 0.0  &
        0.0 0.0 182.4800025 314.6900015

PROP-DATA PRKBV-1
```

```
    IN-UNITS ENG
    PROP-LIST PRKBV
    BPVAL WATER METHA-01 -.0778000000 0.0 0.0 -459.6699923  &
        1340.329993
    BPVAL METHA-01 WATER -.0778000000 0.0 0.0 -459.6699923  &
        1340.329993

PROP-DATA UNIQ-1
    IN-UNITS ENG
    PROP-LIST UNIQ
    BPVAL GLYCEROL WATER .3575000000 -127.4470190 0.0 0.0  &
        77.00000338 553.9999996 0.0
    BPVAL WATER GLYCEROL .8232000000 -261.0345579 0.0 0.0  &
        77.00000338 553.9999996 0.0
    BPVAL GLYCEROL PG .4210000000 -8.234459934 0.0 0.0  &
        191.4800025 357.6200011 0.0
    BPVAL PG GLYCEROL -.2466000000 -112.8707991 0.0 0.0  &
        191.4800025 357.6200011 0.0
    BPVAL GLYCEROL ETHYL-01 0.0 327.0122974 0.0 0.0  &
        205.7000024 307.0400015 0.0
    BPVAL ETHYL-01 GLYCEROL 0.0 -319.0148974 0.0 0.0  &
        205.7000024 307.0400015 0.0
    BPVAL WATER PG 0.0 -492.1070361 0.0 0.0 59.00000353  &
        212.0000023 0.0
    BPVAL PG WATER 0.0 451.2850164 0.0 0.0 59.00000353  &
        212.0000023 0.0
    BPVAL WATER N-PROP -2.388600000 1109.333151 0.0 0.0  &
        77.00000338 212.0000023 0.0
    BPVAL N-PROP WATER 1.826100000 -1202.000210 0.0 0.0  &
        77.00000338 212.0000023 0.0
    BPVAL WATER ETHYL-01 -.4787000000 140.8377589 0.0 0.0  &
        86.72000331 386.0600009 0.0
    BPVAL ETHYL-01 WATER .4661000000 49.24979961 0.0 0.0  &
        86.72000331 386.0600009 0.0
    BPVAL PG N-PROP -.7915000000 943.5014925 0.0 0.0  &
        213.4400023 347.7200012 0.0
    BPVAL N-PROP PG 1.948700000 -2146.453363 0.0 0.0  &
        213.4400023 347.7200012 0.0
    BPVAL PG ETHYL-01 .4147000000 -859.2713931 0.0 0.0  &
        182.4800025 314.6900015 0.0
    BPVAL ETHYL-01 PG .2677000000 173.6895586 0.0 0.0  &
        182.4800025 314.6900015 0.0

STREAM S-101
    SUBSTREAM MIXED TEMP=70. PRES=30. MASS-FLOW=19392.4873
    MASS-FLOW GLYCEROL 15513.99 / WATER 2908.873 / SODIU-01  &
        775.6994 / METHA-01 193.9249

STREAM S-102
    SUBSTREAM MIXED TEMP=70. PRES=30. MOLE-FLOW=1.
    MASS-FRAC WATER 1.

STREAM S-117
    SUBSTREAM MIXED TEMP=70. PRES=1000. MOLE-FLOW=1.
```

```
    MOLE-FRAC HYDROGEN 1.

BLOCK M-101 MIXER

BLOCK M-102 MIXER
    PARAM PRES=25.

BLOCK M-103 MIXER
    PARAM PRES=-5.

BLOCK FSPLIT FSPLIT
    FRAC S-113 0.34

BLOCK S-101 SEP
    PARAM PRES=-5.
    FRAC STREAM=S-104 SUBSTREAM=MIXED COMPS=SODIU-01 FRACS=1.
    FLASH-SPECS S-104 NPHASE=1 FREE-WATER=NO PHASE=S
    FLASH-SPECS S-105 PRES=0. DELT=15.

BLOCK C-102 HEATER
    PARAM TEMP=225. PRES=-5.

BLOCK C-103 HEATER
    PARAM TEMP=90. PRES=-5.

BLOCK H-101 HEATER
    PARAM TEMP=242. PRES=-5.

BLOCK F-101 FLASH2
    PARAM PRES=560. DUTY=0.

BLOCK F-102 FLASH2
    PARAM PRES=0. DUTY=0.

BLOCK V-101 FLASH2
    PARAM TEMP=225. PRES=0.

BLOCK HX-101 HEATX
    PARAM T-HOT=80. CALC-METHOD=TASCPLUS-RIG
    HETRAN-PARAM INPUT-FILE= &
    'EDR_HX101.EDR'
    FEEDS HOT=S-109 COLD=S-106
    PRODUCTS HOT=S-110 COLD=S-107
    PROPERTIES PENG-ROB FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES / PENG-ROB FREE-WATER=STEAM-TA  &
        SOLU-WATER=3 TRUE-COMPS=YES
    HOT-SIDE DP-OPTION=CONSTANT
    COLD-SIDE DP-OPTION=CONSTANT

BLOCK HX-102 HEATX
    PARAM T-COLD=410. CALC-METHOD=TASCPLUS-RIG
    HETRAN-PARAM INPUT-FILE= &
    'EDR_HX102.EDR'
    FEEDS HOT=S-123 COLD=S-115
```

```
    PRODUCTS HOT=S-124 COLD=S-116
    PROPERTIES PENG-ROB FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES / PENG-ROB FREE-WATER=STEAM-TA  &
        SOLU-WATER=3 TRUE-COMPS=YES
    HOT-SIDE DP-OPTION=CONSTANT
    COLD-SIDE DP-OPTION=CONSTANT

BLOCK HX-103 HEATX
    PARAM DECR-HOT=20. CALC-METHOD=TASCPLUS-RIG
    HETRAN-PARAM INPUT-FILE= &
    'EDR_HX103.EDR'
    FEEDS HOT=S-126 COLD=S-119
    PRODUCTS HOT=S-127 COLD=S-120
    PROPERTIES PENG-ROB FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES / PENG-ROB FREE-WATER=STEAM-TA  &
        SOLU-WATER=3 TRUE-COMPS=YES
    HOT-SIDE DP-OPTION=CONSTANT
    COLD-SIDE DP-OPTION=CONSTANT

BLOCK D-101 RADFRAC
    PARAM NSTAGE=6
    COL-CONFIG CONDENSER=TOTAL
    FEEDS S-108 4
    PRODUCTS S-109 1 L / S-114 6 L
    P-SPEC 1 20.
    COL-SPECS MOLE-B=375.5 MOLE-RR=0.2

BLOCK D-102 RADFRAC
    PARAM NSTAGE=16
    COL-CONFIG CONDENSER=PARTIAL-V-L
    FEEDS S-133 10
    PRODUCTS S-136 1 L / S-134 16 L / S-137 1 V
    P-SPEC 1 20.
    COL-SPECS MOLE-B=164.3 MOLE-RR=0.13 T1=130.

BLOCK R-101 RSTOIC
    PARAM PRES=-15. DUTY=0. SERIES=YES
    STOIC 1 MIXED GLYCEROL -1. / HYDROGEN -1. / PG 1. /  &
        WATER 1.
    STOIC 2 MIXED GLYCEROL -2. / HYDROGEN -4. / ISO-PROP 1. / &
        N-PROP 1. / WATER 4.
    CONV 1 MIXED GLYCEROL 0.985
    CONV 2 MIXED GLYCEROL 1.

BLOCK P-100 PUMP
    PARAM PRES=587.

BLOCK P-101 PUMP
    PARAM PRES=42.

BLOCK P-102 PUMP
    PARAM PRES=30.

BLOCK CP-101 COMPR
```

```
    PARAM TYPE=ISENTROPIC PRES=600. SEFF=0.8

BLOCK T-101 COMPR
    PARAM TYPE=ISENTROPIC PRES=600. SEFF=0.8 MODEL-TYPE=TURBINE

BLOCK VALVE VALVE
    PARAM P-OUT=30.

DESIGN-SPEC DS-1
    DEFINE MIXH2 MOLE-FLOW STREAM=S-119 SUBSTREAM=MIXED  &
        COMPONENT=HYDROGEN
    SPEC "MIXH2" TO "665.5535"
    TOL-SPEC ".1"
    VARY STREAM-VAR STREAM=S-117 SUBSTREAM=MIXED  &
        VARIABLE=MOLE-FLOW
    LIMITS "0" "400"

DESIGN-SPEC DS-2
    DEFINE WATFRAC MASS-FRAC STREAM=S-103 SUBSTREAM=MIXED  &
        COMPONENT=WATER
    SPEC "WATFRAC" TO ".5"
    TOL-SPEC ".01"
    VARY STREAM-VAR STREAM=S-102 SUBSTREAM=MIXED  &
        VARIABLE=MOLE-FLOW
    LIMITS "0" "800"

EO-CONV-OPTI

SENSITIVITY S-1
    DEFINE METHREC MOLE-FLOW STREAM=S-103 SUBSTREAM=MIXED  &
        COMPONENT=METHA-01
    TABULATE 1 "METHREC"
    VARY BLOCK-VAR BLOCK=FSPLIT SENTENCE=FRAC VARIABLE=FRAC  &
        ID1=S-113
    RANGE LOWER="0" UPPER=".5" NPOINT="20"

CONV-OPTIONS
    WEGSTEIN MAXIT=70

STREAM-REPOR MOLEFLOW MOLEFRAC MASSFRAC

DISABLE
    SENSITIVITY S-1
;
;
;
;
;
```

ASPEN SIMULATION REPORT

```
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 1

                        RUN CONTROL SECTION

RUN CONTROL INFORMATION
----------------------

THIS COPY OF ASPEN PLUS LICENSED TO UNIVERSITY OF PENNSYLVAN

TYPE OF RUN: NEW

INPUT FILE NAME: _1152wfu.inm

OUTPUT PROBLEM DATA FILE NAME: _1152wfu
LOCATED IN:


PDF SIZE USED FOR INPUT TRANSLATION:
  NUMBER OF FILE RECORDS (PSIZE) =     0
  NUMBER OF IN-CORE RECORDS      =   256
PSIZE NEEDED FOR SIMULATION    =   256

CALLING PROGRAM NAME:         apmain
LOCATED IN:                 C:\PROGRA~1\ASPENT~1\ASPENP~2.2\Engine\xeq

SIMULATION REQUESTED FOR ENTIRE FLOWSHEET
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 2

                         FLOWSHEET SECTION

FLOWSHEET CONNECTIVITY BY STREAMS
---------------------------------

  STREAM     SOURCE     DEST         STREAM     SOURCE     DEST
  S-117      ----       T-101        S-102      ----       M-102
  S-101      ----       M-102        S-133      VALVE      D-102
  S-137      D-102      ----         S-136      D-102      ----
  S-134      D-102      C-103        S-130      V-101      CP-101
  S-129      V-101      M-103        S-115      P-100      HX-102
  S-121      R-101      F-101        S-131      CP-101     M-101
  S-119      M-101      HX-103       S-118      T-101      M-101
  S-127      HX-103     C-102        S-120      HX-103     R-101
  S-128      C-102      V-101        S-135      C-103      ----
  S-103      M-102      S-101        S-110      HX-101     FSPLIT
  S-107      HX-101     H-101        S-109      D-101      HX-101
  S-114      D-101      P-100        S-108      H-101      D-101
  S-113      FSPLIT     ----         S-111      FSPLIT     P-102
  S-123      F-101      HX-102       S-122      F-101      M-103
  S-124      HX-102     F-102        S-116      HX-102     R-101
  S-126      F-102      HX-103       S-125      F-102      M-103
  S-132      M-103      VALVE        S-104      S-101      ----
  S-105      S-101      P-101        S-106      P-101      HX-101
```

```
  S-112     P-102     M-102

 FLOWSHEET CONNECTIVITY BY BLOCKS
 -------------------------------

  BLOCK        INLETS                         OUTLETS
  VALVE        S-132                          S-133
  D-102        S-133                          S-137 S-136 S-134
  V-101        S-128                          S-130 S-129
  P-100        S-114                          S-115
  R-101        S-116 S-120                    S-121
  CP-101       S-130                          S-131
  M-101        S-131 S-118                    S-119
  T-101        S-117                          S-118
  HX-103       S-126 S-119                    S-127 S-120
  C-102        S-127                          S-128
  C-103        S-134                          S-135
  M-102        S-101 S-102 S-112              S-103
  HX-101       S-109 S-106                    S-110 S-107
  D-101        S-108                          S-109 S-114
  H-101        S-107                          S-108
  FSPLIT       S-110                          S-113 S-111
  F-101        S-121                          S-123 S-122
  HX-102       S-123 S-115                    S-124 S-116
  F-102        S-124                          S-126 S-125
  M-103        S-122 S-129 S-125              S-132
  S-101        S-103                          S-104 S-105
  P-101        S-105                          S-106
  P-102        S-111                          S-112
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 3

                          FLOWSHEET SECTION

 CONVERGENCE STATUS SUMMARY
 --------------------------

  DESIGN-SPEC SUMMARY
  ===================


  DESIGN                                                  CONV
  SPEC      ERROR        TOLERANCE    ERR/TOL      VARIABLE   STAT  BLOCK
  ------    -----        ---------    -------      --------   ----  -----
  DS-1      0.34537E-01  0.10000      0.34537       171.84     #    $OLVER03
  DS-2      0.43373E-02  0.10000E-01  0.43373       298.88     #    $OLVER04

  TEAR STREAM SUMMARY
  ===================


  STREAM    MAXIMUM                   MAXIMUM     VARIABLE            CONV
  ID        ERROR        TOLERANCE    ERR/TOL     ID                  STAT  BLOCK
  ------    -------      ---------    --------    --------            ----  -----
  S-108     0.18110E-08  0.22262E-06  0.81349E-02 METHA-01MOLEFLOW #   $OLVER01
```

```
  S-106    0.10204E-04  0.11994E-04  0.85077     WATER MOLEFLOW   #   $OLVER01
  S-121    0.12667E-06  0.62868E-07   2.0148    ISO-PROPMOLEFLOW *   $OLVER02
  S-119    0.11910E-06  0.46937E-07   2.5376    ISO-PROPMOLEFLOW *   $OLVER02

  #  = CONVERGED
  *  = NOT CONVERGED
  LB = AT LOWER BOUNDS
  UB = AT UPPER BOUNDS

 DESIGN-SPEC:  DS-1
 ------------------

  SAMPLED VARIABLES:
    MIXH2    : HYDROGENMOLEFLOW IN STREAM S-119 SUBSTREAM MIXED

  SPECIFICATION:
    MAKE MIXH2 APPROACH 665.554
    WITHIN          0.100000

  MANIPULATED VARIABLES:
    VARY     : TOTAL MOLEFLOW IN STREAM S-117 SUBSTREAM MIXED
    LOWER LIMIT =           0.0                    LBMOL/HR
    UPPER LIMIT =         400.000                  LBMOL/HR
    FINAL VALUE =         171.838                  LBMOL/HR

  VALUES OF ACCESSED FORTRAN VARIABLES:
    VARIABLE      VALUE AT START      FINAL VALUE     UNITS
                  OF LOOP
    --------      --------------      -----------     -----
    MIXH2           665.588            665.588       LBMOL/HR

 DESIGN-SPEC:  DS-2
 ------------------

  SAMPLED VARIABLES:
    WATFRAC  : WATER MASSFRAC IN STREAM S-103 SUBSTREAM MIXED
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 4

                          FLOWSHEET SECTION

 DESIGN-SPEC:  DS-2 (CONTINUED)

  SPECIFICATION:
    MAKE WATFRAC APPROACH 0.50000
    WITHIN          0.0100000

  MANIPULATED VARIABLES:
    VARY     : TOTAL MOLEFLOW IN STREAM S-102 SUBSTREAM MIXED
    LOWER LIMIT =           0.0                    LBMOL/HR
    UPPER LIMIT =         800.000                  LBMOL/HR
    FINAL VALUE =         298.877                  LBMOL/HR

  VALUES OF ACCESSED FORTRAN VARIABLES:
    VARIABLE      VALUE AT START      FINAL VALUE     UNITS
```

```
                OF LOOP
    --------    --------------    -----------    -----
    WATFRAC       0.504337          0.504337

 CONVERGENCE BLOCK:  $OLVER01
 ----------------------------
    Tear Stream  :  S-108      S-106
    Tolerance used:  0.100D-03  0.100D-03
    Trace molefrac:  0.100D-05  0.100D-05

    MAXIT=   70 WAIT   1 ITERATIONS BEFORE ACCELERATING
    QMAX =   0.0     QMIN =  -5.0
    METHOD: WEGSTEIN      STATUS: CONVERGED
    TOTAL NUMBER OF ITERATIONS:    59

