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Optimal production of biobutanol via hydrogenation of butyric acid

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Optimal Production of Biobutanol via Hydrogenation of Butyric Acid

An Undergraduate Honors College Thesis

in the

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College of Engineering
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by

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This thesis is approved.

Thesis Advisor:

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Thesis Committee:

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PREFACE

International Design Contest has been a great platform for me to apply the knowledge gained in my fluid mechanics, reactor design, mass transfer, heat transfer, and analytical chemistry classes, making it a solid capstone project. I am grateful to my advisors Dr. Roy Penny and Dr. Hestekin for giving me the opportunity to be part of this great experience. As part of the six member team, I have contributed specifically in defining the problem, collecting and relating background information, purchasing the equipment, reducing and analyzing data, designing process flow diagram (PFD) for the process and conducting the experiments. Since we opted for open task one of the challenges we faced was to define the problem. I worked with my advisors to come up with a problem definition for our project. I helped in introducing the project with background information, definition of key components, importance of the objectives and solution methods utilized to solve the problem. Getting equipment part took great deal of time and carefulness; I was also part of this process. I also worked on analyzing and reduction of gas chromatograph results for product samples as well as kinetics study of the reaction. I designed process flow diagrams for hydrogenator unit. I was also key player in running the equipment to conduct the experiment. From all these activcities I have gained valuable knowledge of reactor design, kinetics modeling and practical aspects of unit operation. The full report on the project I was involved in is presented in Appendix-A.

APPENDIX- A

Optimal Production of

Biobutanol via Hydrogenation of Butyric Acid

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Biobutanol via Hydrogenation of Butyric Acid

Hogdrogenation

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EXECUTIVE SUMMARY

Butanol is a primary alcohol most commonly used industrially as a solvent. It is largely produced petrochemically using fossil fuel feedstocks. The global butanol market has steadily increased in recent years and is projected to continue increasing at an annual rate of 3.2%. Additionally, the possibility of introducing butanol to the fuel market presents the opportunity to further grow the industry. Because of the increasing demand and its production from fossil fuels, there is a need to manufacture butanol more sustainably and efficiently to help the environment and improve the world economy.

Currently, biobutanol is not produced commercially; however, its development has reached the pilot plant stage in several locations around the world. Current research and development efforts can be improved. There are two main methods of production, the Acetone Butanol Ethanol (ABE) process and a two-step fermentation process. Neither method is commercially viable. The Hogdrogenation process improves upon the second step of the two-step fermentation process.

Experimental data shows a 100% conversion rate for butyric acid, and 88% selectivity for butanol can be achieved at a temperature of 349°F and a residence time of 1.13min. Through a careful economic analysis of a full scale design, the process is shown to be economically favorable. The selected full scale plant produces 30 million gal/year; the fixed capital investment is $154,488,948 and the operating cost is $58,642,217. At a selling price of $4.00 per gallon, the rate of return on investment is 37.8% with a net present value following a ten year lifetime of $17.02 million.

INTRODUCTION

Butanol is a straight chain primary alcohol that can be applied in a variety of industries. Traditionally, it has been used as a solvent and as an intermediate in several consumer products, but butanol also has the potential to be an alternative, sustainable transportation fuel source. It is currently produced by petrochemical processing at the rate of 950 million gallons per year with a market value of over $4 billion per year[1]. Specifically, butanol is synthesized using propylene (a co-product of fossil fuel processing) as the primary feedstock. A modification of the Klass Model, a model used to estimate the future availability of fossil fuels, predicts the depletion time for oil, coal and gas to be approximately 35, 107 and 37 years, respectively which underscores the need for both alternative fuel sources and alternative means of producing petroleum based

products[2]. In addition to the future scarcity of fossil fuels, the production of petrochemical butanol also produces carbon dioxide, a greenhouse gas, as a by-product[3]. The increasing demand for butanol coupled with the negative aspects of petrochemical sources demonstrates the need for a renewable means of butanol production[4].

Biobutanol refers to butanol production from renewable, biological feedstock. This technology has been implemented for over 100 years in the form of ABE fermentation. ABE produces acetone, butanol, and ethanol in a 3:6:1 ratio from potato starch via fermentation by C. tyrobutyricum. Using this method, butanol is produced in two stages; first, the sugars are converted to organic acids and then converted to the solvents by an additional metabolic pathway[5]. This process is difficult to control and requires extensive separation processes to obtain pure butanol with a yield of only 25% of product carbon vs. feed carbon[6].

In 1998, Ramey developed an improved two-step method for butanol conversion from fermentation utilizing two different strains of bacteria in individual fermenters. The first fermenter converts the sugars to butyric acid while the second fermenter produces butanol from the butyric acid. The second fermentation is achieved by either separating the butyric acid from the fermentation broth or by directly feeding the first fermentation broth to the second fermenter. Ideally, this process has a theoretical conversion of 40%[6].

As global butanol demand continues to increase, the need to develop an economical and sustainable alternative for biobutanol production also increases. Such a method would need to address the low yield rates of current biobutanol production techniques while remaining an environmentally conscious alternative to petrochemical production of butanol. Presented in this report is a potential solution to the problems facing biobutanol production with an experimental demonstration of a key step in the process.

TASK PARAMETERS

The purpose of this task is to optimize the conversion of biobutanol by utilizing a hydrotreater to convert butyric acid to butanol:

Operating Conditions
1. Feed Streams
   a. 95:5 by Volume Mixture of Charcoal fluid: Butyric Acid
   b. H_2
2. Temperature Range: 300-350°F

3. Pressure Range: 600-2000 psig
4. Catalyst Bed Height: 22.375"

Task Premises

1. Develop a scalable hydrogenation process for the production of butanol from butyric acid
2. Design a bench-scale apparatus to demonstrate the process
3. Determine hazards of operation and develop safety procedures
4. Determine optimal temperature, pressure, and residence time for butanol selectivity
5. Develop a kinetic model to predict the conversion of butyric acid to butanol and butane
6. Determine the economic viability of the proposed technology

EXISTING TECHNOLOGY

Currently, a common method of biobutanol production includes a primary fermentation step where sugar is fermented using C. tyrobutyricum (or other similar strains) to yield butyric acid. The butyric acid then undergoes an additional fermentation step with C. acetobutylicum (or other similar strains) to produce butanol[1]. Among other problems, bacteria suffer from product inhibition, which adversely affects costs. Two alternative routes from butyric acid to butanol, which involve direct hydrogenation are discussed below.

Esterification followed by hydrogenation

Hydrogenation of an organic acid will generally first require the activation of the carbonyl group. A common method of activating the carbonyl group is by using an alcohol to form an ester that will then be hydrolyzed into two alcohols. Since conventional esterification is a reversible mechanism, the conversion is less than 100% and in most laboratory studies the highest conversion is around 80%. Furthermore, the catalytic hydrogenation of esters to alcohols suffers from the equilibrium limitation. At optimum conditions in practice, the hydrogenation reaction is stopped when 5 to 10% of residual esters still remain[7].

Direct Hydrogenation

A less common method of converting butyric acid to butanol is by direct hydrogenation. This method uses a selective catalyst under high temperature and high pressure to activate the carbonyl group and achieve the hydrogenation of the acid to the alcohol. A trickle bed reactor is typically used which is costly and inefficient. In this method, the feed stream must be vaporized before contacting the hydrogen gas and reacting at the surface of the catalyst. The product stream then must be cooled and sent to a gas separator. The H_2 gas has to be compressed to be

recycled in the system. This requires an excessive amount of hydrogen constantly flowing through the reactor around 1000 to 5000 SCF/bbl of liquid, which requires a large reactor volume. Another drawback is the extreme conditions of operation, reaching up to 5000 psi and 900F[8].