                  *** FINAL VALUES ***

VAR#  TEAR STREAM VAR  STREAM   SUBSTREA COMPONEN ATTRIBUT ELEMENT      UNIT
VALUE       PREV VALUE       ERR/TOL
----  ---------------  -------- -------- -------- -------- -------- ----------- -----------    ------------    ------------
   1  TOTAL MOLEFLOW   S-108    MIXED                          LBMOL/HR     1138.0639      1138.0639      4.8677-05
   2  TOTAL MOLEFLOW   S-106    MIXED                          LBMOL/HR     1138.1451      1138.0639        0.7134
   3  MOLE-FLOW       S-108    MIXED    GLYCEROL              LBMOL/HR      168.4574       168.4574      3.6901-
07
   4  MOLE-FLOW       S-108    MIXED    ACETOL                LBMOL/HR       0.0           0.0           0.0
   5  MOLE-FLOW       S-108    MIXED    WATER                 LBMOL/HR      951.9378       951.9378     -9.2861-
05
   6  MOLE-FLOW       S-108    MIXED    HYDROGEN              LBMOL/HR       0.0           0.0           0.0
   7  MOLE-FLOW       S-108    MIXED    PG                 LBMOL/HR       0.0           0.0           0.0
   8  MOLE-FLOW       S-108    MIXED    N-PROP                LBMOL/HR       0.0           0.0           0.0
   9  MOLE-FLOW       S-108    MIXED    ETHYL-01              LBMOL/HR       0.0           0.0           0.0
  10  MOLE-FLOW       S-108    MIXED    ISO-PROP              LBMOL/HR       0.0           0.0           0.0
  11  MOLE-FLOW       S-108    MIXED    SODIU-01              LBMOL/HR       0.0           0.0           0.0
  12  MOLE-FLOW       S-108    MIXED    METHA-01              LBMOL/HR      17.6687        17.6687      8.1349-
03
  13  PRESSURE        S-108    MIXED                       PSIA          36.8160        36.8160     -9.8423-05
  14  MASS ENTHALPY    S-108    MIXED                          BTU/LB      -4866.9331     -4866.9332      6.7809-05
  15  MOLE-FLOW       S-106    MIXED    GLYCEROL              LBMOL/HR      168.4574       168.4574
4.3773-06
  16  MOLE-FLOW       S-106    MIXED    ACETOL                LBMOL/HR       0.0           0.0           0.0
  17  MOLE-FLOW       S-106    MIXED    WATER                 LBMOL/HR      952.0188       951.9378        0.8508
  18  MOLE-FLOW       S-106    MIXED    HYDROGEN              LBMOL/HR       0.0           0.0           0.0
  19  MOLE-FLOW       S-106    MIXED    PG                 LBMOL/HR       0.0           0.0           0.0
  20  MOLE-FLOW       S-106    MIXED    N-PROP                LBMOL/HR       0.0           0.0           0.0
  21  MOLE-FLOW       S-106    MIXED    ETHYL-01              LBMOL/HR       0.0           0.0           0.0
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 5

                      FLOWSHEET SECTION

 CONVERGENCE BLOCK:  $OLVER01 (CONTINUED)
  22  MOLE-FLOW       S-106    MIXED    ISO-PROP              LBMOL/HR       0.0           0.0           0.0
  23  MOLE-FLOW       S-106    MIXED    SODIU-01              LBMOL/HR       0.0           0.0           0.0
  24  MOLE-FLOW       S-106    MIXED    METHA-01              LBMOL/HR      17.6689        17.6687        0.1111
  25  PRESSURE        S-106    MIXED                       PSIA          42.0000        42.0000        0.0
```

```
 26  MASS ENTHALPY    S-106    MIXED                           BTU/LB      -5003.8462     -5003.7658        -0.1608

                   *** ITERATION HISTORY ***
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 6

                      FLOWSHEET SECTION

 CONVERGENCE BLOCK:  $OLVER01 (CONTINUED)

    TEAR STREAMS AND TEAR VARIABLES:

    ITERATION   MAX-ERR/TOL   STREAM ID     VARIABLE       SUBSTREA COMPONEN ATTRIBUT
ELEMENT
    ---------   -----------   ---------     ---------------- -------- -------- -------- -------
        1     0.1000E+07    S-106         PRESSURE        MIXED
        2     0.1000E+05    S-108         PRESSURE        MIXED
        3      6573.       S-106        MOLE-FLOW       MIXED    METHA-01
        4      6573.       S-108        MOLE-FLOW       MIXED    METHA-01
        5      2606.       S-106        MOLE-FLOW       MIXED    METHA-01
        6      2606.       S-108        MOLE-FLOW       MIXED    METHA-01
        7      1358.       S-106        MOLE-FLOW       MIXED    METHA-01
        8      1358.       S-108        MOLE-FLOW       MIXED    METHA-01
        9      785.3       S-106        MOLE-FLOW       MIXED    METHA-01
       10       785.3       S-108        MOLE-FLOW       MIXED    METHA-01
       11       478.2       S-106        MOLE-FLOW       MIXED    METHA-01
       12       478.2       S-108        MOLE-FLOW       MIXED    METHA-01
       13       448.4       S-106        MOLE-FLOW       MIXED    WATER
       14       448.4       S-108        MOLE-FLOW       MIXED    WATER
       15       283.2       S-106        MOLE-FLOW       MIXED    WATER
       16       283.2       S-108        MOLE-FLOW       MIXED    WATER
       17      -236.2       S-106        MOLE-FLOW       MIXED    WATER
       18      -236.2       S-108        MOLE-FLOW       MIXED    WATER
       19      -159.6       S-106        MOLE-FLOW       MIXED    WATER
       20      -159.6       S-108        MOLE-FLOW       MIXED    WATER
       21      -107.0       S-106        MOLE-FLOW       MIXED    WATER
       22      -107.0       S-108        MOLE-FLOW       MIXED    WATER
       23      -71.40       S-106        MOLE-FLOW       MIXED    WATER
       24      -71.40       S-108        MOLE-FLOW       MIXED    WATER
       25      -47.45       S-106        MOLE-FLOW       MIXED    WATER
       26      -47.45       S-108        MOLE-FLOW       MIXED    WATER
       27      -31.46       S-106        MOLE-FLOW       MIXED    WATER
       28      -31.46       S-108        MOLE-FLOW       MIXED    WATER
       29      -20.82       S-106        MOLE-FLOW       MIXED    WATER
       30      -20.82       S-108        MOLE-FLOW       MIXED    WATER
       31      -13.77       S-106        MOLE-FLOW       MIXED    WATER
       32      -13.77       S-108        MOLE-FLOW       MIXED    WATER
       33       200.2       S-106        MOLE-FLOW       MIXED    WATER
       34       200.2       S-108        MOLE-FLOW       MIXED    WATER
       35       129.5       S-106        MOLE-FLOW       MIXED    WATER
       36       129.5       S-108        MOLE-FLOW       MIXED    WATER
       37       84.36       S-106        MOLE-FLOW       MIXED    WATER
       38       84.36       S-108        MOLE-FLOW       MIXED    WATER
       39       55.20       S-106        MOLE-FLOW       MIXED    WATER
       40       55.20       S-108        MOLE-FLOW       MIXED    WATER
```

```
      41      36.23       S-106        MOLE-FLOW       MIXED    WATER
      42      36.23       S-108        MOLE-FLOW       MIXED    WATER
      43      23.82       S-106        MOLE-FLOW       MIXED    WATER
      44      23.82       S-108        MOLE-FLOW       MIXED    WATER
      45      15.68       S-106        MOLE-FLOW       MIXED    WATER
      46      15.68       S-108        MOLE-FLOW       MIXED    WATER
      47      10.33       S-106        MOLE-FLOW       MIXED    WATER
      48      10.33       S-108        MOLE-FLOW       MIXED    WATER
      49      6.811       S-106        MOLE-FLOW       MIXED    WATER
      50      6.811       S-108        MOLE-FLOW       MIXED    WATER
      51      4.491       S-106        MOLE-FLOW       MIXED    WATER
      52      4.491       S-108        MOLE-FLOW       MIXED    WATER
      53      2.962       S-106        MOLE-FLOW       MIXED    WATER
      54      2.962       S-108        MOLE-FLOW       MIXED    WATER
      55      1.954       S-106        MOLE-FLOW       MIXED    WATER
      56      1.954       S-108        MOLE-FLOW       MIXED    WATER
      57      1.289       S-106        MOLE-FLOW       MIXED    WATER
      58      1.289       S-108        MOLE-FLOW       MIXED    WATER
      59     0.8508       S-106        MOLE-FLOW       MIXED    WATER
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 7

                        FLOWSHEET SECTION

 CONVERGENCE BLOCK:  $OLVER02
 ----------------------------
    Tear Stream  :  S-121      S-119
    Tolerance used:  0.100D-03  0.100D-03
    Trace molefrac:  0.100D-05  0.100D-05

    MAXIT=   70 WAIT   1 ITERATIONS BEFORE ACCELERATING
    QMAX =   0.0     QMIN =  -5.0
    METHOD: WEGSTEIN      STATUS: NOT CONVERGED
    TOTAL NUMBER OF ITERATIONS:    70

    *********************************************************************
    *                                                                   *
    *    BLOCK NOT CONVERGED                                            *
    *                                                                   *
    *    EXCEEDED MAXIMUM NUMBER OF ITERATIONS                          *
    *                                                                   *
    *********************************************************************



                     *** FINAL VALUES ***

VAR#  TEAR STREAM VAR  STREAM   SUBSTREA COMPONEN ATTRIBUT ELEMENT      UNIT
VALUE       PREV VALUE       ERR/TOL
----  --------------  -------- -------- -------- -------- -------- ----------- -----------   ------------   ------------
   1  TOTAL MOLEFLOW   S-121    MIXED                          LBMOL/HR     1063.1236     1063.1301    -6.0587-
02
   2  TOTAL MOLEFLOW   S-119    MIXED                          LBMOL/HR      687.6446      687.6236        0.3051
   3  MOLE-FLOW       S-121    MIXED    GLYCEROL               LBMOL/HR       0.0           0.0           0.0
   4  MOLE-FLOW       S-121    MIXED    ACETOL                 LBMOL/HR       0.0           0.0           0.0
   5  MOLE-FLOW       S-121    MIXED    WATER                  LBMOL/HR      395.0384      395.0385     -3.6307-
```

```
03
  6  MOLE-FLOW       S-121    MIXED    HYDROGEN                LBMOL/HR      494.5852       494.5904       -
0.1047
  7  MOLE-FLOW       S-121    MIXED    PG                   LBMOL/HR      166.1698       166.1698     -2.0683-04
  8  MOLE-FLOW       S-121    MIXED    N-PROP               LBMOL/HR       2.2627         2.2628        -0.4908
  9  MOLE-FLOW       S-121    MIXED    ETHYL-01             LBMOL/HR       0.0            0.0           0.0
 10  MOLE-FLOW       S-121    MIXED    ISO-PROP             LBMOL/HR       4.9886         4.9896        -2.0148
*
 11  MOLE-FLOW       S-121    MIXED    SODIU-01             LBMOL/HR       0.0            0.0           0.0
 12  MOLE-FLOW       S-121    MIXED    METHA-01             LBMOL/HR     7.8826-02      7.8827-02     -
1.7315-02
 13  PRESSURE        S-121    MIXED                         PSIA          566.0365       566.0365      3.6707-04
 14  MASS ENTHALPY    S-121    MIXED                        BTU/LB      -3269.7542     -3269.7482     -1.8293-02
 15  MOLE-FLOW       S-119    MIXED    GLYCEROL             LBMOL/HR       0.0            0.0           0.0
 16  MOLE-FLOW       S-119    MIXED    ACETOL               LBMOL/HR       0.0            0.0           0.0
 17  MOLE-FLOW       S-119    MIXED    WATER                LBMOL/HR      17.0797        17.0791        0.3245
 18  MOLE-FLOW       S-119    MIXED    HYDROGEN             LBMOL/HR      665.5880       665.5687
0.2907
 19  MOLE-FLOW       S-119    MIXED    PG                   LBMOL/HR       0.2401         0.2401        0.6432
 20  MOLE-FLOW       S-119    MIXED    N-PROP               LBMOL/HR       0.9994         0.9993        1.1812
*
 21  MOLE-FLOW       S-119    MIXED    ETHYL-01             LBMOL/HR       0.0            0.0           0.0
 22  MOLE-FLOW       S-119    MIXED    ISO-PROP             LBMOL/HR       3.7261         3.7252        2.5376
*
 23  MOLE-FLOW       S-119    MIXED    SODIU-01             LBMOL/HR       0.0            0.0           0.0
 24  MOLE-FLOW       S-119    MIXED    METHA-01             LBMOL/HR     1.1240-02      1.1240-02
0.4400
 25  PRESSURE        S-119    MIXED                         PSIA          600.0000       600.0000       0.0
 26  MASS ENTHALPY    S-119    MIXED                        BTU/LB       -933.0325      -933.0067      -0.2767

                    *** ITERATION HISTORY ***
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 8

                       FLOWSHEET SECTION

 CONVERGENCE BLOCK:  $OLVER02 (CONTINUED)

    TEAR STREAMS AND TEAR VARIABLES:

    ITERATION   MAX-ERR/TOL   STREAM ID     VARIABLE       SUBSTREA COMPONEN ATTRIBUT
ELEMENT
    ---------   -----------   ---------     ---------------- -------- -------- -------- -------
         1      0.1000E+07    S-121         PRESSURE        MIXED
         2      0.1065E+05    S-121         TOTAL MOLEFLOW   MIXED
         3     -0.1585E+05    S-119         MASS ENTHALPY    MIXED
         4       9985.        S-121         MOLE-FLOW       MIXED    HYDROGEN
         5      0.5834E+05    S-119         MOLE-FLOW       MIXED    N-PROP
         6       7194.        S-121         MOLE-FLOW       MIXED    ISO-PROP
         7       6614.        S-119         MOLE-FLOW       MIXED    ISO-PROP
         8       3313.        S-121         MOLE-FLOW       MIXED    ISO-PROP
         9       3234.        S-119         MOLE-FLOW       MIXED    ISO-PROP
        10       1945.        S-121         MOLE-FLOW       MIXED    ISO-PROP
        11       1936.        S-119         MOLE-FLOW       MIXED    ISO-PROP
        12       1263.        S-121         MOLE-FLOW       MIXED    ISO-PROP
```

```
 13    1257.     S-119     MOLE-FLOW     MIXED   ISO-PROP
 14    858.2     S-121     MOLE-FLOW     MIXED   ISO-PROP
 15    846.1     S-119     MOLE-FLOW     MIXED   ISO-PROP
 16    594.0     S-121     MOLE-FLOW     MIXED   ISO-PROP
 17    586.1     S-119     MOLE-FLOW     MIXED   ISO-PROP
 18    419.1     S-121     MOLE-FLOW     MIXED   ISO-PROP
 19    411.9     S-119     MOLE-FLOW     MIXED   ISO-PROP
 20    298.2     S-121     MOLE-FLOW     MIXED   ISO-PROP
 21    299.5     S-119     MOLE-FLOW     MIXED   ISO-PROP
 22    218.7     S-121     MOLE-FLOW     MIXED   ISO-PROP
 23    221.3     S-119     MOLE-FLOW     MIXED   ISO-PROP
 24    162.6     S-121     MOLE-FLOW     MIXED   ISO-PROP
 25    152.5     S-119     MOLE-FLOW     MIXED   ISO-PROP
 26    112.6     S-121     MOLE-FLOW     MIXED   ISO-PROP
 27    114.7     S-119     MOLE-FLOW     MIXED   ISO-PROP
 28    84.91     S-121     MOLE-FLOW     MIXED   ISO-PROP
 29    92.68     S-119     MOLE-FLOW     MIXED   ISO-PROP
 30    68.76     S-121     MOLE-FLOW     MIXED   ISO-PROP
 31    64.77     S-119     MOLE-FLOW     MIXED   ISO-PROP
 32    48.13     S-121     MOLE-FLOW     MIXED   ISO-PROP
 33   -42.06     S-119     MOLE-FLOW     MIXED   WATER
 34    30.77     S-121     MOLE-FLOW     MIXED   ISO-PROP
 35    34.70     S-119     MOLE-FLOW     MIXED   ISO-PROP
 36    25.84     S-121     MOLE-FLOW     MIXED   ISO-PROP
 37    25.36     S-119     MOLE-FLOW     MIXED   ISO-PROP
 38    18.90     S-121     MOLE-FLOW     MIXED   ISO-PROP
 39    18.19     S-119     MOLE-FLOW     MIXED   ISO-PROP
 40    13.56     S-121     MOLE-FLOW     MIXED   ISO-PROP
 41    13.34     S-119     MOLE-FLOW     MIXED   ISO-PROP
 42    9.949     S-121     MOLE-FLOW     MIXED   ISO-PROP
 43    9.575     S-119     MOLE-FLOW     MIXED   ISO-PROP
 44    7.144     S-121     MOLE-FLOW     MIXED   ISO-PROP
 45    6.780     S-119     MOLE-FLOW     MIXED   ISO-PROP
 46    5.060     S-121     MOLE-FLOW     MIXED   ISO-PROP
 47    4.609     S-119     MOLE-FLOW     MIXED   ISO-PROP
 48    3.441     S-121     MOLE-FLOW     MIXED   ISO-PROP
 49    3.048     S-119     MOLE-FLOW     MIXED   ISO-PROP
 50    46.01     S-119     MOLE-FLOW     MIXED   WATER
 51   -44.90     S-119     MOLE-FLOW     MIXED   WATER
 52   -9.995     S-121     MOLE-FLOW     MIXED   N-PROP
 53   -4.637     S-119     MOLE-FLOW     MIXED   N-PROP
 54    10.84     S-119     MOLE-FLOW     MIXED   PG
 55   -3.499     S-119     MOLE-FLOW     MIXED   METHA-01
 56    2.375     S-119     MOLE-FLOW     MIXED   ISO-PROP
 57    1.774     S-121     MOLE-FLOW     MIXED   ISO-PROP
 58    1.939     S-119     MOLE-FLOW     MIXED   ISO-PROP
 59    1.448     S-121     MOLE-FLOW     MIXED   ISO-PROP
 60    46.09     S-119     MOLE-FLOW     MIXED   WATER
 61   -43.64     S-119     MOLE-FLOW     MIXED   WATER
 62   -9.446     S-121     MOLE-FLOW     MIXED   N-PROP
 63   -4.204     S-119     MOLE-FLOW     MIXED   ISO-PROP
 64    7.608     S-119     MOLE-FLOW     MIXED   N-PROP
 65   -6.505     S-119     MOLE-FLOW     MIXED   N-PROP
 66    4.037     S-119     MOLE-FLOW     MIXED   ISO-PROP
```

```
      67     -3.626       S-119        MOLE-FLOW       MIXED    ISO-PROP
      68      3.239       S-119        MOLE-FLOW       MIXED    ISO-PROP
      69     -2.698       S-119        MOLE-FLOW       MIXED    ISO-PROP
      70      2.538       S-119        MOLE-FLOW       MIXED    ISO-PROP
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 9

                       FLOWSHEET SECTION

 CONVERGENCE BLOCK:  $OLVER03
 ----------------------------
    SPECS: DS-1
    MAXIT=   30 STEP-SIZE=    1.0000    % OF RANGE
            MAX-STEP=       100.    % OF RANGE
            XTOL=       1.000000E-08
    THE NEW ALGORITHM WAS USED WITH BRACKETING=NO
    METHOD: SECANT        STATUS: CONVERGED
    TOTAL NUMBER OF ITERATIONS:   152
    NUMBER OF ITERATIONS ON LAST OUTER LOOP:     1