DEVELOPED TECHNOLOGY

In this study, a desulfurization technology is adapted to optimize the conversion of butyric acid to butanol[8]. This adaptation is referred to as Hogdrogenation. In this process, high pressure hydrogen gas is dissolved into a liquid feed stream consisting of the reacting species and an inert, easily separable diluent, such as charcoal starter or diesel, that enters a liquid phase packed bed reactor where the feed reacts at the surface of the catalyst. This technology has several advantages over existing methods. Trickle bed reactors are gas continuous with gas circulation rates several times greater than reaction requirements. Hogdrogenation utilizes a liquid recycle stream to ensure the concentration of dissolved hydrogen entering the reactor is greater than reaction requirements. This eliminates the need for expensive hydrogen recycle compressors essential for trickle bed reactors. The adiabatic temperature in the Hogdrogenation reactor is much lower than that of a trickle bed reactor due to the increase in thermal mass experienced by the liquid phase reactor as a result of the liquid recycle. The temperature rise in this technology is limited by the concentration of hydrogen dissolved in the liquid. This eliminates the possibility of runaway reaction yielding a safer process[8].

The hydrogenation process detailed in this study is well understood and easily controlled. The technology has the potential of 100% conversion at high yield of organic acids to alcohol making it an ideal candidate for butanol production. Multiple commercial units, desulfurizing hydrocarbons, exist showcasing the economic viability of this process, but there is no published literature covering the technology for hydrogenating butyric acid to butanol.

EXPERIMENTAL APPARATUS

A diagram of the experimental apparatus is presented in Figure 1. The entire apparatus can be broken down into the containment box, piping and reactor system, and the controls and data acquisition. Each of these portions is described in detail below.
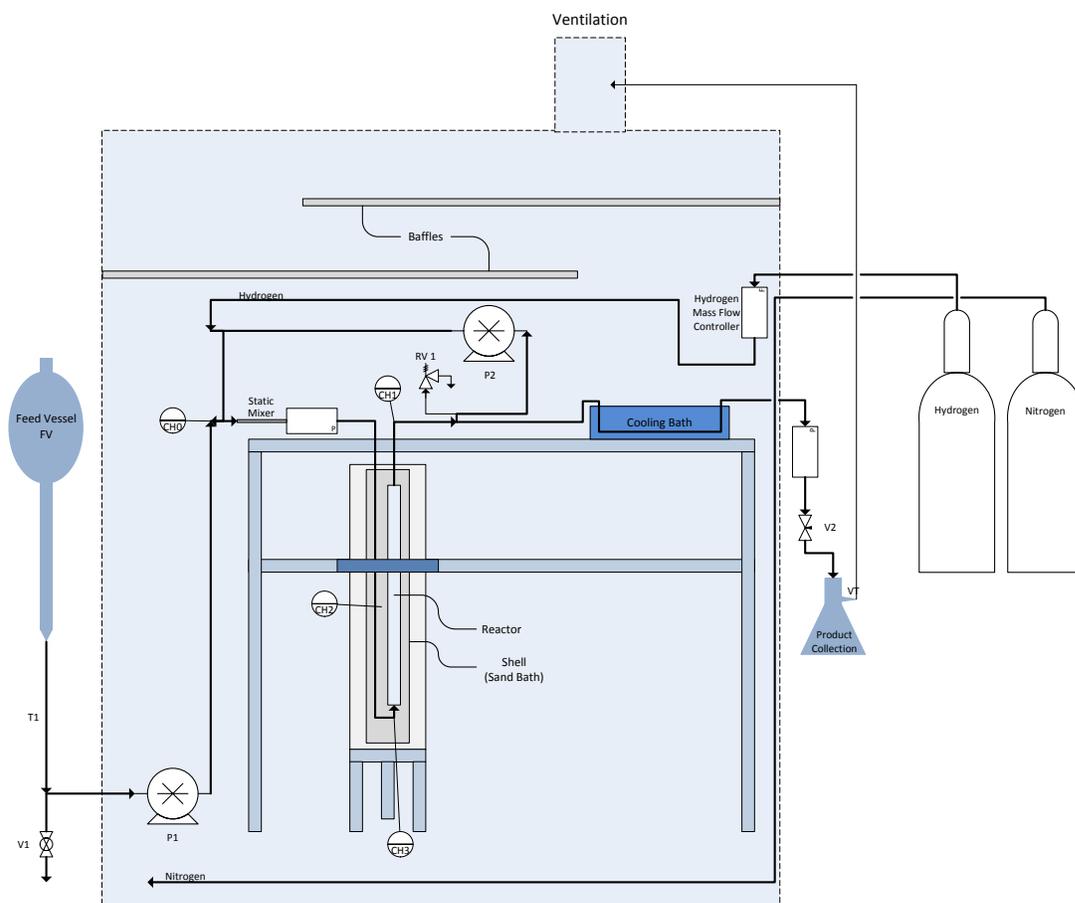
Figure 1. A detailed Process Flow Diagram of the experiment apparatus

Containment Box

The containment box was constructed as a safety feature to handle H_2, the diluent and butyric acid. The box was sized such that a box full of nitrogen mixed with vaporized reactor contents would be below the explosive limit when mixed with air. The N_2 purge is vented, through a 6" flexible duct, to a hood or exhaust duct indoors and to the atmosphere outdoors. Baffles and a weak explosion vent were additional safety features. The weak explosion vent was sized for an overpressure corresponding to a sudden release of the entire system contents as vapor using equations for low pressure venting[9]. The containment box was constructed out of plywood on two sided and transparent polycarbonate on other two sides. On the outside right wall of the box, there are two strap locations for H_2 and N_2 bottles.

Figure 2. The containment box and the piping and reactor system are shown.

Figure 3. Shown are the strapped cylinders, product vessel, and weak explosion vent.

Piping and Reactor System

The reactor system begins at the feed vessel which consists of a 1000 mL separatory funnel and a 250 mL graduated cylinder that have been joined. A Waters 501 HPLC feed pump is connected to the graduated cylinder using Tygon tubing. A 1/16" sheathed J type thermocouple is inserted into the feed line prior to entering a static mixer. Following the static mixer is a pressure for monitoring the reactor inlet pressure. The reactor consists of a ¾" OD, ½" ID x 24" long stainless steel (SS) tube enclosed in a 2 ½" SS shell to which pool filter sand is added to serve as a sand bath. The sand bath is heated by high temperature heating taped wrapped spirally around the shell. At least 2" of high temperature blanket insulation is wrapped around the reactor shell to prevent heat loss. The reactor is packed with 81.62 g of Axens HT-438 nickel-molybdenum (bulk density = 1.14 g/mL) catalyst resulting in a total bed length of 22.375". The catalyst bed was held in place with 2 mm wire mesh at each end of the reactor. 3 mm glass beads were added to promote axial dispersion at the entrance and exit of the bed for a total length of 0.62" at the inlet and 1.5" at the exit. Additional thermocouples are inserted into the reactor inlet and outlet and the center of the sand bath for monitoring the temperature across the bed. A relief valve was placed at the reactor outlet pipe. Following the reactor the stream splits into the product and recycle lines. The recycle is controlled by a second HPLC pump. The

recycle line is joined by the hydrogen line before returning into the feed line. A hydrogen mass flow controller is mounted on the wall of the containment box and controls the flow rate of hydrogen into the system. Meanwhile the product line passes through a water bath and out of the containment box to a needle valve to reduce it to ambient conditions. The water bath is at room temperature which is sufficient due to the small mass flow rate in the product stream. The product collects in an Erlenmeyer flask with tubing that goes to the ventilation duct for any exiting hydrogen.