                    *** FINAL VALUES ***


VAR#  MANIPUL/TEAR-VAR VARIABLE DESCRIPTION                          UNIT        VALUE      PREV
VALUE       ERR/TOL
----  ---------------- ------------------------                 ----------- ------------   ------------   ------------
  1  TOTAL MOLEFLOW   S-117.MIXED                            LBMOL/HR     171.8376      171.8376        0.3454

                    *** ITERATION HISTORY ***

    DESIGN-SPEC ID: DS-1
    ITERATED:  TOTAL MOLEFLOW IN STREAM S-117 SUBSTREAM MIXED

    ITERATION  VARIABLE        ERROR         ERR/TOL
    ---------  --------        -----         -------
        1     171.8          0.3454E-01    0.3454

 CONVERGENCE BLOCK:  $OLVER04
 ----------------------------
    SPECS: DS-2
    MAXIT=   30 STEP-SIZE=    1.0000    % OF RANGE
            MAX-STEP=       100.    % OF RANGE
            XTOL=       1.000000E-08
    THE NEW ALGORITHM WAS USED WITH BRACKETING=NO
    METHOD: SECANT        STATUS: CONVERGED
    TOTAL NUMBER OF ITERATIONS:   127
    NUMBER OF ITERATIONS ON LAST OUTER LOOP:     1

                    *** FINAL VALUES ***


VAR#  MANIPUL/TEAR-VAR VARIABLE DESCRIPTION                          UNIT        VALUE      PREV
VALUE       ERR/TOL
----  ---------------- ------------------------                 ----------- ------------   ------------   ------------
  1  TOTAL MOLEFLOW   S-102.MIXED                            LBMOL/HR     298.8769      298.8769        0.4337
```

```
                *** ITERATION HISTORY ***
```

```
                          FLOWSHEET SECTION

CONVERGENCE BLOCK:  $OLVER04 (CONTINUED)

   DESIGN-SPEC ID: DS-2
   ITERATED:  TOTAL MOLEFLOW IN STREAM S-102 SUBSTREAM MIXED

   ITERATION  VARIABLE        ERROR         ERR/TOL
   ---------  --------        -----         -------
       1      298.9          0.4337E-02     0.4337

COMPUTATIONAL SEQUENCE
----------------------

SEQUENCE USED WAS:
  $OLVER01 D-101 HX-101 FSPLIT P-102
  |  $OLVER04 M-102
  |  (RETURN $OLVER04)
  |  S-101 P-101 H-101
  (RETURN $OLVER01)
  P-100
  *$OLVER02 F-101 *HX-102 F-102 *HX-103 R-101 C-102 V-101 CP-101
  |  $OLVER03 T-101 M-101
  |  (RETURN $OLVER03)
  (RETURN *$OLVER02)
  M-103 VALVE D-102 C-103

OVERALL FLOWSHEET BALANCE
-------------------------

                   ***  MASS AND ENERGY BALANCE  ***
                       IN          OUT       GENERATION   RELATIVE DIFF.
 CONVENTIONAL COMPONENTS
       (LBMOL/HR)
   GLYCEROL          168.457      0.286352E-03  -168.457      0.468770E-09
   ACETOL            0.00000       0.00000       0.00000       0.00000
   WATER             460.344       631.246       170.983      0.128936E-03
   HYDROGEN          171.838      0.839947      -170.983      0.824471E-04
   PG                0.00000       165.930       165.930      0.723638E-07
   N-PROP            0.00000       1.26342       1.26342      0.552076E-05
   ETHYL-01          0.00000       0.00000       0.00000       0.00000
   ISO-PROP          0.00000       1.26348       1.26342     -0.474970E-04
   SODIU-01          13.2729       13.2729       0.00000       0.00000
   METHA-01          6.05218       6.05197       0.00000      0.348543E-04
 TOTAL BALANCE
 MOLE(LBMOL/HR)        819.963       819.868       0.00000      0.116746E-03
 MASS(LB/HR   )        25123.2       25121.7                    0.596787E-04
 ENTHALPY(BTU/HR  )   -0.107053E+09 -0.116457E+09               0.807452E-01
```

```
                  PHYSICAL PROPERTIES SECTION

 COMPONENTS
 ----------

  ID      TYPE  FORMULA       NAME OR ALIAS                   REPORT NAME
  GLYCEROL C    C3H8O3        C3H8O3                          GLYCEROL
  ACETOL   C    C3H6O2-D1     C3H6O2-D1                       ACETOL
  WATER    C    H2O           H2O                             WATER
  HYDROGEN C    H2            H2                              HYDROGEN
  PG       C    C3H8O2-2      C3H8O2-2                        PG
  N-PROP   C    C3H8O-1       C3H8O-1                         N-PROP
  ETHYL-01 C    C2H6O2        C2H6O2                          ETHYL-01
  ISO-PROP C    C3H8O-2       C3H8O-2                         ISO-PROP
  SODIU-01 C    NACL          NACL                            SODIU-01
  METHA-01 C    CH4O          CH4O                            METHA-01

  LISTID        SUPERCRITICAL COMPONENT LIST
  HC-1          HYDROGEN
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 12

                     U-O-S BLOCK SECTION

 BLOCK:  C-102    MODEL: HEATER
 ------------------------------
  INLET STREAM:          S-127
  OUTLET STREAM:         S-128
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                ***  MASS AND ENERGY BALANCE  ***
                              IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)           888.498        888.498        0.00000
     MASS(LB/HR   )           12004.1        12004.1        0.00000
     ENTHALPY(BTU/HR  )      -0.443889E+08   -0.518861E+08    0.144493

                  ***  INPUT DATA  ***
  TWO    PHASE  TP  FLASH
  SPECIFIED TEMPERATURE              F                   225.000
  PRESSURE DROP                      PSI                 5.00000
  MAXIMUM NO. ITERATIONS                                      30
  CONVERGENCE TOLERANCE                                  0.000100000



                   ***  RESULTS  ***
  OUTLET TEMPERATURE    F                              225.00
  OUTLET PRESSURE       PSIA                           553.28
  HEAT DUTY             BTU/HR                       -0.74972E+07
  OUTLET VAPOR FRACTION                                0.58054
  PRESSURE-DROP CORRELATION PARAMETER                  0.27858E+06
```

```
  V-L PHASE EQUILIBRIUM :

    COMP         F(I)        X(I)        Y(I)        K(I)
    WATER        0.36651     0.82793     0.33113E-01 0.39995E-01
    HYDROGEN     0.55587     0.36804E-03 0.95724      2600.8
    PG           0.70286E-01 0.16692     0.46548E-03 0.27886E-02
    N-PROP       0.21637E-02 0.24765E-02 0.19376E-02 0.78236
    ISO-PROP     0.50959E-02 0.21508E-02 0.72239E-02  3.3586
    METHA-01     0.77815E-04 0.15535E-03 0.21791E-04 0.14027
 ASPEN PLUS   PLAT: WIN32    VER: 24.0                 04/11/2011  PAGE 13

                         U-O-S BLOCK SECTION

 BLOCK:  C-103    MODEL: HEATER
 ------------------------------
  INLET STREAM:         S-134
  OUTLET STREAM:        S-135
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                  ***  MASS AND ENERGY BALANCE  ***
                               IN           OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)           164.300       164.300       0.00000
     MASS(LB/HR   )          12379.8       12379.8        0.00000
     ENTHALPY(BTU/HR  )     -0.324322E+08  -0.350141E+08   0.737392E-01

                  ***  INPUT DATA  ***
  TWO    PHASE  TP  FLASH
  SPECIFIED TEMPERATURE          F                     90.0000
  PRESSURE DROP                  PSI                    5.00000
  MAXIMUM NO. ITERATIONS                                   30
  CONVERGENCE TOLERANCE                                  0.000100000




                  ***  RESULTS  ***
  OUTLET TEMPERATURE    F                               90.000
  OUTLET PRESSURE       PSIA                            15.000
  HEAT DUTY             BTU/HR                      -0.25819E+07
  OUTLET VAPOR FRACTION                                  0.0000
  PRESSURE-DROP CORRELATION PARAMETER                      0.13144E+08




  V-L PHASE EQUILIBRIUM :

    COMP         F(I)        X(I)        Y(I)        K(I)
    WATER        0.12859E-01 0.12859E-01 0.92786     0.12296
    PG           0.98714     0.98714     0.72136E-01 0.12451E-03
    N-PROP       0.22134E-07 0.22134E-07 0.17198E-05 0.13239
    ISO-PROP     0.55639E-11 0.55639E-11 0.21457E-08 0.65712
    METHA-01     0.99242E-08 0.99242E-08 0.14898E-05 0.25580
 ASPEN PLUS   PLAT: WIN32    VER: 24.0                 04/11/2011  PAGE 14
```

```
                    U-O-S BLOCK SECTION

BLOCK:  CP-101   MODEL: COMPR
----------------------------
 INLET STREAM:          S-130
 OUTLET STREAM:         S-131
 PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

               ***  MASS AND ENERGY BALANCE  ***
                         IN            OUT        RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)           515.807        515.807         0.00000
    MASS(LB/HR   )          1605.65        1605.65        0.141608E-15
    ENTHALPY(BTU/HR  )      -0.181851E+07   -0.174555E+07   -0.401195E-01

                   ***  INPUT DATA  ***

 ISENTROPIC CENTRIFUGAL COMPRESSOR
  OUTLET PRESSURE  PSIA                              600.000
  ISENTROPIC EFFICIENCY                               0.80000
  MECHANICAL EFFICIENCY                               1.00000

                   ***  RESULTS  ***

  INDICATED  HORSEPOWER REQUIREMENT  HP                 28.6734
  BRAKE      HORSEPOWER REQUIREMENT  HP                 28.6734
  NET WORK REQUIRED                 HP                28.6734
  POWER LOSSES                   HP                 0.0
  ISENTROPIC HORSEPOWER REQUIREMENT  HP                 22.9387
  CALCULATED OUTLET TEMP  F                          244.417
  ISENTROPIC TEMPERATURE  F                          240.520
  EFFICIENCY (POLYTR/ISENTR) USED                        0.80000
  OUTLET VAPOR FRACTION                              1.00000
  HEAD DEVELOPED,       FT-LBF/LB                 28,286.7
  MECHANICAL EFFICIENCY USED                           1.00000
  INLET HEAT CAPACITY RATIO                          1.38825
  INLET VOLUMETRIC FLOW RATE , CUFT/HR                6,949.72
  OUTLET VOLUMETRIC FLOW RATE, CUFT/HR                6,597.33
  INLET  COMPRESSIBILITY FACTOR                        1.01458
  OUTLET COMPRESSIBILITY FACTOR                        1.01566
  AV. ISENT. VOL. EXPONENT                           1.40856
  AV. ISENT. TEMP EXPONENT                           1.38215
  AV. ACTUAL VOL. EXPONENT                           1.55791
  AV. ACTUAL TEMP EXPONENT                           1.52663
ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 15

                    U-O-S BLOCK SECTION

BLOCK:  CP-101   MODEL: COMPR (CONTINUED)

BLOCK:  D-101    MODEL: RADFRAC
-------------------------------
  INLETS   - S-108    STAGE   4
  OUTLETS  - S-109    STAGE   1
```

```
          S-114    STAGE   6
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

               ***  MASS AND ENERGY BALANCE  ***
                          IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          1138.06        1138.06        0.00000
     MASS(LB/HR   )          33229.6        33229.6      -0.217931E-11
     ENTHALPY(BTU/HR  )     -0.161726E+09   -0.162466E+09    0.455082E-02
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 16

                      U-O-S BLOCK SECTION

BLOCK:  D-101    MODEL: RADFRAC (CONTINUED)



                 **********************
                 ****  INPUT DATA  ****
                 **********************

  ****   INPUT PARAMETERS   ****

   NUMBER OF STAGES                                  6
   ALGORITHM OPTION                                  STANDARD
   ABSORBER OPTION                                   NO
   INITIALIZATION OPTION                             STANDARD
   HYDRAULIC PARAMETER CALCULATIONS                  NO
   INSIDE LOOP CONVERGENCE METHOD                    BROYDEN
   DESIGN SPECIFICATION METHOD                       NESTED
   MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS                25
   MAXIMUM NO. OF INSIDE LOOP ITERATIONS                 10
   MAXIMUM NUMBER OF FLASH ITERATIONS                    30
   FLASH TOLERANCE                                   0.000100000
   OUTSIDE LOOP CONVERGENCE TOLERANCE                0.000100000

  ****   COL-SPECS   ****

   MOLAR VAPOR DIST / TOTAL DIST                     0.0
   MOLAR REFLUX RATIO                                0.20000
   MOLAR BOTTOMS RATE          LBMOL/HR              375.500

  ****    PROFILES   ****

   P-SPEC         STAGE   1  PRES, PSIA              20.0000

                  *******************
                  ****  RESULTS  ****
                  *******************


  ***   COMPONENT SPLIT FRACTIONS   ***

                      OUTLET STREAMS
```

```
                  --------------
             S-109       S-114
   COMPONENT:
   GLYCEROL    .49995E-05   1.0000
   WATER       .78257       .21743
   METHA-01    .99617       .38252E-02
```

```
                        U-O-S BLOCK SECTION

 BLOCK:  D-101    MODEL: RADFRAC (CONTINUED)


  ***    SUMMARY OF KEY RESULTS    ***

   TOP STAGE TEMPERATURE         F                    221.380
   BOTTOM STAGE TEMPERATURE      F                    247.890
   TOP STAGE LIQUID FLOW         LBMOL/HR             152.513
   BOTTOM STAGE LIQUID FLOW      LBMOL/HR             375.500
   TOP STAGE VAPOR FLOW          LBMOL/HR               0.0
   BOILUP VAPOR FLOW             LBMOL/HR             896.933
   MOLAR REFLUX RATIO                                   0.20000
   MOLAR BOILUP RATIO                                   2.38864
   CONDENSER DUTY (W/O SUBCOOL)  BTU/HR              -0.164793+08
   REBOILER DUTY                 BTU/HR               0.157399+08

  ****   MAXIMUM FINAL RELATIVE ERRORS   ****

   DEW POINT                     0.37845E-06  STAGE=  5
   BUBBLE POINT                  0.14269E-05  STAGE=  5
   COMPONENT MASS BALANCE        0.92840E-06  STAGE=  2 COMP=GLYCEROL
   ENERGY BALANCE                0.93821E-06  STAGE=  1


  ****    PROFILES   ****

  **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
           FROM THE STAGE INCLUDING ANY SIDE PRODUCT.

                              ENTHALPY
 STAGE TEMPERATURE   PRESSURE          BTU/LBMOL         HEAT DUTY
     F          PSIA          LIQUID       VAPOR       BTU/HR

   1   221.38       20.000     -0.12036E+06  -99448.      -.16479+08
   2   229.97       20.000     -0.12067E+06 -0.10235E+06
   3   230.24       20.000     -0.12096E+06 -0.10241E+06
   4   233.48       20.000     -0.14016E+06 -0.10245E+06
   5   234.16       20.000     -0.14034E+06 -0.10270E+06
   6   247.89       20.000     -0.18824E+06 -0.10273E+06   .15740+08

 STAGE     FLOW RATE              FEED RATE             PRODUCT RATE
        LBMOL/HR               LBMOL/HR              LBMOL/HR
    LIQUID     VAPOR      LIQUID    VAPOR    MIXED      LIQUID    VAPOR
   1  915.1      0.000                          762.5639
```

```
  2  153.1      915.1
  3  151.7      915.6                 17.2337
  4  1278.      897.0      1120.8301
  5  1272.      902.3
  6  375.5      896.9                                375.5000
ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 18

                         U-O-S BLOCK SECTION

BLOCK:  D-101    MODEL: RADFRAC (CONTINUED)

   ****  MASS FLOW PROFILES  ****

STAGE     FLOW RATE                 FEED RATE              PRODUCT RATE
          LB/HR                   LB/HR                  LB/HR
     LIQUID      VAPOR       LIQUID     VAPOR    MIXED       LIQUID     VAPOR
  1 0.1678E+05  0.000                               .13985+05
  2  2764.     0.1678E+05
  3  2760.     0.1675E+05             329.1384
  4 0.3558E+05 0.1642E+05  .32900+05
  5 0.3548E+05 0.1634E+05
  6 0.1924E+05 0.1623E+05                                .19245+05

                    ****   MOLE-X-PROFILE     ****
  STAGE     GLYCEROL      WATER        METHA-01
     1    0.11044E-05   0.97692       0.23082E-01
     2    0.11364E-03   0.99763       0.22605E-02
     3    0.21073E-02   0.99595       0.19438E-02
     4    0.13209       0.86465       0.32605E-02
     5    0.13306       0.86615       0.79037E-03
     6    0.44862       0.55120       0.17999E-03

                    ****   MOLE-Y-PROFILE     ****
  STAGE     GLYCEROL      WATER        METHA-01
     1    0.73210E-08   0.81160       0.18840
     2    0.11044E-05   0.97692       0.23082E-01
     3    0.19916E-04   0.98038       0.19601E-01
     4    0.35090E-03   0.98115       0.18501E-01
     5    0.36087E-03   0.99510       0.45424E-02
     6    0.94577E-03   0.99801       0.10459E-02

                    ****   K-VALUES           ****
  STAGE     GLYCEROL      WATER        METHA-01
     1    0.66287E-02   0.83078        8.1622
     2    0.97191E-02   0.97924        10.211
     3    0.94510E-02   0.98437        10.084
     4    0.26566E-02    1.1347        5.6743
     5    0.27122E-02    1.1489        5.7473
     6    0.21082E-02    1.8106        5.8109

                    ****   MASS-X-PROFILE     ****
  STAGE     GLYCEROL      WATER        METHA-01
     1    0.55463E-05   0.95967       0.40328E-01
     2    0.57963E-03   0.99541       0.40115E-02
```

```
    3   0.10664E-01  0.98591      0.34225E-02
    4   0.43685      0.55939      0.37518E-02
    5   0.43947      0.55962      0.90826E-03
    6   0.80614      0.19375      0.11253E-03
```

```
                       U-O-S BLOCK SECTION

BLOCK:  D-101    MODEL: RADFRAC (CONTINUED)