Controls and Data Acquisition

All of the controls are attached to the left wall of the containment box on either side of the feed vessel platform to allow for complete operation of the system without opening of the containment box. On the left side of the platform are two power strips that supply all of the power necessary for the pumps, heat tapes, and controllers. Also on the left side are two switches for external control of the pumps. On the right side of the feed vessel is a data acquisition docking station, and 4 variable voltage controllers, the bottom three of which control the heat tapes. The top voltage controller adjusts the hydrogen mass flow controller. The first of the three heat tape controllers controls the heat tapes on the recycle loop. The bottom two controllers are for the heat tapes on the reactor shell to control the sand bath temperature. The data acquisition station transfers the thermocouple output to a computer for real-time monitoring.

EXPERIMENTAL PROCEDURE

Prior to operation, always ensure that the ventilation duct is in place, the explosion vent is covered (a taped sheet of paper is suitable), there is at least 2" of water in the water bath, the door is closed, and that the nitrogen is flowing at 2 psig. Wait 15 min after turning on the nitrogen for the box to be filled. The only exception to this rule is when first pressure checking the system which is detailed below. If the door must be open during operation place a fan such that it will blow into the box to minimize the flow of nitrogen into the room.

First-Time Operation

Pressure Checking the System

Close the needle valve and start a flow of hydrogen. Wait for the system to reach the pressure limits set by the relief valve. As the pressure builds, use soapy water to test each connection for leaks. Tighten any leaking connections. Once the system has reached pressure, continue to the drying procedure.

Drying

Slowly open the needle valve to lower the pressure until it stabilizes between 300 and 600 psig. Next close the box and start nitrogen flow. After 15 min, turn on the heating tapes and heat the reactor to between 200 and 250°F. Let the system run for 2 hours while maintaining the temperature and pressure. Continue to the sulfiding procedure.

Sulfiding

For our catalyst, a sulfiding procedure must be performed to prevent the catalyst from breaking down at high temperatures. For this process simply follow the instructions provided by the catalyst vendor.

General Operation

Startup

Ensure that the feed pump is set to 3 mL/min and recycle pump P2 is set to 6 mL/min with 1050 psig max output. Set the hydrogen controller to 30 sccm. Fill the feed vessel to the 250 mL line with pure solvent. Turn on the feed pump .When the pressure begins to rise, turn on the recycle pump and heating tapes. Begin ramping the temperature to the desired value at no more than 200°F/hr. Adjust the needle valve to obtain the desired pressure. Once the set pressure is obtained, adjust the feed pump to the desired flow rate. When the temperature is within 40°F of the set point, drain the feed vessel of the pure solvent to the top of the Tygon tubing and begin feeding the butyric acid/solvent solution. Adjust the hydrogen controller to the desired flow rate for sampling. Once the set temperature has been reached, flush out three system volumes before moving to the sampling procedure.

Sampling

Hold the temperature and pressure steady at the desired set points by adjusting the controls for the heat tapes and needle valve. Remove any liquid in the product flask and allow a sufficient volume for analysis to collect (a few milliliters is sufficient for gas chromatography). After collecting the sample, adjust the conditions to the next set point and repeat the sampling procedure allowing at least two system volumes to pass before collection at each set point.

Shutdown

Turn off all heating elements. Drain the feed vessel of any remaining feed to the top of the Tygon tubing. Begin feeding pure solvent in small amounts to the first line on the cylinder to dilute the previous feed. Next, fill to the 250 mL mark. Set the feed pump to a high flow rate to

increase the temperature reduction and flush the system. Once the temperature drops below 400°F, turn off the pumps. Turn off hydrogen controller, close the hydrogen valve leading to the hydrogen controller, and close the hydrogen bottle valve. Depressurize the system by slowly opening the needle valve. Turn off the nitrogen and all power strips.

ANALYTICAL METHODS

Jones Oxidation for Alcohols

The Jones reagent is a chromic acid in a sulfuric acid solution. The test is performed by reacting two drops of a solution with 1 mL of pure acetone and one drop of Jones reagent. The presence of aldehydes and primary or secondary alcohols will be indicated by the formation of a green color within 15 seconds[10].

Gas Chromatograph Analysis

The final concentrations of butyric acid and butanol in the product stream are determined by gas chromatography to determine the conversion and selectivity. Our analysis was performed with a Shimadzu Model 2014 gas chromatograph operating with a flame ionization detector at 300°C, an automated sample injector at 300°C, and a capillary column at 35°C. Standard samples were prepared from ACS grade butyric acid, butanol, and charcoal starter.

EXPERIMENTAL RESULTS

Various temperatures, pressures, and flow rates were tested to determine the optimal operating conditions. Tom Potts, one of the graduate students at University of Arkansas, used the temperatures, pressures and flow rates ranged from 310°F to 350°F, 650 psig to 2100g psi and 1.5 mL/min – 3.5 mL/min, respectively. The data along with calculated conversions and selectivity he got is shown in Table 1.

Table 1. Experimental data: temperature, residence time, conversion rate, and selectivity

Pressure (psig)	Temperature (°F)	Space Velocity (min^{-1})	Conversion rate (butyric acid)	Selectivity for butanol	Selectivity for butane
2068	309.5	0.453	0.97	0.76	0.14
2086	348.8	0.884	1	0.86	0.14
2086	348.8	0.884	1	0.88	0.12
733	312.5	0.833	1	0.43	0.44
733	312.5	0.833	1	0.41	0.46
719	329.75	0.863	1	0.41	0.5
719	329.75	0.863	1	0.42	0.5

729	349.5	0.923	1	0.42	0.57
729	349.5	0.923	1	0.43	0.56
695	346.67	0.48	0.99	0.4	0.58
695	346.67	0.48	0.99	0.41	0.57
712	328.5	0.453	0.98	0.38	0.61
712	328.5	0.453	0.98	0.38	0.61
724	310.5	0.437	0.96	0.38	0.66
724	310.5	0.437	0.96	0.73	0.31

The peculiar result that some selectivities do not sum to unity is attributed to error in the gas chromatography analysis, but it is still being investigated.

Data Reduction

The two simultaneous hydrogenation reactions are given below:

$$C_3H_7COOH + 2H_2 \rightarrow C_4H_9OH + H_2O \quad k1 \qquad (1)$$

$$C_4H_9OH + H_2 \quad \rightarrow C_4H_{10} + H_2O \quad k2 \qquad (2)$$
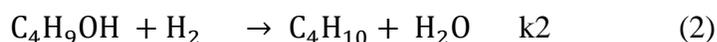
The Arrhenius equation (7) is used to correlate rate constants with temperature.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \qquad (7)$$

A kinetic model predicting the Activation energy and Arrhenius constant was developed from the experimental data using Matlab and Excel's Solver program. This model can predict the rate constants at specific temperature which is then used to determine the theoretical concentrations of butyric acid, butanol and butane.