                   ****   MASS-Y-PROFILE     ****
  STAGE     GLYCEROL      WATER        METHA-01
    1   0.32638E-07  0.70778      0.29222
    2   0.55463E-05  0.95967      0.40328E-01
    3   0.10027E-03  0.96556      0.34336E-01
    4   0.17658E-02  0.96584      0.32392E-01
    5   0.18356E-02  0.99013      0.80389E-02
    6   0.48122E-02  0.99334      0.18515E-02

BLOCK:  D-102    MODEL: RADFRAC
-------------------------------
   INLETS   - S-133    STAGE  10
   OUTLETS  - S-137    STAGE   1
              S-136    STAGE   1
              S-134    STAGE  16
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                            IN             OUT       RELATIVE DIFF.
   TOTAL BALANCE
      MOLE(LBMOL/HR)           547.323        547.323      -0.207714E-15
      MASS(LB/HR   )           19591.2        19591.2      -0.928471E-15
      ENTHALPY(BTU/HR  )      -0.781100E+08   -0.795924E+08    0.186258E-01
```

```
                       U-O-S BLOCK SECTION

BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)



                   **********************
                   ****  INPUT DATA  ****
                   **********************

  ****   INPUT PARAMETERS   ****

   NUMBER OF STAGES                                  16
   ALGORITHM OPTION                                STANDARD
   INITIALIZATION OPTION                             STANDARD
   HYDRAULIC PARAMETER CALCULATIONS                    NO
   INSIDE LOOP CONVERGENCE METHOD                    NEWTON
   DESIGN SPECIFICATION METHOD                     NESTED
   MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS              25
```

```
   MAXIMUM NO. OF INSIDE LOOP ITERATIONS                 10
   MAXIMUM NUMBER OF FLASH ITERATIONS                    30
   FLASH TOLERANCE                              0.000100000
   OUTSIDE LOOP CONVERGENCE TOLERANCE                    0.000100000

  ****   COL-SPECS   ****

   MOLAR REFLUX RATIO                             0.13000
   MOLAR BOTTOMS RATE           LBMOL/HR              164.300
   CONDENSER TEMPERATURE         F                    130.000

  ****    PROFILES   ****

   P-SPEC         STAGE   1  PRES, PSIA                 20.0000

                  *******************
                  ****  RESULTS  ****
                  *******************


  ***   COMPONENT SPLIT FRACTIONS   ***

                    OUTLET STREAMS
                    --------------
            S-137       S-136       S-134
   COMPONENT:
   WATER      .85286E-03   .99356      .55898E-02
   HYDROGEN    .99992      .83472E-04   0.0000
   PG         .53556E-05   .22549E-01   .97745
   N-PROP      .72514      .27486      .28784E-05
```

```
BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)

  ***   COMPONENT SPLIT FRACTIONS   ***

                    OUTLET STREAMS
                    --------------
            S-137       S-136       S-134
   COMPONENT:
   ISO-PROP    .96809      .31911E-01   .72352E-09
   METHA-01    .12954E-01   .98702      .24125E-04


  ***    SUMMARY OF KEY RESULTS    ***

   TOP STAGE TEMPERATURE         F                    130.000
   BOTTOM STAGE TEMPERATURE       F                   364.027
   TOP STAGE LIQUID FLOW         LBMOL/HR              49.7930
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR              164.300
   TOP STAGE VAPOR FLOW           LBMOL/HR               3.30330
   BOILUP VAPOR FLOW            LBMOL/HR              252.798
```

```
   MOLAR REFLUX RATIO                              0.13000
   MOLAR BOILUP RATIO                              1.53864
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR          -8,588,640.
   REBOILER DUTY                 BTU/HR          7,106,170.

  ****   MAXIMUM FINAL RELATIVE ERRORS   ****

   DEW POINT                    0.33817E-05  STAGE= 15
   BUBBLE POINT                 0.52790E-05  STAGE=  1
   COMPONENT MASS BALANCE        0.72629E-08  STAGE=  5 COMP=ISO-PROP
   ENERGY BALANCE               0.44363E-06  STAGE= 14

 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 22

                         U-O-S BLOCK SECTION

 BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)

  ****    PROFILES   ****

  **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
        FROM THE STAGE INCLUDING ANY SIDE PRODUCT.

                              ENTHALPY
 STAGE TEMPERATURE   PRESSURE           BTU/LBMOL         HEAT DUTY
     F           PSIA          LIQUID       VAPOR       BTU/HR

   1   130.00       20.000     -0.12347E+06  -83091.      -.85886+07
   2   231.02       20.000     -0.12239E+06 -0.10332E+06
   3   231.13       20.000     -0.12289E+06 -0.10343E+06
   4   231.20       20.000     -0.12323E+06 -0.10349E+06
   8   231.41       20.000     -0.12462E+06 -0.10363E+06
   9   231.52       20.000     -0.12591E+06 -0.10369E+06
  10   233.20       20.000     -0.14789E+06 -0.10399E+06
  11   233.32       20.000     -0.14788E+06 -0.10398E+06
  12   233.34       20.000     -0.14790E+06 -0.10398E+06
  15   316.56       20.000     -0.19288E+06 -0.12300E+06
  16   364.03       20.000     -0.19740E+06 -0.16184E+06   .71062+07

 STAGE     FLOW RATE                FEED RATE             PRODUCT RATE
        LBMOL/HR                 LBMOL/HR              LBMOL/HR
    LIQUID     VAPOR      LIQUID    VAPOR    MIXED      LIQUID    VAPOR
   1  429.5     3.303                          379.7197    3.3033
   2  55.17     432.8
   3  55.06     438.2
   4  54.99     438.1
   8  54.64     437.8
   9  54.02     437.7              91.8493
  10  511.4      345.2      455.4736
  11  511.5      347.1
  12  511.4      347.2
  15  417.1      285.0
  16  164.3      252.8                                164.3000
```

```
   ****  MASS FLOW PROFILES  ****

 STAGE     FLOW RATE                FEED RATE             PRODUCT RATE
          LB/HR                   LB/HR                  LB/HR
      LIQUID      VAPOR       LIQUID     VAPOR    MIXED       LIQUID     VAPOR
   1  8003.       136.2                              7075.3126  136.1601
   2  1063.       8139.
   3  1081.       8274.
   4  1093.       8292.
   8  1142.       8336.
   9  1179.       8353.           1803.4776
  10 0.1898E+05  6587.      .17788+05
  11 0.1897E+05  6596.
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 23

                           U-O-S BLOCK SECTION

 BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)

   ****  MASS FLOW PROFILES  ****

 STAGE     FLOW RATE                FEED RATE             PRODUCT RATE
          LB/HR                   LB/HR                  LB/HR
      LIQUID      VAPOR       LIQUID     VAPOR    MIXED       LIQUID     VAPOR
  12 0.1898E+05  6593.
  15 0.2930E+05  9912.
  16 0.1238E+05 0.1692E+05                              .12380+05

                   ****   MOLE-X-PROFILE     ****
   STAGE     WATER        HYDROGEN       PG           N-PROP        ISO-PROP
      1    0.98895       0.18464E-06   0.98535E-02   0.91452E-03   0.10618E-03
      2    0.97846       0.68408E-08   0.21505E-01   0.98687E-05   0.16374E-05
      3    0.97215       0.73785E-08   0.27815E-01   0.11224E-04   0.19598E-05
      4    0.96779       0.78268E-08   0.32174E-01   0.12617E-04   0.22329E-05
      8    0.95039       0.97553E-08   0.49569E-01   0.19399E-04   0.36102E-05
      9    0.93447       0.11705E-07   0.65473E-01   0.27469E-04   0.53297E-05
     10     0.67126       0.14078E-10   0.32845       0.22769E-03   0.27967E-04
     11     0.67151       0.66732E-15   0.32843       0.46357E-04   0.16307E-05
     12     0.67128       0.31658E-19   0.32871       0.94426E-05   0.95170E-07
     15     0.10060        0.0000       0.89940       0.15563E-06   0.72542E-10
     16     0.12859E-01   0.95267E-22   0.98714       0.22134E-07   0.55639E-11

                   ****   MOLE-X-PROFILE     ****
   STAGE     METHA-01
      1    0.17568E-03
      2    0.20983E-04
      3    0.19715E-04
      4    0.20420E-04
      8    0.23301E-04
      9    0.25804E-04
     10     0.33827E-04
     11     0.14080E-04
     12     0.58571E-05
     15     0.11739E-06
```

```
  16    0.99242E-08

                   ****   MOLE-Y-PROFILE     ****
 STAGE     WATER        HYDROGEN      PG           N-PROP       ISO-PROP
    1    0.97583E-01   0.25425       0.26902E-03   0.27734       0.37029
    2    0.98215       0.19407E-02   0.97804E-02   0.30243E-02   0.29314E-02
    3    0.98091       0.19168E-02   0.11248E-01   0.28845E-02   0.28836E-02
    4    0.98012       0.19173E-02   0.12039E-01   0.28853E-02   0.28843E-02
    8    0.97817       0.19186E-02   0.13980E-01   0.28880E-02   0.28864E-02
    9    0.97741       0.19192E-02   0.14739E-01   0.28892E-02   0.28873E-02
   10    0.98091       0.43733E-06   0.16624E-01   0.16420E-02   0.70432E-03
   11    0.98288       0.20742E-10   0.16693E-01   0.33545E-03   0.41205E-04
   12    0.98320       0.98310E-15   0.16713E-01   0.68283E-04   0.24024E-05
   15    0.71131        0.0000       0.28869       0.10907E-05   0.10955E-08
   16    0.15763       0.43055E-18   0.84237       0.24239E-06   0.11607E-09
ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 24

                         U-O-S BLOCK SECTION

BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)

                   ****   MOLE-Y-PROFILE     ****
 STAGE     METHA-01
    1    0.26504E-03
    2    0.17636E-03
    3    0.15688E-03
    4    0.15675E-03
    8    0.15717E-03
    9    0.15733E-03
   10    0.11946E-03
   11    0.49834E-04
   12    0.20738E-04
   15    0.13554E-05
   16    0.18723E-06

                   ****   K-VALUES          ****
 STAGE     WATER        HYDROGEN      PG           N-PROP       ISO-PROP
    1    0.98673E-01   0.13770E+07   0.27302E-01    303.26       3487.3
    2     1.0038       0.28369E+06   0.45479       306.45       1790.3
    3     1.0090       0.25979E+06   0.40438       257.00       1471.3
    4     1.0127       0.24496E+06   0.37417       228.69       1291.7
    8     1.0292       0.19668E+06   0.28204       148.88       799.55
    9     1.0459       0.16396E+06   0.22512       105.18       541.75
   10      1.4613       31064.      0.50612E-01    7.2116       25.184
   11      1.4637       31082.      0.50828E-01    7.2362       25.267
   12      1.4647       31053.      0.50844E-01    7.2314       25.244
   15      7.0704       6467.1      0.32098       7.0087       15.102
   16      12.259       4519.5      0.85334       10.951       20.862

                   ****   K-VALUES          ****
 STAGE     METHA-01
    1     1.5087
    2     8.4048
    3     7.9573
```

```
    4     7.6762
    8     6.7452
    9     6.0971
   10      3.5313
   11      3.5394
   12      3.5407
   15      11.547
   16      18.866

                   ****   MASS-X-PROFILE     ****
  STAGE     WATER        HYDROGEN      PG           N-PROP       ISO-PROP
    1    0.95616      0.19976E-07   0.40241E-01   0.29496E-02   0.34246E-03
    2    0.91499      0.71582E-09   0.84943E-01   0.30785E-04   0.51077E-05
    3    0.89211      0.75766E-09   0.10782       0.34358E-04   0.59994E-05
    4    0.87680      0.79346E-09   0.12312       0.38130E-04   0.67482E-05
    8    0.81938      0.94113E-09   0.18051       0.55792E-04   0.10383E-04
    9    0.77154      0.10814E-08   0.22833       0.75655E-04   0.14679E-04
   10     0.32593      0.76490E-12   0.67363       0.36879E-03   0.45299E-04
   11     0.32614      0.36267E-16   0.67377       0.75106E-04   0.26421E-05
   12     0.32590      0.17199E-20   0.67408       0.15293E-04   0.15413E-06
   15    0.25799E-01    0.0000       0.97420       0.13313E-06   0.62055E-10
```

```
                        U-O-S BLOCK SECTION

BLOCK:  D-102    MODEL: RADFRAC (CONTINUED)

                   ****   MASS-X-PROFILE     ****
  STAGE     WATER        HYDROGEN      PG           N-PROP       ISO-PROP
   16    0.30745E-02   0.25488E-23   0.99693       0.17653E-07   0.44376E-11

                   ****   MASS-X-PROFILE     ****
  STAGE     METHA-01
    1    0.30211E-03
    2    0.34900E-04
    3    0.32178E-04
    4    0.32905E-04
    8    0.35730E-04
    9    0.37894E-04
   10     0.29213E-04
   11     0.12163E-04
   12     0.50576E-05
   15     0.53540E-07
   16     0.42203E-08

                   ****   MASS-Y-PROFILE     ****
  STAGE     WATER        HYDROGEN      PG           N-PROP       ISO-PROP
    1    0.42649E-01   0.12435E-01   0.49664E-03   0.40435       0.53986
    2    0.94088      0.20803E-03   0.39576E-01   0.96646E-02   0.93679E-02
    3    0.93584      0.20464E-03   0.45329E-01   0.91801E-02   0.91773E-02
    4    0.93282      0.20419E-03   0.48397E-01   0.91605E-02   0.91573E-02
    8    0.92544      0.20311E-03   0.55866E-01   0.91145E-02   0.91096E-02
    9    0.92258      0.20271E-03   0.58766E-01   0.90971E-02   0.90914E-02
   10     0.92612      0.46203E-07   0.66295E-01   0.51714E-02   0.22183E-02
```

```
   11   0.93187      0.22005E-11  0.66853E-01  0.10609E-02  0.13032E-03
   12   0.93277      0.10437E-15  0.66973E-01  0.21610E-03  0.76031E-05
   15   0.36842       0.0000      0.63158      0.18846E-05  0.18928E-08
   16   0.42423E-01  0.12966E-19  0.95758      0.21761E-06  0.10421E-09

                 ****   MASS-Y-PROFILE    ****
  STAGE    METHA-01
    1   0.20603E-03
    2   0.30050E-03
    3   0.26620E-03
    4   0.26534E-03
    8   0.26447E-03
    9   0.26413E-03
   10    0.20060E-03
   11   0.84035E-04
   12   0.34993E-04
   15   0.12487E-05
   16   0.89620E-07
 ASPEN PLUS   PLAT: WIN32    VER: 24.0                04/11/2011  PAGE 26

                       U-O-S BLOCK SECTION

 BLOCK:  F-101    MODEL: FLASH2
 ------------------------------
  INLET STREAM:          S-121
  OUTLET VAPOR STREAM:   S-123
  OUTLET LIQUID STREAM:  S-122
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

               ***  MASS AND ENERGY BALANCE  ***
                          IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          1063.13        1063.13        0.00000
     MASS(LB/HR   )          21196.9        21196.9       0.343256E-15
     ENTHALPY(BTU/HR  )     -0.693085E+08   -0.693085E+08   -0.166199E-06

                   ***  INPUT DATA  ***
  TWO    PHASE  PQ  FLASH
  SPECIFIED PRESSURE    PSIA                        560.000
  SPECIFIED HEAT DUTY   BTU/HR                          0.0
  MAXIMUM NO. ITERATIONS                             30
  CONVERGENCE TOLERANCE                                 0.000100000

                    ***  RESULTS  ***
  OUTLET TEMPERATURE    F                            455.16
  OUTLET PRESSURE       PSIA                        560.00
  VAPOR FRACTION                                0.92669



  V-L PHASE EQUILIBRIUM :

    COMP           F(I)         X(I)          Y(I)          K(I)
    WATER          0.37158       0.34956       0.37332        1.0680
```

```
    HYDROGEN        0.46522       0.44429E-02    0.50167        112.92
    PG             0.15630       0.64158       0.11791       0.18378
    N-PROP          0.21285E-02    0.18346E-02    0.21517E-02     1.1728
    ISO-PROP        0.46933E-02    0.25308E-02    0.48644E-02     1.9221
    METHA-01        0.74146E-04    0.49110E-04    0.76126E-04     1.5501
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 27

                       U-O-S BLOCK SECTION

BLOCK:  F-102    MODEL: FLASH2
------------------------------
  INLET STREAM:         S-124
  OUTLET VAPOR STREAM:   S-126
  OUTLET LIQUID STREAM:  S-125
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                            IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)           985.192        985.192      -0.115396E-15
     MASS(LB/HR   )           16879.8        16879.8      -0.215523E-15
     ENTHALPY(BTU/HR  )      -0.585529E+08   -0.585529E+08   -0.872072E-07

                    ***  INPUT DATA  ***
  TWO    PHASE  PQ  FLASH
  PRESSURE DROP        PSI                           0.0
  SPECIFIED HEAT DUTY   BTU/HR                          0.0
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000

                     ***  RESULTS  ***
  OUTLET TEMPERATURE    F                              429.05
  OUTLET PRESSURE       PSIA                         559.14
  VAPOR FRACTION                                 0.90185



  V-L PHASE EQUILIBRIUM :

    COMP             F(I)          X(I)           Y(I)          K(I)
    WATER           0.37332       0.43594       0.36651       0.84074
    HYDROGEN        0.50167       0.36870E-02    0.55587        150.77
    PG             0.11791       0.55554       0.70286E-01    0.12652
    N-PROP          0.21517E-02    0.20419E-02    0.21637E-02     1.0596
    ISO-PROP        0.48644E-02    0.27370E-02    0.50959E-02     1.8619
    METHA-01        0.76126E-04    0.60607E-04    0.77815E-04     1.2839

BLOCK:  FSPLIT   MODEL: FSPLIT
------------------------------
  INLET STREAM:         S-110
  OUTLET STREAMS:       S-113       S-111
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 28
```

```
                    U-O-S BLOCK SECTION

BLOCK:  FSPLIT   MODEL: FSPLIT (CONTINUED)