Matlab development

The kinetic model was developed using three separate Matlab programs. The first program defines the reaction order of all the species (reactants and products) in the model and defines the differential equations. The second program takes the temperatures, concentrations, and residence times and solves the differential equations for the experimental k values. The values of the rate constants are then tabulated in excel, and the Solver function is used to perform a least squares minimization for the values of the frequency factors, activation energies, and model k values for the two reactions. The third Matlab program uses the data from Excel to

output predicted final concentrations of butyric acid, butanol, and butane which was compared with the experimental results.

Results and discussion

Upon analysis of the products, it was discovered that all of the butyric acid was converted to butanol when the temperature was above 350°F, and those data points were not considered during the kinetic modeling. The values chosen for n for this phase of the study were -1/2, 0, 1, 2, and ½ with 0 giving the best fit to the experimental data. This can be explained by considering that excess hydrogen in the vapor phase is in constant equilibrium with the liquid phase, so as hydrogen is reacted in the liquid phase, it will be replenished by hydrogen from the vapor phase. The activation energies for the two reactions obtained from the solution of the coupled differential equations are 84.2 kJ/mol and 22.3 kJ/mol for reactions (1) and (2) respectively. The table below shows the activation energies determined from the experimental data for reactions (1) and (2) mentioned above.

Conclusion

1-butanol was produced in a liquid-phase catalytic reactor by the catalytic hydrogenation of butyric acid. A model of the parallel-series reactions was generated and correlated to experimental values for varying temperatures and residence times. The Arrhenius frequency factors and the activation energies for both reactions have been estimated. The activation energy of the first reaction was estimated to be 84.2 kJ/mole, and the activation energy of the second reaction was estimated to be 22.3 kJ/mole. From these values, the conversion of butyric acid and the selectivity for butanol as functions of the reaction conditions were developed. It was found that the model predicted maximum yield of n-butanol per mass of butyric acid occurs at higher temperatures and shorter residence times The assumption that both reactions (1) and (2) are zero order with respect to hydrogen needs to be further investigated. Other reaction orders are currently being studied for better consistency with literature values and experimental data. Less active catalysts should also be investigated to promote selectivity for butanol over butane. The GC conditions also need to continue to be investigated to determine the source of error in the overall mass balance of our results.

FULL SCALE DESIGN

The capacity of the full-scale plant described in this study is 30 million gallons of butanol per year. The analysis details the entire production process from the handling of the feedstock to

the final separation of butanol with a particular emphasis on the novel hydrogenation step. Figure 4 presents a block diagram of the process.
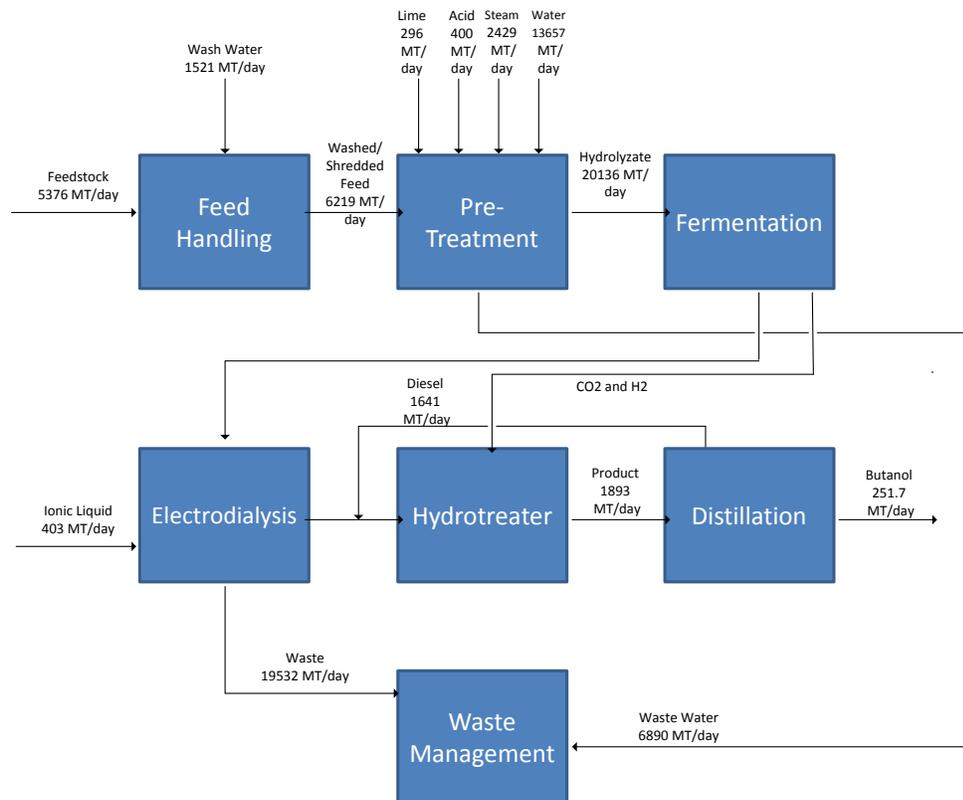
Figure 4. A block flow diagram of full scale biobutanol production process

Handling and Pre-treatment

The plant was designed to convert corn stover, a cellulosic feed source that has previously demonstrated potential as a feedstock[11], to butanol. The corn stover is brought to the plant in 200 truckloads (27 MT/TL = 60,000 lb/TL) per day where it is washed and shredded. After the metal impurities are removed, the feed is treated with a dilute acid solution (1.9W% aqueous sulfuric acid solution) to maximize exposure of the cellulose in fermentation. It is worth noting that several cellulosic feedstocks such as bark, sawdust, switchgrass, algae, etc. under optimized pre-treatment conditions could be used in this plant design. This highlights the versatility cellulosic feed sources.

Fermentation

Butyric acid is continuously produced by fermentation using the bacterium *Clostridium tyrobutyricum*. The process is run in a continuous mode by recycling the cells in the product stream following separation with an ultrafiltration membrane. Using this method, butyric acid

selectivities as high as 95% with productivities as high as 1.13 $gL^{-1}h^{-1}$ have been observed[12], but there is one drawback. The butyric acid is produced in low concentrations in the fermentation broth which must be removed before mixing with the hydrotreater diluent and feeding to the reactor to avoid poisoning the hydrogenation catalyst. Fermentation also produces hydrogen as a byproduct in a stoichiometric ratio to butyric acid which could be fed to the hydrogenation reactor to alleviate potentially all of the hydrogen cost

Separation--Electrodialysis

The method of choice for separating the butyric acid from the fermentation broth is electrodialysis to concentrate the feed followed by distillation. Electrodialysis allows for separation of the butyric acid in a much more efficient and economical manner than direct distillation and is also more environmentally friendly than the current method of choice for extraction which uses a two-phase liquid extraction that produces massive volumes of gypsum salt as a byproduct that must be landfilled[13]. This process was scaled from the lab to industrial plant scale for the current economic analysis using data from[12] for the fermentation and ongoing research in our department that has not yet been published using electrodialysis.