              ***  MASS AND ENERGY BALANCE  ***
                         IN            OUT       RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)          762.564        762.564        0.00000
    MASS(LB/HR   )          13984.8        13984.8      -0.130069E-15
    ENTHALPY(BTU/HR  )     -0.939180E+08  -0.939180E+08   0.158661E-15

                 ***  INPUT DATA  ***

 FRACTION OF FLOW              STRM=S-113    FRAC=        0.34000

                  ***  RESULTS  ***

 STREAM= S-113         SPLIT=        0.34000     KEY=  0    STREAM-ORDER=   1
       S-111                    0.66000          0                 2

BLOCK:  H-101    MODEL: HEATER
------------------------------
  INLET STREAM:         S-107
  OUTLET STREAM:        S-108
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

              ***  MASS AND ENERGY BALANCE  ***
                         IN            OUT       RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)          1138.06        1138.06       0.486765E-08
    MASS(LB/HR   )          33229.6        33229.6       0.908441E-08
    ENTHALPY(BTU/HR  )     -0.164137E+09  -0.161726E+09  -0.146863E-01

                 ***  INPUT DATA  ***
  TWO    PHASE  TP  FLASH
  SPECIFIED TEMPERATURE              F                   242.000
  PRESSURE DROP                   PSI                  5.00000
  MAXIMUM NO. ITERATIONS                                  30
  CONVERGENCE TOLERANCE                                  0.000100000


ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 29

                    U-O-S BLOCK SECTION

BLOCK:  H-101    MODEL: HEATER (CONTINUED)

                  ***  RESULTS  ***
  OUTLET TEMPERATURE    F                          242.00
  OUTLET PRESSURE       PSIA                     36.816
  HEAT DUTY           BTU/HR                  0.24106E+07
  OUTLET VAPOR FRACTION                            0.0000
  PRESSURE-DROP CORRELATION PARAMETER                     0.20788E+07
```

```
 V-L PHASE EQUILIBRIUM :

   COMP          F(I)       X(I)        Y(I)        K(I)
   GLYCEROL      0.14802    0.14802     0.37835E-03 0.17172E-02
   WATER         0.83645    0.83645     0.92100     0.73970
   METHA-01      0.15525E-01 0.15525E-01 0.78625E-01  3.4022

BLOCK:  HX-101   MODEL: HEATX
-----------------------------
 THIS BLOCK RUNS WITH ASPEN EDR 25.0  WITH ADVANCED METHOD FOR SHELL&TUBE
 HOT SIDE:
 ---------
 INLET STREAM:        S-109
 OUTLET STREAM:       S-110
 PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
 COLD SIDE:
 ----------
 INLET STREAM:        S-106
 OUTLET STREAM:       S-107
 PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

             ***  MASS AND ENERGY BALANCE  ***
                        IN          OUT      RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)           1900.71        1900.63       0.427128E-04
    MASS(LB/HR   )         47215.8        47214.4       0.310346E-04
    ENTHALPY(BTU/HR  )     -0.258065E+09   -0.258055E+09   -0.387716E-04

               ***  INPUT DATA  ***

 FLASH SPECS FOR HOT SIDE:
 TWO    PHASE     FLASH
 MAXIMUM NO. ITERATIONS                           30
 CONVERGENCE TOLERANCE                              0.000100000
ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 30

                    U-O-S BLOCK SECTION

BLOCK:  HX-101   MODEL: HEATX (CONTINUED)

 FLASH SPECS FOR COLD SIDE:
 TWO    PHASE     FLASH
 MAXIMUM NO. ITERATIONS                           30
 CONVERGENCE TOLERANCE                              0.000100000

 SHELL&TUBE INPUT FILE NAME                            EDR_HX101.EDR
 SHELL&TUBE PROGRAM MODE                                DESIGN

 HEAT CURVE GENERATION
   HOT  HEAT CURVE GENERATED BY                        ASPEN PLUS
   COLD HEAT CURVE GENERATED BY                         ASPEN PLUS
```

```
                   ***  OVERALL RESULTS  ***

   STREAMS:
            --------------------------------------
            |                                    |
   S-109  ----->|          HOT  (SHELL)          |-----> S-110
   T=  2.2138D+02  |                             |    T=  8.0000D+01
   P=  2.0000D+01  |                             |    P=  1.9741D+01
   V=  0.0000D+00  |                             |    V=  0.0000D+00
            |                                    |
   S-107  <-----|          COLD (TUBE)           |<----- S-106
   T=  1.5183D+02  |                             |    T=  6.9907D+01
   P=  4.1816D+01  |                             |    P=  4.2000D+01
   V=  0.0000D+00  |                             |    V=  0.0000D+00
            --------------------------------------

   UNIT RESULTS:
     CALCULATED HEAT DUTY          BTU/HR            2136339.4528
     CALCULATED (REQUIRED) AREA     SQFT                2043.4209
     ACTUAL EXCHANGER AREA         SQFT                2052.0350
     % OVER (UNDER) DESIGN (DIRTY)                        0.4216
     % OVER (UNDER) DESIGN (CLEAN)                        0.4216
     AVERAGE COEFFICIENT (DIRTY)    BTU/HR-SQFT-R          33.9741
     AVERAGE COEFFICIENT (CLEAN)    BTU/HR-SQFT-R          33.9741
     UA (DIRTY)                  BTU/HR-R           69423.3987
     LMTD (CORRECTED)             F                    30.7726
     LMTD CORRECTION FACTOR                               0.9989
     NUMBER OF SHELLS IN SERIES                             1
     NUMBER OF SHELLS IN PARALLEL                           1
 ASPEN PLUS   PLAT: WIN32    VER: 24.0                04/11/2011  PAGE 31

                        U-O-S BLOCK SECTION

 BLOCK:  HX-101   MODEL: HEATX (CONTINUED)

   SHELLSIDE RESULTS:
     AVERAGE WALL TEMPERATURE         F                    122.8254
     CLEAN PRESSURE DROP              PSI                    0.2593
     WINDOW PRESSURE DROP             PSI                    0.0007
     PRESSURE DROP IN ENDS            PSI                    0.0007
     CROSSFLOW PRESSURE DROP          PSI                    0.0029
     BULK FILM COEFFICIENT            BTU/HR-SQFT-R          131.2348
     WALL FILM COEFFICIENT            BTU/HR-SQFT-R          131.2348
     THERMAL RESISTANCE               HR-SQFT-R/BTU            0.0076
     MAXIMUM FOULING RESISTANCE       HR-SQFT-R/BTU            0.000062
     FOULING RESISTANCE               HR-SQFT-R/BTU            0.0000
     CROSSFLOW VELOCITY               FT/SEC                 0.0885
     WINDOW VELOCITY                  FT/SEC                 0.1210
     MIDPOINT VELOCITY                FT/SEC                 0.1047
     SHELL ENTRANCE RHOV^2            LB/FT-SQSEC            95.0789
     SHELL EXIT RHOV^2                LB/FT-SQSEC            87.2858
     BUNDLE ENTRANCE RHOV^2           LB/FT-SQSEC             0.4808
     BUNDLE EXIT RHOV^2               LB/FT-SQSEC             0.4414
     FOULING % OF OVERALL RESISTANCE                          0.0000
```

```
    FILM % OF OVERALL RESISTANCE                     25.8880
    FRICTIONAL PRESSURE DROP        PSI              0.2593

  TUBESIDE RESULTS:
    AVERAGE WALL TEMPERATURE        F                115.0198
    CLEAN PRESSURE DROP             PSI              0.1840
    BULK FILM COEFFICIENT           BTU/HR-SQFT-R    46.3992
    WALL FILM COEFFICIENT           BTU/HR-SQFT-R    46.3992
    THERMAL RESISTANCE              HR-SQFT-R/BTU    0.0216
    MAXIMUM FOULING RESISTANCE      HR-SQFT-R/BTU    0.000062
    FOULING RESISTANCE              HR-SQFT-R/BTU    0.0000
    INPUT VELOCITY                  FT/SEC           0.1329
    OUTLET VELOCITY                 FT/SEC           0.1384
    MIDPOINT VELOCITY               FT/SEC           0.1384
    FOULING % OF OVERALL RESISTANCE                  0.0000
    FILM % OF OVERALL RESISTANCE                     73.2214
    FRICTIONAL PRESSURE DROP        PSI              0.1840

 BLOCK:  HX-102   MODEL: HEATX
 ----------------------------
  THIS BLOCK RUNS WITH ASPEN EDR 25.0  WITH ADVANCED METHOD FOR SHELL&TUBE
  HOT SIDE:
  ---------
  INLET STREAM:          S-123
  OUTLET STREAM:         S-124
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
  COLD SIDE:
  ----------
  INLET STREAM:          S-115
  OUTLET STREAM:         S-116
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
```

```
 BLOCK:  HX-102   MODEL: HEATX (CONTINUED)


    ***********************************************************************
    *                                                                     *
    *    A POTENTIAL TUBE VIBRATIEON PROBLEM IS INDICATED                 *
    *                                                                     *
    ***********************************************************************



                   ***  MASS AND ENERGY BALANCE  ***
                              IN             OUT        RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          1360.69        1360.69        0.00000
     MASS(LB/HR   )          36124.6        36124.6        0.00000
     ENTHALPY(BTU/HR  )     -0.127173E+09  -0.127173E+09   0.234345E-15

                     ***  INPUT DATA  ***
```

```
  FLASH SPECS FOR HOT SIDE:
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000

  FLASH SPECS FOR COLD SIDE:
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000

  SHELL&TUBE INPUT FILE NAME                                EDR_HX102.EDR
  SHELL&TUBE PROGRAM MODE                                    DESIGN

  HEAT CURVE GENERATION
    HOT  HEAT CURVE GENERATED BY                          ASPEN PLUS
    COLD HEAT CURVE GENERATED BY                          ASPEN PLUS

                    ***  OVERALL RESULTS  ***

  STREAMS:
              --------------------------------------
              |                                    |
  S-123     ----->|          HOT  (SHELL)          |-----> S-124
  T=  4.5516D+02  |                                |      T=  4.2905D+02
  P=  5.6000D+02  |                                |      P=  5.5914D+02
  V=  1.0000D+00  |                                |      V=  9.0185D-01
              |                                    |
  S-116     <-----|          COLD (TUBE)           |<----- S-115
  T=  4.1000D+02  |                                |      T=  2.5213D+02
  P=  5.8104D+02  |                                |      P=  5.8700D+02
  V=  0.0000D+00  |                                |      V=  0.0000D+00
              --------------------------------------
```

```
                          U-O-S BLOCK SECTION

 BLOCK:  HX-102   MODEL: HEATX (CONTINUED)

  UNIT RESULTS:
    CALCULATED HEAT DUTY          BTU/HR           1990193.7789
    CALCULATED (REQUIRED) AREA     SQFT                 66.0988
    ACTUAL EXCHANGER AREA         SQFT                 72.8456
    % OVER (UNDER) DESIGN (DIRTY)                      10.2072
    % OVER (UNDER) DESIGN (CLEAN)                      10.2072
    AVERAGE COEFFICIENT (DIRTY)    BTU/HR-SQFT-R         344.7762
    AVERAGE COEFFICIENT (CLEAN)    BTU/HR-SQFT-R         344.7762
    UA (DIRTY)                  BTU/HR-R           22789.2816
    LMTD (CORRECTED)              F                  87.3303
    LMTD CORRECTION FACTOR                             0.9052
    NUMBER OF SHELLS IN SERIES                         1
    NUMBER OF SHELLS IN PARALLEL                           1

  SHELLSIDE RESULTS:
    AVERAGE WALL TEMPERATURE         F                     441.7477
```

```
    CLEAN PRESSURE DROP              PSI                       0.8597
    WINDOW PRESSURE DROP              PSI                       0.2903
    PRESSURE DROP IN ENDS            PSI                       0.2903
    CROSSFLOW PRESSURE DROP          PSI                       0.2178
    BULK FILM COEFFICIENT            BTU/HR-SQFT-R            754.8609
    WALL FILM COEFFICIENT            BTU/HR-SQFT-R            754.8609
    THERMAL RESISTANCE               HR-SQFT-R/BTU             0.0013
    MAXIMUM FOULING RESISTANCE       HR-SQFT-R/BTU             0.000148
    FOULING RESISTANCE               HR-SQFT-R/BTU             0.0000
    CROSSFLOW VELOCITY               FT/SEC                   17.0614
    WINDOW VELOCITY                  FT/SEC                   30.5421
    MIDPOINT VELOCITY                FT/SEC                   23.8017
    SHELL ENTRANCE RHOV^2            LB/FT-SQSEC              332.0135
    SHELL EXIT RHOV^2                LB/FT-SQSEC              296.9255
    BUNDLE ENTRANCE RHOV^2           LB/FT-SQSEC              246.7540
    BUNDLE EXIT RHOV^2               LB/FT-SQSEC              220.2565
    FOULING % OF OVERALL RESISTANCE                            0.0000
    FILM % OF OVERALL RESISTANCE                              45.6741
    FRICTIONAL PRESSURE DROP         PSI                       0.8866

  TUBESIDE RESULTS:
    AVERAGE WALL TEMPERATURE         F                        397.6940
    CLEAN PRESSURE DROP              PSI                       5.9635
    BULK FILM COEFFICIENT            BTU/HR-SQFT-R            770.4299
    WALL FILM COEFFICIENT            BTU/HR-SQFT-R            770.4299
    THERMAL RESISTANCE               HR-SQFT-R/BTU             0.0013
    MAXIMUM FOULING RESISTANCE       HR-SQFT-R/BTU             0.000148
    FOULING RESISTANCE               HR-SQFT-R/BTU             0.0000
    INPUT VELOCITY                   FT/SEC                    4.9940
    OUTLET VELOCITY                  FT/SEC                    5.4123
    MIDPOINT VELOCITY                FT/SEC                    5.4123
    FOULING % OF OVERALL RESISTANCE                            0.0000
    FILM % OF OVERALL RESISTANCE                              44.7511
    FRICTIONAL PRESSURE DROP         PSI                       5.9310
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 34

                          U-O-S BLOCK SECTION

 BLOCK:  HX-103   MODEL: HEATX
 -----------------------------
   THIS BLOCK RUNS WITH ASPEN EDR 25.0  WITH ADVANCED METHOD FOR SHELL&TUBE
   HOT SIDE:
   ---------
   INLET STREAM:         S-126
   OUTLET STREAM:        S-127
   PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
   COLD SIDE:
   ----------
   INLET STREAM:         S-119
   OUTLET STREAM:        S-120
   PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE


     ***********************************************************************
```

```
  *                                             *
  *    A POTENTIAL TUBE VIBRATIEON PROBLEM IS INDICATED              *
  *                                             *
  *******************************************************************


                *** MASS AND ENERGY BALANCE ***
                          IN           OUT       RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)         1576.12       1576.12        0.00000
    MASS(LB/HR   )         13956.0       13956.0        0.00000
    ENTHALPY(BTU/HR  )     -0.450774E+08  -0.450774E+08  -0.165284E-15

                   *** INPUT DATA ***

  FLASH SPECS FOR HOT SIDE:
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000

  FLASH SPECS FOR COLD SIDE:
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000

  SHELL&TUBE INPUT FILE NAME                              EDR_HX103.EDR
  SHELL&TUBE PROGRAM MODE                                  DESIGN

  HEAT CURVE GENERATION
    HOT  HEAT CURVE GENERATED BY                        ASPEN PLUS
    COLD HEAT CURVE GENERATED BY                        ASPEN PLUS
 ASPEN PLUS   PLAT: WIN32     VER: 24.0              04/11/2011  PAGE 35

                      U-O-S BLOCK SECTION

 BLOCK:  HX-103   MODEL: HEATX (CONTINUED)

                   *** OVERALL RESULTS ***

  STREAMS:
            --------------------------------------
            |                                    |
  S-126    ----->|        HOT  (SHELL)         |-----> S-127
  T=  4.2905D+02  |                              |     T=  4.0905D+02
  P=  5.5914D+02  |                              |     P=  5.5828D+02
  V=  1.0000D+00  |                              |     V=  9.3825D-01
            |                                    |
  S-120    <-----|        COLD (TUBE)          |<----- S-119
  T=  4.1649D+02  |                              |     T=  2.0241D+02
  P=  5.9891D+02  |                              |     P=  6.0000D+02
  V=  1.0000D+00  |                              |     V=  9.9431D-01
            --------------------------------------

  UNIT RESULTS:
```

```
    CALCULATED HEAT DUTY          BTU/HR           1132628.0668
    CALCULATED (REQUIRED) AREA     SQFT                 156.3568
    ACTUAL EXCHANGER AREA         SQFT                 164.4385
    % OVER (UNDER) DESIGN (DIRTY)                        5.1688
    % OVER (UNDER) DESIGN (CLEAN)                        5.1688
    AVERAGE COEFFICIENT (DIRTY)    BTU/HR-SQFT-R         145.2866
    AVERAGE COEFFICIENT (CLEAN)    BTU/HR-SQFT-R         145.2866
    UA (DIRTY)                   BTU/HR-R           22716.5518
    LMTD (CORRECTED)              F                   49.8592
    LMTD CORRECTION FACTOR                            0.7197
    NUMBER OF SHELLS IN SERIES                        1
    NUMBER OF SHELLS IN PARALLEL                         1

  SHELLSIDE RESULTS:
    AVERAGE WALL TEMPERATURE         F                    421.1405
    CLEAN PRESSURE DROP             PSI                  0.8607
    WINDOW PRESSURE DROP             PSI                  0.3807
    PRESSURE DROP IN ENDS           PSI                  0.3807
    CROSSFLOW PRESSURE DROP          PSI                  0.1580
    BULK FILM COEFFICIENT           BTU/HR-SQFT-R          569.6667
    WALL FILM COEFFICIENT           BTU/HR-SQFT-R          569.6667
    THERMAL RESISTANCE              HR-SQFT-R/BTU            0.0018
    MAXIMUM FOULING RESISTANCE       HR-SQFT-R/BTU           0.000178
    FOULING RESISTANCE              HR-SQFT-R/BTU            0.0000
    CROSSFLOW VELOCITY              FT/SEC                13.7680
    WINDOW VELOCITY                FT/SEC                27.6842
    MIDPOINT VELOCITY              FT/SEC                20.7261
    SHELL ENTRANCE RHOV^2           LB/FT-SQSEC            125.6469
    SHELL EXIT RHOV^2              LB/FT-SQSEC            466.0312
    BUNDLE ENTRANCE RHOV^2           LB/FT-SQSEC             36.9687
    BUNDLE EXIT RHOV^2              LB/FT-SQSEC             53.8235
    FOULING % OF OVERALL RESISTANCE                         0.0000
    FILM % OF OVERALL RESISTANCE                         25.5038
    FRICTIONAL PRESSURE DROP         PSI                  0.8735
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 36