Hydrogenation
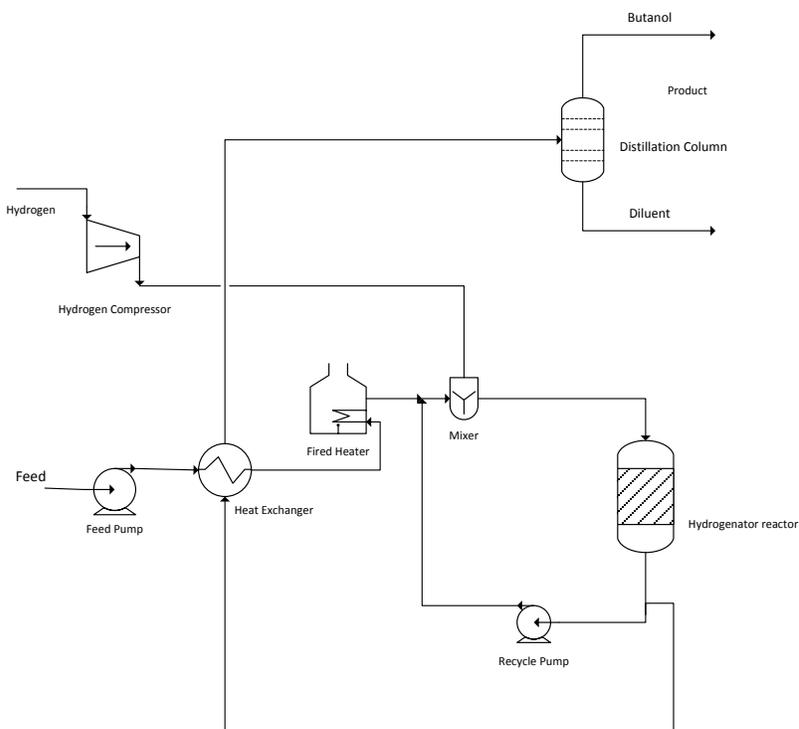
Figure 5. A process flow diagram of full scale butyric acid hydrogenation step

The electrodialysis product is fed to the hydrogenation unit. The feed is pumped to a heat exchanger where heat is recovered from the product line. The feed then passes to a fired heater. The fired heater heats the feed to a temperature of 250°F before sending the feed to a static mixer. The static mixer mixes hydrogen coming from a hydrogen feed line with the feed coming from the fired heater and the recycle stream. The feed then passes to the hydrogenation reactor packed with nickel-molybdenum catalyst. The reactor is isothermally held at a temperature of 500°F. The outlet stream of the reactor bifurcates into a recycle stream and the distillation feed stream. Recycling is used primarily to recover the unreacted hydrogen[8].

Separation---Distillation

The product from the hydrogenation is distilled in a distillation column to produce solvent grade butanol. The feed to the distillation consists of the light key butanol and heavy key diluent, assumed to be diesel for our purposes, along with other impurities. The large difference in the molecular weight of butanol compared to the components of the chosen diluent makes the distillation process easy and economic. The butanol exits through the top of the column and the diluent along with other impurities goes out the bottom. The diluent is then recycled back to the hydrotreater.

Waste Water Management

Waste water treatment for bioethanol plants has been thoroughly studied by the National Renewable Energy Laboratory[14]. The water is treated mainly using activated sludge. Activated sludge is a biochemical process for treating sewage and industrial wastewater that uses air (or oxygen) and microorganisms to biologically oxidize organic pollutants, producing a waste sludge (or floc) containing the oxidized material. This process is very costly and not environmentally sustainable.

For our process, by employing recycle in the fermentation the amount of water needing to be treated is dramatically reduced. Research is also currently underway that could lead to an even greater reduction in the need for waste water treatment by incorporating an onsite treatment scheme compatible with the fermentation process that would allow for additional recycle. This doubles as a reduction in the waste produced and cost of treatment while also reducing the amount of water that has to be brought in to the system.

ECONOMIC ANALYSIS

The full-scale process beginning with fermentation and ending with the separation of butanol from the product stream was analyzed for economic viability and compared with competing technologies for producing butanol. The analysis was performed for a ten year plant lifetime producing 30 million gallons of butanol per year. The total costs for the plant were divided into the fixed capital investment which was spent entirely in a three year construction period preceding the ten year plant lifetime and a yearly cost of manufacturing during operation. A selling price for butanol of $4 per gallon was assumed based on the current market price for solvent-grade butanol. Additional assumptions were a yearly tax rate of 45%, an internal rate of return of 5%, and 20% recovery of the fixed capital investment at the end of the plant lifetime.

The fixed capital investment (FCI) represents the total cost of equipment for the entire plant. The breakdown of the FCI, separated for each processing step, is displayed in Table 1. Equipment was sized for a ten million gallon per year plant using CHEMCAD and scaled to 30 million gallons using an assumed cost exponent of 0.6[15]. To account for extra expenses in construction (engineering, process development, buildings and infrastructure, etc.) a Lang Factor of 3.63 which corresponds to a typical solid-fluid processing plant[15] was used. It was suggested that a factor of five be used, but due to the scale and continuous nature of our process, a lower value is more appropriate. The contribution of the pretreatment of the cellulosic feedstock and wastewater treatment were not considered in the economic comparison because they are identical for all fermentation processes.

Table 3. The breakdown of the estimated fixed capital investment for a biomass to butanol plant using hydrotreating is displayed.

Equipment	Quantity	Unit Price	Total Purchased Cost
Fermenter			
Feed pumps	6	$11,000	$66,000
Fermenter vessel	2	$1,800,000	$3,600,000
Pump to inoculum vessel	2	$6,000	$12,000
Inoculum fermenter vessel	1	$1,800,000	$1,800,000
Total			**$5,478,000**
Butyric Acid Separation			
Electrodialysis Unit	3	$1,200,313	$3,600,940

Ionic Liquid for ED	1	$5,551,573	$5,551,573
Feed pumps	2	$5,200	$10,400
Distillation preheater	1	$25,000	$25,000
Distillation Column	1	$811,000	$811,000
Column condenser	1	$82,380	$82,380
Column reboiler	1	$54,191	$54,191
Total			**$10,135,484**
Hydrotreating			
Hydrotreater	1	$5,800,000	$5,800,000
Hydrogen Plant	1	$520,000	$520,000
Distillation Column	1	$81,483	$81,483
Total			**$6,401,483**
Total Equipment Cost			**$22,014,967**
Scaled Plant FCI			**$154,488,948.29**

The yearly cost of manufacturing (COM) is broken down in Table 2. The raw material and utility costs were calculated for an output of 30 million gallons of butanol per year. To be conservative, it was not assumed that all of the hydrogen could be obtained from fermentation but rather that half would come from fermentation and half from an onsite hydrogen plant. Based on feedback industry professionals and the number of steps in our process, it was estimated that 24 operators would be necessary for continuous operation. The cost of labor was calculated assuming an average salary of $60,000. The other manufacturing costs were estimated based on the scaled fixed capital investment and cost of labor using established rules-of-thumb[15].

Table 4. The various costs of manufacturing are broken down for a 30 million gallon per year biomass to butanol plant using hydrotreating. The method of estimating the cost of each contributor to the total cost is given.