                       U-O-S BLOCK SECTION

 BLOCK:  HX-103   MODEL: HEATX (CONTINUED)

  TUBESIDE RESULTS:
    AVERAGE WALL TEMPERATURE         F                    405.7931
    CLEAN PRESSURE DROP             PSI                  1.0853
    BULK FILM COEFFICIENT           BTU/HR-SQFT-R          206.1210
    WALL FILM COEFFICIENT           BTU/HR-SQFT-R          206.1210
    THERMAL RESISTANCE              HR-SQFT-R/BTU            0.0049
    MAXIMUM FOULING RESISTANCE       HR-SQFT-R/BTU           0.000178
    FOULING RESISTANCE              HR-SQFT-R/BTU            0.0000
    INPUT VELOCITY                FT/SEC                40.3146
    OUTLET VELOCITY               FT/SEC                53.5906
    MIDPOINT VELOCITY              FT/SEC                53.5906
    FOULING % OF OVERALL RESISTANCE                         0.0000
    FILM % OF OVERALL RESISTANCE                         70.4861
    FRICTIONAL PRESSURE DROP         PSI                  1.0606
```

```
BLOCK:  M-101    MODEL: MIXER
-----------------------------
  INLET STREAMS:        S-131      S-118
  OUTLET STREAM:        S-119
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                             IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          687.645        687.624       0.305083E-04
     MASS(LB/HR   )          1952.06        1951.94       0.584380E-04
     ENTHALPY(BTU/HR  )     -0.182133E+07   -0.182118E+07   -0.861022E-04

                    ***  INPUT DATA  ***
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                                30
  CONVERGENCE TOLERANCE                                  0.000100000
  OUTLET PRESSURE:  MINIMUM OF INLET STREAM PRESSURES

BLOCK:  M-102    MODEL: MIXER
-----------------------------
  INLET STREAMS:        S-101      S-102      S-112
  OUTLET STREAM:        S-103
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 37

                        U-O-S BLOCK SECTION

BLOCK:  M-102    MODEL: MIXER (CONTINUED)

                 ***  MASS AND ENERGY BALANCE  ***
                             IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          1151.42        1151.42        0.00000
     MASS(LB/HR   )          34006.8        34006.8        0.00000
     ENTHALPY(BTU/HR  )     -0.169033E+09   -0.169033E+09    0.176311E-15

                    ***  INPUT DATA  ***
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                                30
  CONVERGENCE TOLERANCE                                  0.000100000
  OUTLET PRESSURE   PSIA                             25.0000

BLOCK:  M-103    MODEL: MIXER
-----------------------------
  INLET STREAMS:        S-122      S-129      S-125
  OUTLET STREAM:        S-132
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                             IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          547.323        547.323        0.00000
```

```
    MASS(LB/HR   )          19591.2        19591.2       0.371389E-15
    ENTHALPY(BTU/HR  )     -0.781100E+08   -0.781100E+08   -0.381543E-15

                 ***  INPUT DATA  ***
  TWO    PHASE     FLASH
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                 0.000100000
  PRESSURE DROP   PSI                            5.00000

BLOCK:  P-100    MODEL: PUMP
----------------------------
  INLET STREAM:         S-114
  OUTLET STREAM:        S-115
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 38

                        U-O-S BLOCK SECTION

BLOCK:  P-100    MODEL: PUMP (CONTINUED)

               ***  MASS AND ENERGY BALANCE  ***
                              IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          375.500        375.500        0.00000
     MASS(LB/HR   )          19244.9        19244.9      -0.189036E-15
     ENTHALPY(BTU/HR  )     -0.706840E+08   -0.706100E+08   -0.104774E-02

                 ***  INPUT DATA  ***
   OUTLET PRESSURE  PSIA                          587.000
   DRIVER EFFICIENCY                            1.00000

   FLASH SPECIFICATIONS:
   LIQUID PHASE CALCULATION
   NO FLASH PERFORMED
   MAXIMUM NUMBER OF ITERATIONS                           30
   TOLERANCE                                 0.000100000

                  ***  RESULTS  ***
   VOLUMETRIC FLOW RATE  CUFT/HR                     267.014
   PRESSURE CHANGE  PSI                           567.000
   NPSH AVAILABLE   FT-LBF/LB                         0.0
   FLUID POWER  HP                            11.0107
   BRAKE POWER  HP                             29.1061
   ELECTRICITY  KW                            21.7044
   PUMP EFFICIENCY USED                            0.37829
   NET WORK REQUIRED  HP                           29.1061
   HEAD DEVELOPED FT-LBF/LB                         1,132.83

BLOCK:  P-101    MODEL: PUMP
----------------------------
  INLET STREAM:         S-105
  OUTLET STREAM:        S-106
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE
```

```
              ***  MASS AND ENERGY BALANCE  ***
                          IN          OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          1138.15       1138.15       0.00000
     MASS(LB/HR   )          33231.1       33231.1       0.00000
     ENTHALPY(BTU/HR  )     -0.166287E+09  -0.166283E+09  -0.249300E-04
```

```
                    U-O-S BLOCK SECTION

 BLOCK:  P-101    MODEL: PUMP (CONTINUED)

                 ***  INPUT DATA  ***
   OUTLET PRESSURE  PSIA                            42.0000
   DRIVER EFFICIENCY                              1.00000

   FLASH SPECIFICATIONS:
   LIQUID PHASE CALCULATION
   NO FLASH PERFORMED
   MAXIMUM NUMBER OF ITERATIONS                          30
   TOLERANCE                                  0.000100000

                  ***  RESULTS  ***
   VOLUMETRIC FLOW RATE  CUFT/HR                    471.696
   PRESSURE CHANGE  PSI                            22.0000
   NPSH AVAILABLE   FT-LBF/LB                       40.1994
   FLUID POWER  HP                              0.75471
   BRAKE POWER  HP                               1.62926
   ELECTRICITY  KW                              1.21494
   PUMP EFFICIENCY USED                            0.46322
   NET WORK REQUIRED  HP                             1.62926
   HEAD DEVELOPED FT-LBF/LB                           44.9679

 BLOCK:  P-102    MODEL: PUMP
 ----------------------------
  INLET STREAM:         S-111
  OUTLET STREAM:        S-112
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

              ***  MASS AND ENERGY BALANCE  ***
                          IN          OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)          503.292       503.292       0.00000
     MASS(LB/HR   )          9229.94       9229.94       0.00000
     ENTHALPY(BTU/HR  )     -0.619858E+08  -0.619849E+08  -0.156051E-04

                 ***  INPUT DATA  ***
   OUTLET PRESSURE  PSIA                            30.0000
   DRIVER EFFICIENCY                              1.00000

   FLASH SPECIFICATIONS:
   LIQUID PHASE CALCULATION
   NO FLASH PERFORMED
   MAXIMUM NUMBER OF ITERATIONS                          30
```

```
   TOLERANCE                                            0.000100000
```

```
                         U-O-S BLOCK SECTION

BLOCK:  P-102    MODEL: PUMP (CONTINUED)

                      ***  RESULTS  ***
   VOLUMETRIC FLOW RATE  CUFT/HR                      150.641
   PRESSURE CHANGE  PSI                          10.2593
   NPSH AVAILABLE   FT-LBF/LB                        44.9718
   FLUID POWER  HP                           0.11240
   BRAKE POWER  HP                            0.38016
   ELECTRICITY  KW                           0.28349
   PUMP EFFICIENCY USED                            0.29566
   NET WORK REQUIRED  HP                             0.38016
   HEAD DEVELOPED FT-LBF/LB                            24.1115

BLOCK:  R-101    MODEL: RSTOIC
------------------------------
  INLET STREAMS:         S-116       S-120
  OUTLET STREAM:         S-121
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                         IN          OUT       GENERATION   RELATIVE DIFF.
  TOTAL BALANCE
  MOLE(LBMOL/HR)        1063.12       1063.13       0.00000     -0.605872E-05
  MASS(LB/HR   )        21196.8       21196.9                 -0.379189E-05
  ENTHALPY(BTU/HR  )   -0.693083E+08 -0.693085E+08               0.196263E-05

                     ***  INPUT DATA  ***
  STOICHIOMETRY MATRIX:

   REACTION #   1:
    SUBSTREAM MIXED   :
    GLYCEROL  -1.00    WATER      1.00    HYDROGEN  -1.00    PG        1.00

   REACTION #   2:
    SUBSTREAM MIXED   :
    GLYCEROL  -2.00    WATER      4.00    HYDROGEN  -4.00    N-PROP     1.00
    ISO-PROP   1.00


  REACTION CONVERSION SPECS: NUMBER=    2
    REACTION #   1:
    SUBSTREAM:MIXED    KEY COMP:GLYCEROL CONV FRAC: 0.9850
    REACTION #   2:
    SUBSTREAM:MIXED    KEY COMP:GLYCEROL CONV FRAC:  1.000




  TWO    PHASE  PQ  FLASH
```

```
  PRESSURE DROP        PSI                          15.0000
  SPECIFIED HEAT DUTY   BTU/HR                          0.0
  MAXIMUM NO. ITERATIONS                              30
  CONVERGENCE TOLERANCE                                0.000100000
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 41

                      U-O-S BLOCK SECTION

BLOCK:  R-101    MODEL: RSTOIC (CONTINUED)
  SERIES REACTIONS
  GENERATE COMBUSTION REACTIONS FOR FEED SPECIES          NO

                    ***  RESULTS  ***
  OUTLET TEMPERATURE    F                            455.84
  OUTLET PRESSURE       PSIA                         566.04
  VAPOR FRACTION                                   0.92623



  REACTION EXTENTS:

    REACTION         REACTION
    NUMBER           EXTENT
                  LBMOL/HR
    1              165.93
    2              1.2634

  V-L PHASE EQUILIBRIUM :

    COMP             F(I)          X(I)          Y(I)          K(I)
    WATER           0.37158       0.35104       0.37322        1.0632
    HYDROGEN        0.46522       0.45085E-02   0.50191        111.32
    PG              0.15630       0.64002       0.11778        0.18402
    N-PROP          0.21284E-02   0.18411E-02   0.21513E-02    1.1684
    ISO-PROP        0.46924E-02   0.25428E-02   0.48636E-02    1.9127
    METHA-01        0.74146E-04   0.49353E-04   0.76121E-04    1.5424

BLOCK:  S-101    MODEL: SEP
---------------------------
  INLET STREAM:          S-103
  OUTLET STREAMS:        S-104      S-105
  PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                 ***  MASS AND ENERGY BALANCE  ***
                          IN            OUT       RELATIVE DIFF.
   TOTAL BALANCE
     MOLE(LBMOL/HR)           1151.42        1151.42       0.394945E-15
     MASS(LB/HR   )           34006.8        34006.8       0.213956E-15
     ENTHALPY(BTU/HR  )      -0.169033E+09   -0.168638E+09   -0.233928E-02
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 42

                      U-O-S BLOCK SECTION

BLOCK:  S-101    MODEL: SEP (CONTINUED)
```

```
                  ***  INPUT DATA  ***

   INLETT PRESSURE DROP   PSI                          5.00000

   FLASH SPECS FOR STREAM S-104
   ONE    PHASE  TP  FLASH   SPECIFIED PHASE IS  SOLID
   PRESSURE DROP        PSI                         0.0
   MAXIMUM NO. ITERATIONS                             30
   CONVERGENCE TOLERANCE                                0.000100000

   FLASH SPECS FOR STREAM S-105
   TWO    PHASE  TP  FLASH
   SPECIFIED TEMPERATURE CHANGE    F                    15.0000
   PRESSURE DROP        PSI                         0.0
   MAXIMUM NO. ITERATIONS                             30
   CONVERGENCE TOLERANCE                                0.000100000

   FRACTION OF FEED
     SUBSTREAM= MIXED
       STREAM= S-104     CPT= SODIU-01  FRACTION=         1.00000


                  ***  RESULTS  ***

   HEAT DUTY           BTU/HR                       0.39542E+06

  COMPONENT = GLYCEROL
    STREAM     SUBSTREAM    SPLIT FRACTION
    S-105      MIXED               1.00000

  COMPONENT = WATER
    STREAM     SUBSTREAM    SPLIT FRACTION
    S-105      MIXED               1.00000

  COMPONENT = SODIU-01
    STREAM     SUBSTREAM    SPLIT FRACTION
    S-104      MIXED               1.00000

  COMPONENT = METHA-01
    STREAM     SUBSTREAM    SPLIT FRACTION
    S-105      MIXED               1.00000
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 43

                    U-O-S BLOCK SECTION

 BLOCK:  T-101    MODEL: COMPR
 -----------------------------
   INLET STREAM:         S-117
   OUTLET STREAM:        S-118
   PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

               ***  MASS AND ENERGY BALANCE  ***
```

```
                         IN           OUT       RELATIVE DIFF.
    TOTAL BALANCE
      MOLE(LBMOL/HR)          171.838        171.838        0.00000
      MASS(LB/HR   )          346.404        346.404        0.00000
      ENTHALPY(BTU/HR  )      -5244.32       -75785.5       0.930800

                    ***  INPUT DATA  ***

   ISENTROPIC TURBINE
    OUTLET PRESSURE  PSIA                            600.000
    ISENTROPIC EFFICIENCY                             0.80000
    MECHANICAL EFFICIENCY                              1.00000

                    ***  RESULTS  ***

    INDICATED  HORSEPOWER REQUIREMENT  HP               -27.7237
    BRAKE      HORSEPOWER REQUIREMENT  HP               -27.7237
    NET WORK REQUIRED                HP                -27.7237
    POWER LOSSES                     HP                  0.0
    ISENTROPIC HORSEPOWER REQUIREMENT  HP               -34.6546
    CALCULATED OUTLET TEMP  F                          11.7339
    ISENTROPIC TEMPERATURE  F                          -3.14840
    EFFICIENCY (POLYTR/ISENTR) USED                     0.80000
    OUTLET VAPOR FRACTION                              1.00000
    HEAD DEVELOPED,       FT-LBF/LB                 -198,081.
    MECHANICAL EFFICIENCY USED                          1.00000
    INLET HEAT CAPACITY RATIO                          1.41692
    INLET VOLUMETRIC FLOW RATE , CUFT/HR              1,010.06
    OUTLET VOLUMETRIC FLOW RATE, CUFT/HR              1,479.73
    INLET  COMPRESSIBILITY FACTOR                       1.03411
    OUTLET COMPRESSIBILITY FACTOR                       1.02133
    AV. ISENT. VOL. EXPONENT                           1.45958
    AV. ISENT. TEMP EXPONENT                           1.41031
    AV. ACTUAL VOL. EXPONENT                           1.33775
    AV. ACTUAL TEMP EXPONENT                           1.29557
 ASPEN PLUS   PLAT: WIN32     VER: 24.0               04/11/2011  PAGE 44

                      U-O-S BLOCK SECTION

 BLOCK:  T-101    MODEL: COMPR (CONTINUED)

 BLOCK:  V-101    MODEL: FLASH2
 ------------------------------
   INLET STREAM:          S-128
   OUTLET VAPOR STREAM:   S-130
   OUTLET LIQUID STREAM:  S-129
   PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

                ***  MASS AND ENERGY BALANCE  ***
                         IN           OUT       RELATIVE DIFF.
    TOTAL BALANCE
      MOLE(LBMOL/HR)          888.498        888.498        0.00000
      MASS(LB/HR   )          12004.1        12004.1       0.226374E-10
      ENTHALPY(BTU/HR  )      -0.518861E+08   -0.518861E+08    0.143595E-15
```

```
                  ***  INPUT DATA  ***
 TWO    PHASE  TP  FLASH
 SPECIFIED TEMPERATURE F                        225.000
 PRESSURE DROP        PSI                        0.0
 MAXIMUM NO. ITERATIONS                             30
 CONVERGENCE TOLERANCE                             0.000100000

                  ***  RESULTS  ***
 OUTLET TEMPERATURE    F                         225.00
 OUTLET PRESSURE      PSIA                       553.28
 HEAT DUTY           BTU/HR                      0.0000
 VAPOR FRACTION                                  0.58054


ASPEN PLUS   PLAT: WIN32    VER: 24.0               04/11/2011  PAGE 45

                    U-O-S BLOCK SECTION

BLOCK:  V-101    MODEL: FLASH2 (CONTINUED)

 V-L PHASE EQUILIBRIUM :

   COMP             F(I)          X(I)          Y(I)          K(I)
   WATER           0.36651       0.82793       0.33113E-01    0.39995E-01
   HYDROGEN        0.55587       0.36804E-03   0.95724        2600.8
   PG            0.70286E-01    0.16692       0.46548E-03    0.27886E-02
   N-PROP          0.21637E-02   0.24765E-02   0.19376E-02    0.78236
   ISO-PROP        0.50959E-02   0.21508E-02   0.72239E-02    3.3586
   METHA-01        0.77815E-04   0.15535E-03   0.21791E-04    0.14027

BLOCK:  VALVE    MODEL: VALVE
-----------------------------
 INLET STREAM:         S-132
 OUTLET STREAM:        S-133
 PROPERTY OPTION SET:   PENG-ROB  STANDARD PR EQUATION OF STATE

               ***  MASS AND ENERGY BALANCE  ***
                          IN            OUT       RELATIVE DIFF.
  TOTAL BALANCE
    MOLE(LBMOL/HR)           547.323        547.323        0.00000
    MASS(LB/HR   )         19591.2        19591.2        0.00000
    ENTHALPY(BTU/HR  )      -0.781100E+08   -0.781100E+08     0.00000

                  ***  INPUT DATA  ***

  VALVE OUTLET PRESSURE     PSIA                    30.0000
  VALVE FLOW COEF CALC.                          NO

                  FLASH SPECIFICATIONS:
  NPHASE                                   2
  MAX NUMBER OF ITERATIONS                            30
  CONVERGENCE TOLERANCE                               0.000100000
```