Direct Manufacturing Costs	Basis	Cost
Raw Materials	To produce 30 MMgal butanol	$15,766,547
Utilities	To produce 30 MMgal butanol	$11,997,372
Operating Labor	Estimated from Process	$1,440,000
Direct Supervisory and clerical	18% of OL	$259,200
Maintenance and repairs	6% of FCI	$4,379,731
Operating Supplies	0.9% of FCI	$656,960
Laboratory Charges	15% of OL	$216,000

Patents and royalties	3% of base COM*	$1,536,600
Total Direct Manufacturing Costs		**$36,252,410**
Fixed Manufacturing costs		
Depreciation	10% of FCI	$7,299,551
Local Taxes and Insurance	3.2% of FCI	$2,335,856
Plant Overhead	70.8% of OL + 3.6% of FCI	$3,647,358
Total fixed manufacturing costs		**$13,282,766**
General manufacturing costs		
Administrative	17.7% of OL + 0.9% of FCI	$911,840
Distribution and selling	11% of base COM*	$5,634,201
Research and development	5% of base COM*	$2,561,001
Total general manufacturing costs		**$9,107,042**
Total manufacturing costs		**$58,642,217**

*Base COM is estimated COM from FCI, OL, raw materials, and utilities[15]

Using the estimated values for the FCI and COM the profitability of the plant was determined for a ten year lifetime. The cash flows are shown in Table 3. A similar analysis was performed for the ABE method of butanol production with the results shown in Table 4. The results clearly show that the method of hydrotreating for butanol production is more economically viable due to its dramatically lower cost of manufacturing. Additionally, Hogdrogenation's process is far more economical than producing butanol via the petrochemical route. For the petrochemical process, propylene is consumed to produce buteraldehyde which is reduced to butanol in a 1:1 ratio. To produce 30 million gallons of butanol by this method, 115 million pounds of propylene would be consumed which would cost $93,160,000 at the current market value of $0.81 per pound. In addition to propylene, hydrogen and carbon monoxide are also necessary for the reaction which brings the total raw material cost to $103,555,000 ($3.45/gal butanol) assuming that hydrogen is priced at $5 per thousand cubic feet and carbon monoxide can be obtained for a negligible amount as the byproduct of other processes in the plant. The dramatically higher cost of manufacturing more than offsets the reduced capital cost of eliminating the fermentation equipment. The rest of the process would be similar in FCI because hydrogenation under similar conditions is used to reduce buteraldehyde to butanol.

Table 5. Displayed is the cash flow table for a 30 million gallon per year biomass to butanol hydrotreating plant for a ten year lifetime following a three year construction period.

						Butanol via Hydrotreating				
Year	Investment	dk	FCI-sum(dk)	R	COMd	(R-COMd-dk)*(1-t)+dk	Cash Flow	Cum. Cash Flow	Disc. Cash Flow	Cum. Disc. Cash Flow
0	$ (30.00)	$ -	$ 154.49	$ -	$ -	$ -	$ (30.00)	$ (30.00)	$ (30.00)	$ (30.00)
1	$ (92.69)	$ -	$ 154.49	$ -	$ -	$ -	$ (92.69)	$ (122.69)	$ (88.28)	$ (118.28)
2	$ (61.80)	$ -	$ 154.49	$ -	$ -	$ -	$ (61.80)	$ (184.49)	$ (56.05)	$ (174.33)
3	$ -	$30.90	$ 123.59	$120.00	$ 61.63	$ 15.11	$ 15.11	$ (169.38)	$ 13.05	$ (161.28)
4	$ -	$49.44	$ 74.15	$120.00	$ 61.63	$ 4.91	$ 4.91	$ (164.47)	$ 4.04	$ (157.24)
5	$ -	$29.66	$ 44.49	$120.00	$ 61.63	$ 15.79	$ 15.79	$ (148.68)	$ 12.37	$ (144.86)
6	$ -	$17.80	$ 26.70	$120.00	$ 61.63	$ 22.32	$ 22.32	$ (126.36)	$ 16.65	$ (128.21)
7	$ -	$17.80	$ 8.90	$120.00	$ 61.63	$ 22.32	$ 22.32	$ (104.05)	$ 15.86	$ (112.35)
8	$ -	$ 8.90	$ -	$120.00	$ 61.63	$ 27.21	$ 27.21	$ (76.84)	$ 18.42	$ (93.94)
9	$ -	$ -	$ -	$120.00	$ 61.63	$ 32.10	$ 32.10	$ (44.73)	$ 20.69	$ (73.24)
10	$ -	$ -	$ -	$120.00	$ 61.63	$ 32.10	$ 32.10	$ (12.63)	$ 19.71	$ (53.53)
11	$ -	$ -	$ -	$120.00	$ 61.63	$ 32.10	$ 32.10	$ 19.47	$ 18.77	$ (34.76)
12	$ 60.90	$ -	$ -	$120.00	$ 61.63	$ 32.10	$ 93.00	$ 112.48	$ 51.79	$ 17.02

Table 6. The economics of various processes are directly compared.

Process	FCI (million $)	COM (million $)	Production Cost ($/gal)	Payback Period (yr)	Net Present Value (million $)	ROROI
Hydrotreating	$61.7	$70.6	$2.35	9	$17.02	37.8%
ABE Fermentation	$51.4	$108.4	$3.61	>10	-$33.52	22.5%

BUTANOL: POTENTIAL AS BIOFUEL

Approximately one fourth of human-activity-generated carbon dioxide emissions are from the use of fossil derived vehicular fuels for cars and light trucks[11]. Thus, replacement of fossil derived fuel with a (nearly) carbon dioxide-neutral fuel such as biobutanol would be beneficial to the environment. Ethanol is currently the main biofuel, but biobutanol possesses many superior characteristics than ethanol making it an ultimate biofuel.

Butanol is less hydrophilic than ethanol. In comparison to ethanol butanol is less corrosive, less volatile and less explosive. Butanol also has higher energy content than ethanol. butanol's heating value is 105,000 Btu per gallon versus only 84,000 Btu/gal for ethanol produces. Gasoline's heating value is 115,000 Btu per gallon; thus, butanol has a heating value 91% of gasoline's value. Existing pipelines are equipped to carry butanol and it is more compatible with oil infrastructure e.g. butanol mixes well with gasoline. Ethanol can only be used as a fuel additive whereas butanol can be used as an immediate replacement for gasoline with only minor modifications to a vehicle's carburetion and timing. Furthermore, the current feedstocks for ethanol are corn and sugarcane, but butanol can be produced from a variety of

biomasses that do not compete with food sources. The use of corn and sugar for the production of ethanol has increased the cost of corn and sugarcane based foods which drives the importance to develop a biofuel from non-food feedstocks.

REGULATIONS

Community Considerations

The Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) provides United States citizens with information regarding possible exposure to hazardous chemicals. The legislation sections pertaining to this process are Emergency Planning (sections 301-303), Emergency Notification (304), and Community Right-to-Know Requirements (311-312).

The two objectives of EPCRA are to encourage emergency planning and response actions for chemical accidents and to provide local governments and community with information about chemical hazards. To achieve the first objective, a local emergency planning committee (LEPC) will be formed by members of the general public as well as representatives from the company to plan for emergency situations. To properly inform the community of any hazards involved, town hall meetings will be held once building has commenced. Multiple meetings will be necessary to update the community as the construction is occurring. The meetings will consist of overviews of any new developments that the company encounters. There will also be time for the community to freely ask questions to better understand the chemical processing. Should any major changes occur within the plant, other LEPC and town hall meetings will be held to account for risks and convey any issues to the public. All information will be made available upon request for anyone, public or private. Currently, there are no hazardous chemicals that will present any difficulties with the local government and people, but it is imperative to the success of the company to have their support.

Environmental Considerations

For the bench scale apparatus, a safety box encloses the pressurized area of the system to contain the possibility of a hydrogen/diluent leak. Furthermore, the box is constantly purged with nitrogen to ensure that, in the event of system failure, any released flammables will not cross the flammability envelope. In a larger system, these are not likely to be issues and the construction of the proposed system would abide by any local governance on air contamination from possible hydrogen leaks. Should there be a material leak of any kind the first step would be to alert local authorities of the situation. The National Response Center will be alerted afterward

to prepare for any possible threat to the public health ([1-800-222-1222](tel:1-800-222-1222)). To ensure the safety of the work force, evacuation protocols will be established and practiced regularly with routes posted around the plant.