```
                  ***  RESULTS  ***

   VALVE PRESSURE DROP      PSI                    518.280
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 46

                      STREAM SECTION

 S-101 S-102 S-103 S-104 S-105
 -----------------------------

 STREAM ID             S-101      S-102      S-103      S-104      S-105
 FROM :                ----       ----       M-102      S-101      S-101
 TO   :                M-102      M-102      S-101      ----       P-101

 SUBSTREAM: MIXED
 PHASE:                LIQUID     LIQUID     LIQUID     SOLID      LIQUID
 COMPONENTS: LBMOL/HR
   GLYCEROL            168.4569     0.0      168.4574     0.0      168.4574
   ACETOL                0.0        0.0        0.0        0.0        0.0
   WATER               161.4670   298.8769   952.0188     0.0      952.0188
   HYDROGEN              0.0        0.0        0.0        0.0        0.0
   PG                    0.0        0.0        0.0        0.0        0.0
   N-PROP                0.0        0.0        0.0        0.0        0.0
   ETHYL-01              0.0        0.0        0.0        0.0        0.0
   ISO-PROP              0.0        0.0        0.0        0.0        0.0
   SODIU-01             13.2729     0.0       13.2729    13.2729     0.0
   METHA-01              6.0522     0.0       17.6689     0.0       17.6689
 COMPONENTS: MOLE FRAC
   GLYCEROL              0.4823     0.0        0.1463     0.0        0.1480
   ACETOL                0.0        0.0        0.0        0.0        0.0
   WATER                 0.4623     1.0000     0.8268     0.0        0.8365
   HYDROGEN              0.0        0.0        0.0        0.0        0.0
   PG                    0.0        0.0        0.0        0.0        0.0
   N-PROP                0.0        0.0        0.0        0.0        0.0
   ETHYL-01              0.0        0.0        0.0        0.0        0.0
   ISO-PROP              0.0        0.0        0.0        0.0        0.0
   SODIU-01            3.8004-02    0.0      1.1527-02    1.0000     0.0
   METHA-01            1.7329-02    0.0      1.5345-02    0.0      1.5524-02
 COMPONENTS: MASS FRAC
   GLYCEROL              0.8000     0.0        0.4562     0.0        0.4669
   ACETOL                0.0        0.0        0.0        0.0        0.0
   WATER                 0.1500     1.0000     0.5043     0.0        0.5161
   HYDROGEN              0.0        0.0        0.0        0.0        0.0
   PG                    0.0        0.0        0.0        0.0        0.0
   N-PROP                0.0        0.0        0.0        0.0        0.0
   ETHYL-01              0.0        0.0        0.0        0.0        0.0
   ISO-PROP              0.0        0.0        0.0        0.0        0.0
   SODIU-01            4.0000-02    0.0      2.2810-02    1.0000     0.0
   METHA-01            1.0000-02    0.0      1.6648-02    0.0      1.7037-02
 TOTAL FLOW:
   LBMOL/HR            349.2489   298.8769  1151.4180    13.2729  1138.1451
   LB/HR              1.9392+04  5384.3506  3.4007+04   775.6994  3.3231+04
   CUFT/HR             242.1154    86.4478   470.7215     5.7432   471.6956
 STATE VARIABLES:
```

```
  TEMP   F            70.0000    70.0000    54.8014    54.8182    69.8182
  PRES   PSIA          30.0000    30.0000    25.0000    20.0000    20.0000
  VFRAC                0.0        0.0        0.0        0.0        0.0
  LFRAC               1.0000     1.0000     1.0000     0.0        1.0000
  SFRAC               0.0        0.0        0.0        1.0000     0.0
ENTHALPY:
  BTU/LBMOL         -2.0053+05 -1.2384+05 -1.4680+05 -1.7708+05 -1.4610+05
  BTU/LB           -3611.4585 -6874.1822 -4970.5698 -3029.9052 -5003.9710
  BTU/HR           -7.0035+07 -3.7013+07 -1.6903+08 -2.3503+06 -1.6629+08
```

```
                         STREAM SECTION

S-101 S-102 S-103 S-104 S-105 (CONTINUED)

STREAM ID             S-101      S-102      S-103      S-104      S-105

ENTROPY:
  BTU/LBMOL-R         -86.4419   -40.3582   -54.1619   -22.1726   -53.7260
  BTU/LB-R            -1.5568    -2.2402    -1.8338    -0.3794    -1.8401
DENSITY:
  LBMOL/CUFT           1.4425     3.4573     2.4461     2.3111     2.4129
  LB/CUFT             80.0960    62.2844    72.2439   135.0641    70.4503
AVG MW                 55.5263    18.0153    29.5347    58.4425    29.1976
```

```
                         STREAM SECTION

S-106 S-107 S-108 S-109 S-110
-----------------------------

STREAM ID             S-106      S-107      S-108      S-109      S-110
FROM :               P-101      HX-101     H-101      D-101      HX-101
TO   :              HX-101     H-101      D-101      HX-101     FSPLIT


MAX CONV. ERROR:      8.5077-05     0.0     8.1349-07     0.0       0.0
SUBSTREAM: MIXED
PHASE:               LIQUID     LIQUID     LIQUID     LIQUID     LIQUID
COMPONENTS: LBMOL/HR
  GLYCEROL            168.4574   168.4574   168.4574  8.4221-04  8.4221-04
  ACETOL               0.0        0.0        0.0        0.0        0.0
  WATER               952.0188   951.9378   951.9378   744.9620   744.9620
  HYDROGEN             0.0        0.0        0.0        0.0        0.0
  PG                   0.0        0.0        0.0        0.0        0.0
  N-PROP               0.0        0.0        0.0        0.0        0.0
  ETHYL-01             0.0        0.0        0.0        0.0        0.0
  ISO-PROP             0.0        0.0        0.0        0.0        0.0
  SODIU-01             0.0        0.0        0.0        0.0        0.0
  METHA-01            17.6689    17.6687    17.6687    17.6011    17.6011
COMPONENTS: MOLE FRAC
  GLYCEROL             0.1480     0.1480     0.1480  1.1044-06  1.1044-06
  ACETOL               0.0        0.0        0.0        0.0        0.0
  WATER                0.8365     0.8365     0.8365     0.9769     0.9769
```

```
  HYDROGEN            0.0       0.0       0.0       0.0       0.0
  PG                0.0       0.0       0.0       0.0       0.0
  N-PROP            0.0       0.0       0.0       0.0       0.0
  ETHYL-01          0.0       0.0       0.0       0.0       0.0
  ISO-PROP          0.0       0.0       0.0       0.0       0.0
  SODIU-01          0.0       0.0       0.0       0.0       0.0
  METHA-01         1.5524-02  1.5525-02  1.5525-02  2.3082-02  2.3082-02
COMPONENTS: MASS FRAC
  GLYCEROL           0.4669     0.4669     0.4669  5.5463-06  5.5463-06
  ACETOL            0.0       0.0       0.0       0.0       0.0
  WATER             0.5161     0.5161     0.5161     0.9597     0.9597
  HYDROGEN            0.0       0.0       0.0       0.0       0.0
  PG                0.0       0.0       0.0       0.0       0.0
  N-PROP            0.0       0.0       0.0       0.0       0.0
  ETHYL-01          0.0       0.0       0.0       0.0       0.0
  ISO-PROP          0.0       0.0       0.0       0.0       0.0
  SODIU-01          0.0       0.0       0.0       0.0       0.0
  METHA-01         1.7037-02  1.7037-02  1.7037-02  4.0328-02  4.0328-02
TOTAL FLOW:
  LBMOL/HR          1138.1451  1138.0639  1138.0639   762.5639   762.5639
  LB/HR            3.3231+04  3.3230+04  3.3230+04  1.3985+04  1.3985+04
  CUFT/HR           471.7154   491.1869   515.9014   248.6216   228.2434
STATE VARIABLES:
  TEMP   F          69.9067   151.8282   242.0000   221.3804    80.0000
  PRES   PSIA        42.0000    41.8160    36.8160    20.0000    19.7407
  VFRAC             0.0       0.0       0.0       0.0       0.0
  LFRAC             1.0000     1.0000     1.0000     1.0000     1.0000
  SFRAC             0.0       0.0       0.0       0.0       0.0
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 49

                         STREAM SECTION

S-106 S-107 S-108 S-109 S-110 (CONTINUED)

STREAM ID            S-106      S-107      S-108      S-109      S-110

ENTHALPY:
  BTU/LBMOL         -1.4610+05 -1.4422+05 -1.4211+05 -1.2036+05 -1.2316+05
  BTU/LB           -5003.8462 -4939.4756 -4866.9332 -6562.9766 -6715.7386
  BTU/HR           -1.6628+08 -1.6414+08 -1.6173+08 -9.1782+07 -9.3918+07
ENTROPY:
  BTU/LBMOL-R         -53.7228   -50.4286   -47.1981   -35.6303   -40.2390
  BTU/LB-R           -1.8400    -1.7271    -1.6165    -1.9429    -2.1942
DENSITY:
  LBMOL/CUFT           2.4128     2.3170     2.2060     3.0672     3.3410
  LB/CUFT           70.4473    67.6517    64.4108    56.2492    61.2712
AVG MW              29.1976    29.1984    29.1984    18.3391    18.3391
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 50

                         STREAM SECTION

S-111 S-112 S-113 S-114 S-115
-----------------------------
```

```
STREAM ID           S-111     S-112     S-113     S-114     S-115
FROM :              FSPLIT    P-102     FSPLIT    D-101     P-100
TO   :              P-102     M-102     ----      P-100     HX-102

SUBSTREAM: MIXED
PHASE:              LIQUID    LIQUID    LIQUID    LIQUID    LIQUID
COMPONENTS: LBMOL/HR
  GLYCEROL          5.5586-04  5.5586-04  2.8635-04  168.4566   168.4566
  ACETOL              0.0       0.0       0.0       0.0       0.0
  WATER             491.6749   491.6749   253.2871   206.9758   206.9758
  HYDROGEN            0.0       0.0       0.0       0.0       0.0
  PG                  0.0       0.0       0.0       0.0       0.0
  N-PROP              0.0       0.0       0.0       0.0       0.0
  ETHYL-01            0.0       0.0       0.0       0.0       0.0
  ISO-PROP            0.0       0.0       0.0       0.0       0.0
  SODIU-01            0.0       0.0       0.0       0.0       0.0
  METHA-01           11.6167    11.6167    5.9844  6.7587-02  6.7587-02
COMPONENTS: MOLE FRAC
  GLYCEROL          1.1044-06  1.1044-06  1.1044-06    0.4486     0.4486
  ACETOL              0.0       0.0       0.0       0.0       0.0
  WATER               0.9769    0.9769    0.9769    0.5512    0.5512
  HYDROGEN            0.0       0.0       0.0       0.0       0.0
  PG                  0.0       0.0       0.0       0.0       0.0
  N-PROP              0.0       0.0       0.0       0.0       0.0
  ETHYL-01            0.0       0.0       0.0       0.0       0.0
  ISO-PROP            0.0       0.0       0.0       0.0       0.0
  SODIU-01            0.0       0.0       0.0       0.0       0.0
  METHA-01          2.3082-02  2.3082-02  2.3082-02  1.7999-04  1.7999-04
COMPONENTS: MASS FRAC
  GLYCEROL          5.5463-06  5.5463-06  5.5463-06    0.8061     0.8061
  ACETOL              0.0       0.0       0.0       0.0       0.0
  WATER               0.9597    0.9597    0.9597    0.1938    0.1938
  HYDROGEN            0.0       0.0       0.0       0.0       0.0
  PG                  0.0       0.0       0.0       0.0       0.0
  N-PROP              0.0       0.0       0.0       0.0       0.0
  ETHYL-01            0.0       0.0       0.0       0.0       0.0
  ISO-PROP            0.0       0.0       0.0       0.0       0.0
  SODIU-01            0.0       0.0       0.0       0.0       0.0
  METHA-01          4.0328-02  4.0328-02  4.0328-02  1.1253-04  1.1253-04
TOTAL FLOW:
  LBMOL/HR          503.2922   503.2922   259.2717   375.5000   375.5000
  LB/HR            9229.9377  9229.9377  4754.8164  1.9245+04  1.9245+04
  CUFT/HR           150.6406   150.6465    77.6027   267.0142   267.5415
STATE VARIABLES:
  TEMP   F           80.0000    80.0714    80.0000   247.8897   252.1323
  PRES   PSIA        19.7407    30.0000    19.7407    20.0000   587.0000
  VFRAC               0.0       0.0       0.0       0.0       0.0
  LFRAC               1.0000    1.0000    1.0000    1.0000    1.0000
  SFRAC               0.0       0.0       0.0       0.0       0.0
ENTHALPY:
  BTU/LBMOL        -1.2316+05 -1.2316+05 -1.2316+05 -1.8824+05 -1.8804+05
  BTU/LB           -6715.7386 -6715.6338 -6715.7386 -3672.8791 -3669.0308
  BTU/HR           -6.1986+07 -6.1985+07 -3.1932+07 -7.0684+07 -7.0610+07
ASPEN PLUS   PLAT: WIN32     VER: 24.0                04/11/2011  PAGE 51
```

```
                    STREAM SECTION

S-111 S-112 S-113 S-114 S-115 (CONTINUED)

STREAM ID            S-111      S-112      S-113      S-114      S-115

ENTROPY:
  BTU/LBMOL-R         -40.2390   -40.2366   -40.2390   -74.0968   -73.9371
  BTU/LB-R             -2.1942    -2.1940    -2.1942    -1.4458    -1.4426
DENSITY:
  LBMOL/CUFT            3.3410     3.3409     3.3410     1.4063     1.4035
  LB/CUFT              61.2712    61.2688    61.2712    72.0743    71.9322
AVG MW                 18.3391    18.3391    18.3391    51.2513    51.2513
ASPEN PLUS   PLAT: WIN32    VER: 24.0                04/11/2011  PAGE 52

                    STREAM SECTION

S-116 S-117 S-118 S-119 S-120
-----------------------------

STREAM ID            S-116      S-117      S-118      S-119      S-120
FROM :               HX-102     ----       T-101      M-101      HX-103
TO   :               R-101      T-101      M-101      HX-103     R-101


MAX CONV. ERROR:       0.0        0.0        0.0     2.5376-04     0.0
SUBSTREAM: MIXED
PHASE:               LIQUID     VAPOR      VAPOR      MIXED      VAPOR
COMPONENTS: LBMOL/HR
  GLYCEROL            168.4566     0.0        0.0        0.0        0.0
  ACETOL                0.0        0.0        0.0        0.0        0.0
  WATER               206.9758     0.0        0.0       17.0791    17.0791
  HYDROGEN              0.0      171.8376   171.8376   665.5687   665.5687
  PG                    0.0        0.0        0.0        0.2401     0.2401
  N-PROP                0.0        0.0        0.0        0.9993     0.9993
  ETHYL-01              0.0        0.0        0.0        0.0        0.0
  ISO-PROP              0.0        0.0        0.0        3.7252     3.7252
  SODIU-01              0.0        0.0        0.0        0.0        0.0
  METHA-01            6.7587-02    0.0        0.0     1.1240-02  1.1240-02
COMPONENTS: MOLE FRAC
  GLYCEROL              0.4486     0.0        0.0        0.0        0.0
  ACETOL                0.0        0.0        0.0        0.0        0.0
  WATER                 0.5512     0.0        0.0     2.4838-02  2.4838-02
  HYDROGEN              0.0        1.0000     1.0000     0.9679     0.9679
  PG                    0.0        0.0        0.0     3.4915-04  3.4915-04
  N-PROP                0.0        0.0        0.0     1.4533-03  1.4533-03
  ETHYL-01              0.0        0.0        0.0        0.0        0.0
  ISO-PROP              0.0        0.0        0.0     5.4175-03  5.4175-03
  SODIU-01              0.0        0.0        0.0        0.0        0.0
  METHA-01            1.7999-04    0.0        0.0     1.6346-05  1.6346-05
COMPONENTS: MASS FRAC
  GLYCEROL              0.8061     0.0        0.0        0.0        0.0
  ACETOL                0.0        0.0        0.0        0.0        0.0
```

```
  WATER                 0.1938     0.0        0.0        0.1576     0.1576
  HYDROGEN              0.0        1.0000     1.0000     0.6874     0.6874
  PG                    0.0        0.0        0.0     9.3594-03  9.3594-03
  N-PROP                0.0        0.0        0.0     3.0767-02  3.0767-02
  ETHYL-01              0.0        0.0        0.0        0.0        0.0
  ISO-PROP              0.0        0.0        0.0        0.1147     0.1147
  SODIU-01              0.0        0.0        0.0        0.0        0.0
  METHA-01           1.1253-04     0.0        0.0     1.8451-04  1.8451-04
 TOTAL FLOW:
  LBMOL/HR            375.5000   171.8376   171.8376   687.6236   687.6236
  LB/HR             1.9245+04   346.4039   346.4039  1951.9440  1951.9440
  CUFT/HR             289.9531  1010.0551  1479.7311  8233.9153  1.0946+04
 STATE VARIABLES:
  TEMP   F            410.0000    70.0000    11.7339   202.4134   416.4896
  PRES   PSIA         581.0365  1000.0000   600.0000   600.0000   598.9147
  VFRAC                 0.0        1.0000     1.0000     0.9943     1.0000
  LFRAC                 1.0000     0.0        0.0     5.6867-03     0.0
  SFRAC                 0.0        0.0        0.0        0.0        0.0
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 53

                              STREAM SECTION

 S-116 S-117 S-118 S-119 S-120 (CONTINUED)

 STREAM ID             S-116      S-117      S-118      S-119      S-120

 ENTHALPY:
  BTU/LBMOL          -1.8274+05   -30.5191  -441.0296 -2648.5083 -1001.3455
  BTU/LB             -3565.6165   -15.1393  -218.7777  -933.0067  -352.7503
  BTU/HR             -6.8620+07 -5244.3222 -7.5785+04 -1.8212+06 -6.8855+05
 ENTROPY:
  BTU/LBMOL-R          -67.2210    -8.5047    -8.2835    -6.5588    -4.3807
  BTU/LB-R              -1.3116    -4.2188    -4.1091    -2.3105    -1.5432
 DENSITY:
  LBMOL/CUFT             1.2950     0.1701     0.1161  8.3511-02  6.2821-02
  LB/CUFT               66.3723     0.3430     0.2341     0.2371     0.1783
 AVG MW                 51.2513     2.0159     2.0159     2.8387     2.8387
 ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 54