Hydrogen Sulfide (H_2S) is a heavy gas that is produced in the process of sulfiding the nickel molybdenum catalyst. While it can be immediately detected by the "rotten egg" odor, the sensitivity to gas can be lost due to constant exposure. According to OSHA IMIS Code Number 1480, at concentrations above 100 ppm H_2S is considered Immediately Dangerous to Life or Health Concentration (IDLH). The short-term exposure limit (STEL), however, is 5 ppm. The STEL will not be repeated more than 4 times per day with at least 60 minutes between successive exposures[19].

The fermentation step of the process produces carbon dioxide (CO_2). In compliance with the Environmental Protection Agency (EPA), industrial plants producing any greenhouse gasses would need to report the concentrations. The Greenhouse Gas Reporting Program collects and publishes this data for public knowledge, but because the hydrogenation process recycles the CO_2, this is not a necessary procedure. Furthermore, the concentration of CO_2 that comes off the end process is well under the allowable permissible exposure limit (PEL) for general industries of 5,000 ppm or a time weighted average of 9,000 mg/m^3.These values correlate to the allowable limits for the National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH)[22].

Another regulation to consider is the Clean Air Act. After careful investigation, it is determined that the production of butanol through this process does not produce any materials on the list of Hazardous air pollutants[23].

Chemical Considerations

There are several chemicals involved throughout the Hogdrogenation process. In accordance with the OSHA Department of Labor in Title 29 CFR 1910 Subpart I, the facility will provide personal protective equipment (PPE) for all operators and maintenance staff. PPE will be worn in all operating areas of the facility and kept in sanitary conditions when not in use. Also, OSHA requires that Material Safety Data Sheets (MSDS) for each chemical must be on site, so binders containing the MSDS for each chemical will be readily available in the operating areas. Proper safety techniques and training will also be provided to all personnel according to OSHA guidelines which employees will complete early in their employment. These meetings

will cover procedures for emergency situations and safety and be repeated on an annual basis with changing procedures[24].

For the bench scale apparatus the feed mixture of butyric acid and diluent is prepared by hand. In full-scale operation, no feed will be handled. Permissible exposure limit (PEL) is defined as the maximum concentrations that a worker can continuously be exposed to a substance for an 8-hour work day. For butyric acid there is no PEL, but if above 70C, vapor air mixtures of butyric acid may cause explosion[16]. Diesel also has no associated PEL, but is designated by OSHA as a carcinogen. It is also considered an explosive when mixed with vapor and air above $50°C$[17]. The possible explosions are not necessary to consider in large-scale operations because no air mixtures would enter the system. In case of an emergency with a leak, protocol would be followed according to the risk mitigation plans developed using the EPA 40 CFR Part 68 guidelines established in monthly safety meetings and local authority notification procedures according to plans developed in previous LEPC meetings[25].

Worker Safety

Specific safety precautions for manual labor are associated with the high pressure system and H_2S off gas. For operating systems that are at high pressures, OSHA directive number STG 01-10-001 entitled Guidelines for Pressure Vessel Safety will be read and understood before operating the system. A High Pressure Safety training course will also be completed before operating[18].

Furthermore, regulations for H_2S exposure are given by OSHA. Specifically for H_2S, OSHA has varying limits for three different categories: construction (10ppm), maritime (10ppm), and all other industries (20ppm). Similarly, the maximum safe exposure of hydrogen sulfide in a 10 minute period (assuming there is no exposure throughout the other 7 hours and 50 minutes) is 50ppm. The most affected organs are the respiratory system and the eyes. The threshold limit value (TLV) assigned by the American Conference of Governmental Industrial Hygienists (ACGIH) is between 1 ppm and 5 ppm. This corresponds to a time weighted averages (TWA) value of 1.4 mg/m^3 for 1 ppm and a short term exposure limit (STEL) value of 7 mg/m^3 for 5 ppm[21].

Additional Considerations

Another implemented regulation pertaining to the process is the Energy Independence & Security Act of 2007. This piece of legislation is aimed at reducing the US dependence on

unsustainable energy sources and focusing resources on alternative renewable energy, biofuel infrastructure, carbon capture, sequestration, and sustainability. The Hogdrogenation process supports this act by reducing the carbon footprint of the butanol production process, reaching a sustainable feedstock to produce renewable energy, and optimizing the automobile biofuel economy. Furthermore, Hogdrogenation can be an essential part to the act's goal of reducing gasoline consumption by 20% in 10 years[20].

CONCLUSIONS AND RECOMMENDATIONS

1. A bench-scale representation of the Hogdrogenation process showcased the production of butanol from butyric acid.

2. A detailed safety analysis led to the creation of a nitrogen purged containment box that in the event of a catastrophic failure would not release flammable vapor.

3. The experimental procedure showed 100% conversion rate for butyric acid.

4. It also showed 88% selectivity for the production of butanol over butane.

5. The optimal conditions were found to be 349°F, 2028psig and 0.884 min^{-1}.

6. The economic analysis showed that Hogdrogenation had a net present value (NPV) of $17.02 million compare to a NPV of -$33.52 million for ABE.

7. Repeat experimental runs to see if variation is significant.

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Appendix A—Audits

Audit 1: Jon Skeds

March 19, 2013

Subject: Review and comments of HOGdrogeNATION WERC 2013 Report

University of Arkansas School of chemical engineering

Reviewer: Jon M. Skeds

To: Megan Dunn

Dear Ms. Dunn,

At your request, I have reviewed the draft report you sent entitled "Optimal production of biobutanol via hydrogenation of butyric acid". I have provided my comments in the paragraphs below. I am a chemical engineer that graduated from Purdue University with over 35 years of industry experience. The majority of my career has been with engineering companies that design and construct process plants. A significant portion of my career was devoted to reviewing and approving the designs and cost estimates produced by the company's internal engineers and estimators. My comments are based on my industry experience in the field of designing process plants for the refining and chemical industries.

OVERVIEW

It is encouraging to read about your efforts to develop a process of producing biobutanol that would compete favorably from an economic standpoint with existing butanol production technologies. Developing a new technology can be both challenging and rewarding. Commercializing a new technology is a very difficult venture and solid experimental data along with a sound economic analysis are keys to success. I will concentrate my comments mainly on the experimental data and cost analysis.

TECHNOLOGY AND EXPERIMENT DESIGN

You have employed a hydrogenation technology that has been proven in many commercial installations. Almost every refinery in the world uses hydrogenation in the form of hydrotreating applied to product streams such as diesel, gasoline, and naphtha. As such, the hazards and safety precautions are well known to the industry. Therefore, acceptance of the technology from an operational and safety standpoint should be relatively easy. The use of liquid full hydrogenation reactors in your design in lieu of trickle bed reactors will significantly reduce the cost of your design. The safety consideration in your experiment design with your vent system is similar to the safety relief and flare systems employed in commercial facilities. Therefore, my opinion is the hydrogenation technology used in your design is very sound.

EXPERIMENTAL RESULTS

In reviewing the experimental results contained in Table 1, I have several comments. In order for the product samples taken to match the temperature, pressure, and space velocity of the run, the unit must be at steady state. How did you determine the unit was at steady state prior to taking the samples? Most refineries will take samples several minutes apart and then compare them to make sure the unit is at steady state. Some of the runs do not add up to 100% when adding the selectivity of butanol and butane. How do you explain this?