                              STREAM SECTION

 S-121 S-122 S-123 S-124 S-125
 -----------------------------

 STREAM ID             S-121      S-122      S-123      S-124      S-125
 FROM :                R-101      F-101      F-101      HX-102     F-102
 TO   :                F-101      M-103      HX-102     F-102      M-103



 MAX CONV. ERROR:    -2.0148-04    0.0        0.0        0.0        0.0
 SUBSTREAM: MIXED
 PHASE:                MIXED      LIQUID     VAPOR      MIXED      LIQUID
 COMPONENTS: LBMOL/HR
  GLYCEROL              0.0        0.0        0.0        0.0        0.0
```

```
  ACETOL              0.0        0.0        0.0        0.0        0.0
  WATER             395.0385    27.2438   367.7947   367.7947    42.1524
  HYDROGEN          494.5904     0.3463   494.2442   494.2442     0.3565
  PG              166.1698    50.0037   116.1662   116.1662    53.7172
  N-PROP              2.2628     0.1430     2.1199     2.1199     0.1974
  ETHYL-01            0.0        0.0        0.0        0.0        0.0
  ISO-PROP            4.9896     0.1972     4.7924     4.7924     0.2646
  SODIU-01            0.0        0.0        0.0        0.0        0.0
  METHA-01          7.8827-02  3.8275-03  7.4999-02  7.4999-02  5.8603-03
COMPONENTS: MOLE FRAC
  GLYCEROL            0.0        0.0        0.0        0.0        0.0
  ACETOL              0.0        0.0        0.0        0.0        0.0
  WATER               0.3716     0.3496     0.3733     0.3733     0.4359
  HYDROGEN            0.4652  4.4429-03     0.5017     0.5017  3.6870-03
  PG                0.1563     0.6416     0.1179     0.1179     0.5555
  N-PROP            2.1285-03  1.8346-03  2.1517-03  2.1517-03  2.0419-03
  ETHYL-01            0.0        0.0        0.0        0.0        0.0
  ISO-PROP          4.6933-03  2.5308-03  4.8644-03  4.8644-03  2.7370-03
  SODIU-01            0.0        0.0        0.0        0.0        0.0
  METHA-01          7.4146-05  4.9110-05  7.6126-05  7.6126-05  6.0607-05
COMPONENTS: MASS FRAC
  GLYCEROL            0.0        0.0        0.0        0.0        0.0
  ACETOL              0.0        0.0        0.0        0.0        0.0
  WATER               0.3357     0.1137     0.3925     0.3925     0.1557
  HYDROGEN          4.7037-02  1.6169-04  5.9026-02  5.9026-02  1.4740-04
  PG                0.5965     0.8814     0.5237     0.5237     0.8384
  N-PROP            6.4155-03  1.9905-03  7.5472-03  7.5472-03  2.4336-03
  ETHYL-01            0.0        0.0        0.0        0.0        0.0
  ISO-PROP          1.4146-02  2.7458-03  1.7062-02  1.7062-02  3.2619-03
  SODIU-01            0.0        0.0        0.0        0.0        0.0
  METHA-01          1.1916-04  2.8408-05  1.4237-04  1.4237-04  3.8513-05
TOTAL FLOW:
  LBMOL/HR          1063.1301    77.9378   985.1922   985.1922    96.6940
  LB/HR             2.1197+04  4317.1178  1.6880+04  1.6880+04  4875.6888
  CUFT/HR           1.6500+04    89.2728  1.6587+04  1.4834+04    97.9093
STATE VARIABLES:
  TEMP   F          455.8376   455.1614   455.1614   429.0464   429.0460
  PRES   PSIA       566.0365   560.0000   560.0000   559.1403   559.1403
  VFRAC               0.9262     0.0        1.0000     0.9019     0.0
  LFRAC             7.3771-02     1.0000     0.0     9.8148-02     1.0000
  SFRAC               0.0        0.0        0.0        0.0        0.0
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 55

                           STREAM SECTION

S-121 S-122 S-123 S-124 S-125 (CONTINUED)

STREAM ID             S-121      S-122      S-123      S-124      S-125

ENTHALPY:
  BTU/LBMOL         -6.5193+04 -1.6354+05 -5.7413+04 -5.9433+04 -1.5820+05
  BTU/LB            -3269.7482 -2952.3758 -3350.9178 -3468.8219 -3137.3276
  BTU/HR            -6.9308+07 -1.2746+07 -5.6563+07 -5.8553+07 -1.5297+07
ENTROPY:
```

```
  BTU/LBMOL-R         -20.1361   -76.6788   -15.6425   -17.8791   -71.3337
  BTU/LB-R            -1.0099    -1.3843    -0.9130    -1.0435    -1.4147
DENSITY:
  LBMOL/CUFT         6.4431-02     0.8730  5.9395-02  6.6413-02     0.9876
  LB/CUFT             1.2846    48.3587     1.0176     1.1379    49.7980
AVG MW                19.9382    55.3918    17.1335    17.1335    50.4239
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 56

                         STREAM SECTION

S-126 S-127 S-128 S-129 S-130
-----------------------------


STREAM ID              S-126      S-127      S-128      S-129      S-130
FROM :                 F-102      HX-103     C-102      V-101      V-101
TO   :                 HX-103     C-102      V-101      M-103      CP-101

SUBSTREAM: MIXED
PHASE:                 VAPOR      MIXED      MIXED      LIQUID     VAPOR
COMPONENTS: LBMOL/HR
  GLYCEROL               0.0        0.0        0.0        0.0        0.0
  ACETOL                 0.0        0.0        0.0        0.0        0.0
  WATER               325.6423   325.6423   325.6423   308.5626    17.0797
  HYDROGEN            493.8876   493.8876   493.8876     0.1372   493.7505
  PG                   62.4490    62.4490    62.4490    62.2089     0.2401
  N-PROP                1.9224     1.9224     1.9224     0.9230     0.9994
  ETHYL-01               0.0        0.0        0.0        0.0        0.0
  ISO-PROP              4.5277     4.5277     4.5277     0.8016     3.7261
  SODIU-01               0.0        0.0        0.0        0.0        0.0
  METHA-01           6.9139-02  6.9139-02  6.9139-02  5.7899-02  1.1240-02
COMPONENTS: MOLE FRAC
  GLYCEROL               0.0        0.0        0.0        0.0        0.0
  ACETOL                 0.0        0.0        0.0        0.0        0.0
  WATER                 0.3665     0.3665     0.3665     0.8279  3.3113-02
  HYDROGEN              0.5559     0.5559     0.5559  3.6804-04     0.9572
  PG                 7.0286-02  7.0286-02  7.0286-02     0.1669  4.6548-04
  N-PROP             2.1637-03  2.1637-03  2.1637-03  2.4765-03  1.9376-03
  ETHYL-01               0.0        0.0        0.0        0.0        0.0
  ISO-PROP           5.0959-03  5.0959-03  5.0959-03  2.1508-03  7.2239-03
  SODIU-01               0.0        0.0        0.0        0.0        0.0
  METHA-01           7.7815-05  7.7815-05  7.7815-05  1.5535-04  2.1791-05
COMPONENTS: MASS FRAC
  GLYCEROL               0.0        0.0        0.0        0.0        0.0
  ACETOL                 0.0        0.0        0.0        0.0        0.0
  WATER                 0.4887     0.4887     0.4887     0.5346     0.1916
  HYDROGEN           8.2940-02  8.2940-02  8.2940-02  2.6592-05     0.6199
  PG                    0.3959     0.3959     0.3959     0.4552  1.1379-02
  N-PROP             9.6242-03  9.6242-03  9.6242-03  5.3342-03  3.7406-02
  ETHYL-01               0.0        0.0        0.0        0.0        0.0
  ISO-PROP           2.2667-02  2.2667-02  2.2667-02  4.6327-03     0.1395
  SODIU-01               0.0        0.0        0.0        0.0        0.0
  METHA-01           1.8455-04  1.8455-04  1.8455-04  1.7841-04  2.2431-04
TOTAL FLOW:
  LBMOL/HR            888.4982   888.4982   888.4982   372.6911   515.8070
```

```
  LB/HR             1.2004+04  1.2004+04  1.2004+04  1.0398+04  1605.6541
  CUFT/HR           1.4736+04  1.3675+04  7127.7148   178.0009  6949.7139
STATE VARIABLES:
  TEMP   F           429.0460   409.0464   225.0000   225.0000   225.0000
  PRES   PSIA        559.1403   558.2795   553.2795   553.2795   553.2795
  VFRAC                1.0000     0.9382     0.5805     0.0        1.0000
  LFRAC                0.0      6.1755-02    0.4195     1.0000     0.0
  SFRAC                0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL         -4.8685+04 -4.9959+04 -5.8397+04 -1.3434+05 -3525.5544
  BTU/LB            -3603.4643 -3697.8180 -4322.3718 -4814.9205 -1132.5638
  BTU/HR            -4.3256+07 -4.4389+07 -5.1886+07 -5.0068+07 -1.8185+06
ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 57

                          STREAM SECTION

S-126 S-127 S-128 S-129 S-130 (CONTINUED)

STREAM ID            S-126      S-127      S-128      S-129      S-130

ENTROPY:
  BTU/LBMOL-R         -12.0617   -13.5096   -24.1456   -49.0038    -6.1846
  BTU/LB-R             -0.8928    -0.9999    -1.7872    -1.7564    -1.9868
DENSITY:
  LBMOL/CUFT         6.0293-02  6.4970-02     0.1247     2.0938  7.4220-02
  LB/CUFT               0.8146     0.8778     1.6841    58.4178     0.2310
AVG MW                 13.5105    13.5105    13.5105    27.9009     3.1129
ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 58

                          STREAM SECTION

S-131 S-132 S-133 S-134 S-135
-----------------------------

STREAM ID            S-131      S-132      S-133      S-134      S-135
FROM :               CP-101     M-103      VALVE      D-102      C-103
TO   :               M-101      VALVE      D-102      C-103      ----

SUBSTREAM: MIXED
PHASE:               VAPOR      MIXED      MIXED      LIQUID     LIQUID
COMPONENTS: LBMOL/HR
  GLYCEROL               0.0        0.0        0.0        0.0        0.0
  ACETOL                 0.0        0.0        0.0        0.0        0.0
  WATER                17.0797   377.9589   377.9589     2.1127     2.1127
  HYDROGEN            493.7505     0.8399     0.8399  1.5652-20  1.5652-20
  PG                    0.2401   165.9297   165.9297   162.1873   162.1873
  N-PROP                0.9994     1.2634     1.2634  3.6366-06  3.6366-06
  ETHYL-01               0.0        0.0        0.0        0.0        0.0
  ISO-PROP              3.7261     1.2635     1.2635  9.1415-10  9.1415-10
  SODIU-01               0.0        0.0        0.0        0.0        0.0
  METHA-01           1.1240-02  6.7586-02  6.7586-02  1.6305-06  1.6305-06
COMPONENTS: MOLE FRAC
  GLYCEROL               0.0        0.0        0.0        0.0        0.0
  ACETOL                 0.0        0.0        0.0        0.0        0.0
```

```
  WATER              3.3113-02     0.6906     0.6906  1.2859-02  1.2859-02
  HYDROGEN             0.9572  1.5346-03  1.5346-03  9.5267-23  9.5267-23
  PG              4.6548-04     0.3032     0.3032     0.9871     0.9871
  N-PROP            1.9376-03  2.3084-03  2.3084-03  2.2134-08  2.2134-08
  ETHYL-01              0.0        0.0        0.0        0.0        0.0
  ISO-PROP           7.2239-03  2.3085-03  2.3085-03  5.5639-12  5.5639-12
  SODIU-01              0.0        0.0        0.0        0.0        0.0
  METHA-01           2.1791-05  1.2349-04  1.2349-04  9.9242-09  9.9242-09
COMPONENTS: MASS FRAC
  GLYCEROL              0.0        0.0        0.0        0.0        0.0
  ACETOL                0.0        0.0        0.0        0.0        0.0
  WATER                0.1916     0.3476     0.3476  3.0745-03  3.0745-03
  HYDROGEN             0.6199  8.6428-05  8.6428-05  2.5488-24  2.5488-24
  PG              1.1379-02     0.6445     0.6445     0.9969     0.9969
  N-PROP            3.7406-02  3.8755-03  3.8755-03  1.7653-08  1.7653-08
  ETHYL-01              0.0        0.0        0.0        0.0        0.0
  ISO-PROP              0.1395  3.8757-03  3.8757-03  4.4376-12  4.4376-12
  SODIU-01              0.0        0.0        0.0        0.0        0.0
  METHA-01           2.2431-04  1.1054-04  1.1054-04  4.2203-09  4.2203-09
TOTAL FLOW:
  LBMOL/HR            515.8070   547.3230   547.3230   164.3000   164.3000
  LB/HR            1605.6541  1.9591+04  1.9591+04  1.2380+04  1.2380+04
  CUFT/HR           6597.3326   357.4023  1.7899+04   233.5486   193.9751
STATE VARIABLES:
  TEMP   F          244.4171   317.2634   254.7511   364.0271    90.0000
  PRES   PSIA         600.0000   548.2795    30.0000    20.0000    15.0000
  VFRAC               1.0000  1.7993-04     0.1278     0.0        0.0
  LFRAC               0.0        0.9998     0.8722     1.0000     1.0000
  SFRAC               0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL         -3384.1109 -1.4271+05 -1.4271+05 -1.9740+05 -2.1311+05
  BTU/LB           -1087.1259 -3986.9863 -3986.9863 -2619.7765 -2828.3357
  BTU/HR           -1.7455+06 -7.8110+07 -7.8110+07 -3.2432+07 -3.5014+07
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 59

                          STREAM SECTION

S-131 S-132 S-133 S-134 S-135 (CONTINUED)

STREAM ID             S-131      S-132      S-133      S-134      S-135

ENTROPY:
  BTU/LBMOL-R          -6.1443   -56.4712   -56.2361  -111.9337  -135.0044
  BTU/LB-R            -1.9738    -1.5776    -1.5711    -1.4855    -1.7917
DENSITY:
  LBMOL/CUFT         7.8184-02     1.5314  3.0578-02     0.7035     0.8470
  LB/CUFT             0.2434    54.8156     1.0945    53.0072    63.8214
AVG MW                3.1129    35.7946    35.7946    75.3485    75.3485
ASPEN PLUS   PLAT: WIN32     VER: 24.0                 04/11/2011  PAGE 60

                          STREAM SECTION

S-136 S-137
-----------
```

```
STREAM ID            S-136     S-137
FROM :               D-102     D-102
TO   :               ----      ----

SUBSTREAM: MIXED
PHASE:               LIQUID    VAPOR
COMPONENTS: LBMOL/HR
  GLYCEROL              0.0       0.0
  ACETOL                0.0       0.0
  WATER               375.5238    0.3223
  HYDROGEN              7.0112-05    0.8399
  PG                   3.7416  8.8865-04
  N-PROP                0.3473    0.9162
  ETHYL-01              0.0       0.0
  ISO-PROP            4.0319-02    1.2232
  SODIU-01              0.0       0.0
  METHA-01            6.6709-02  8.7551-04
COMPONENTS: MOLE FRAC
  GLYCEROL              0.0       0.0
  ACETOL                0.0       0.0
  WATER                 0.9889  9.7583-02
  HYDROGEN              1.8464-07    0.2543
  PG                 9.8535-03  2.6902-04
  N-PROP              9.1452-04    0.2773
  ETHYL-01              0.0       0.0
  ISO-PROP            1.0618-04    0.3703
  SODIU-01              0.0       0.0
  METHA-01            1.7568-04  2.6504-04
COMPONENTS: MASS FRAC
  GLYCEROL              0.0       0.0
  ACETOL                0.0       0.0
  WATER                 0.9562  4.2649-02
  HYDROGEN              1.9976-08  1.2435-02
  PG                 4.0241-02  4.9664-04
  N-PROP              2.9496-03    0.4044
  ETHYL-01              0.0       0.0
  ISO-PROP            3.4246-04    0.5399
  SODIU-01              0.0       0.0
  METHA-01            3.0211-04  2.0603-04
TOTAL FLOW:
  LBMOL/HR            379.7197    3.3033
  LB/HR              7075.3126   136.1602
  CUFT/HR             117.1993  1020.6045
STATE VARIABLES:
  TEMP   F            130.0000   130.0000
  PRES   PSIA          20.0000    20.0000
  VFRAC                 0.0       1.0000
  LFRAC                 1.0000    0.0
  SFRAC                 0.0       0.0
ENTHALPY:
  BTU/LBMOL          -1.2347+05 -8.3091+04
  BTU/LB             -6626.6697 -2015.8168
  BTU/HR             -4.6886+07 -2.7447+05
```

```
                           STREAM SECTION

S-136 S-137 (CONTINUED)

STREAM ID              S-136      S-137

ENTROPY:
  BTU/LBMOL-R          -39.0904   -47.4015
  BTU/LB-R             -2.0979    -1.1500
DENSITY:
  LBMOL/CUFT            3.2399  3.2366-03
  LB/CUFT              60.3699     0.1334
AVG MW                 18.6330    41.2194
ASPEN PLUS   PLAT: WIN32     VER: 24.0                  04/11/2011  PAGE 62

                        PROBLEM STATUS SECTION

BLOCK STATUS
------------

**************************************************************************
*                                                                        *
* Calculations were completed with errors                                *
*                                                                        *
* The following Unit Operation blocks were                               *
* completed with warnings:                                               *
*   HX-102    HX-103                                                     *
*                                                                        *
* All streams were flashed normally                                      *
*                                                                        *
* The following Convergence blocks were                                  *
* completed with errors:                                                 *
*   $OLVER02                                                             *
*                                                                        *
* All Sensitivity blocks were completed normally                         *
*                                                                        *
**************************************************************************
```