The data in Table 1 show the results but the operating pressure was not recorded. Were all these runs made at the same pressure? Your conclusions state that the optimal run was made at 350 F, 700 psi, and yielded 70% selectivity for butanol. However, Table 1 appears to show 86 or 88% selectivity at these conditions. I believe additional runs around the optimal conditions are warranted to verify the results.

SAFETY , ENVIRONMENTAL, AND GOVERNMENT REGULATIONS

As mentioned earlier, the hydrogenation process has been in use in refineries around the world for several decades. The hydrogenation process goes through a HAZOP (hazardous operation

analysis) in each refinery prior to installation and startup. Therefore, the safety aspect has been extensively examined and designed for. Operator training has also been documented for these installations. Prior to installation of hydrogenation units in refineries, an environmental permit in obtained. Once again this process has been repeated many times and should not be a concern.

COST ANALYSIS

On the surface, the cost analysis looks to favor your process by a wide margin. I would ask the following questions:

- Have you included the cost of engineering the plant? The engineering cost typically runs 15% of the total project cost.
- Have you included off sites such as flare systems, truck loading racks for the products, product and feed storage tanks, buildings, site preparation and fencing, etc?
- I would like to see listed what the hydrogen consumption is per barrel of feed or product. This is normally a large operating expense.
- In most locations, hydrogen is not available for purchase. Have you considered this and if so should you include the cost of a hydrogen plant?

SUMMARY

I am impressed with amount of work that has gone into your report. I have tried to review your report with a critical eye, only pointing out the areas where I have questions and/or comments based on my industry experience. I have not attempted to address the vast majority of the report that contains clear and sufficient detail.

MUELLER®

Memorandum

To: HOGdrogeNATION Team, WERC 2013

From: Karen Reed, P.E.

Date: 4/30/2013

Re: Review of WERC Task 1 Report

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iewed the draft revision of the paper "Optimal Production of Biobutanol via

n of Butyric Acid. I am very impressed with the time and knowledge that

writing of this paper, and would like to congratulate the team on an

d well thought out plan. You have obviously spent many hours

and developing the bench scale and full scale plans for this process.

ve a few comments that I would recommend addressing in the paper. In general, these comments are simply additions that I feel will add to the understanding and robustness of the report. In the description of the experimental containment box, it mentions that three brass door hinges and four brass draw catches are used to attach the front polycarbonate panel. Since these points are, by design, the weakest spots in the construction of the containment chamber, I would like to see a discussion of the potential for an overpressure scenario in the chamber and how this is mitigated by the vent.

Second, In the description of the startup of the system, you mention cooling water in the bath. What temperature water is used for the experiment? Is the temperature of the water critical to the successful operation of the system? This is especially important in

the scale up discussion of the system since cooling tower generated water is generally much less expensive than chiller generated water.

Additionally, in the description of the experimental data shown in Table 1, there is no mention of repeatability of the experimental data in separate experimental runs. It would be worthwhile to note the number of times that this experiment was run and how closely the data from each run matched the previous ones.

I would also recommend including some discussions on what costs are included in the installation factor used for the full scale cost analysis. The capital investment for this equipment will include engineering, instrumentation, piping, control system, structural platforms, and the labor to build and install all of this equipment. Since the fixed capital investment is detailed out as major equipment costs multiplied by the installation factor, these additional items will either need to be added to the cost or shown to already be included.

From a safety standpoint, I would recommend the addition of gas level monitoring throughout the site. You discuss the exposure limits for personnel, and the addition of monitors will help ensure that these limits are maintained.

My last comment has to do with some general housekeeping issues within the report. Since this is simply a draft, I'm assuming that these issues were already planned to be fixed, but I wanted to bring them to your attention just to make sure that nothing is missed. In Table 5, I would recommend adding units of measure to the columns and possibly a more detailed explanation of each column. Also, in the report, there are a couple changes in font and size. I would recommend updating those and having one person reread the report as a whole to ensure continuity and flow throughout.

Again, I am impressed with the amount of effort put into this report and project and I wish you the best at the WERC competition.

Sincerely,

Karen Reed, P.E.

BioPharm Product Manager

Paul Mueller Company

Audit 3: John Parks

Date: March 17, 2012

HOGdrogeNATION Team

Department of Chemical Engineering

University of Arkansas

Subject: Review and comments on WERC 2013 Paper

Dear HOGdrogeNATION Team,

I read your very interesting paper on conversion of biomass to n-butanol. Let me complement you on the nice experimental work you did. I offer these comments for your consideration

Economics

Clear economic analysis it critical to successful projects. You have addressed many of the key elements of the analysis, capital, operating costs, market and project valuation. I would like to see a return on capital calculation along with the NPV calculation that you provided.

The number of operators was estimated using a published method. The number of operators seems high to me, and would seem excessive once scaled up from the 10 million gal base to 30 million gallons. The method was published in 1984, with data undoubtedly from a few years previous to that. Current new plants, fully automated, would require much less labor, even given the fact that this plant handles a lot of solid material coming in.

The new fixed capital seems low to me. When we estimate new capital, we estimate similar to your method, bare equipment multiplied by a factor to get installed cost, but there is also a significant amount of engineering, process design, purchasing cost to add, plus estimating contingency and project reserve. Also missing are utilities, site preparation, product storage, structure, buildings etc. In the end, we see total capital to be closer to 5 times bare equipment than the 1.44 in your analysis.

Another topic to mention is a discussion of the project value with varying diesel costs. Fuel prices vary and there is some point that diesel fuel price could drop such that the economics for this project would begin to look bad. You use $4.00 per gallon for diesel, is that the value at the

refinery or at the pump? Note that the pump price includes taxes and the refinery price is the better comparison price.

Health and Safety

This process has hazards that are properly addressed in the lab setup. Hydrogen looks like that major source of hazard, and there are large amounts of flammable organics to deal with. The containment system in the experimental unit is a nice way to deal with leaks . An oxygen meter inside the containment box would be a nice add.

A section, in the operating procedures, outlining the required personal protective equipment (PPE) should be added. This should clearly define gloves, goggles, fire-resistant clothing etc needed prior to running. Also make sure MSDS are availiable for each chemical in the system.

Legal issues

Along with the health reasons for the above comments on personal protective equipment, and MSDS, there are legal reasons to do so. The MSDS will give reportable quantities, should a release happen. Having defined PPE , that is approved by management, and properly trained to the operators is necessary to keep everyone legal.

General Comments

It would be useful to have a more detailed chemistry section, perhaps in the early part of the paper, showing a bit on the chemistry for sugars to butyric acid and

Units consistency, the paper mostly uses ^{O}F, but sometimes switches to ^{O}K.

The data table on page 14 does not list pressures for the individual runs. One fun thing to do is to run the data thru a statistical program and develop an empirical model of the data, sometimes a surface map can show interesting information on where stable operating areas are located.

Background and Experience

 I have worked as a Chemical Engineer for Albemarle Corporation since 1976, with about 20 years of process design experience, along with a few years in plant process technology, and process evaluation.

I currently manage and oversee the R&D activities for Albemarle's $750 million Fine Chemicals division. I have B.S. degree in Chemical Engineering from The University of Arkansas, and am holder or co-holder of 11 US patents.

If there are any further questions or comments regarding my evaluation I can be reached at225-235-2202 or email: john.parks@albemarle.com.