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05 May 2017

Dear Dr. Anthony,

We are pleased to present you with a full design report for a butanol plant capable of producing 13,800 metric tons of butanol per year when operating a full capacity. Work on this project began at the end of January 2017, with the release of the design project and specifications.

This report includes the evaluation of a continuous process, utilizing ethanol reacted over a hydroxyapatite catalyst. Sections of this report include our conclusions and recommendations, as well as a complete process description with a process flow diagram. In addition, we discuss health, safety, and environmental hazards associated with this process. Several design specifications are included to make this design inherently safer. Finally, we include a full costing report of our process, as well as several profitability measures.

Our finalized design process is capable of producing butanol with 99% purity. We calculated this plant to have a net present worth of $46 million over a 15-year project life. In addition, we calculated the return on investment to be 41%, making this project highly profitable.

Please feel free to contact us with any questions or concerns.

Best Regards,

Diane Collard

Martha Floy

Matthew Webb

BASE CASE DESIGN FOR THE CONVERSION OF ETHANOL TO BUTANOL PROCESS

Submitted as a Part of Course Requirements in CHE 571

Diane Collard,
Martha Floy,
Matthew Webb,

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ABSTRACT

The purpose of this report is to design an n-butanol plant producing 13,800 metric tons of butanol when operating at full capacity. The n-butanol process is an addition to an existing medium-sized bioethanol plant. Our design is based upon reacting ethanol over a hydroxyapatite catalyst.

In order to model our process, we used Aspen Plus as a process simulator. In addition, we made sure to check the results given by the simulator with several correlations, mass balance calculations, and literature data.

Our research led us to the development of a continuous processing design producing n-butanol with 99.9% purity. Side product streams produce waste hydrogen and hydrocarbons sent to a flare and waste water streams.

Also included in this report is an in-depth discussion of the health and safety hazards involved with this process. Chosen design specifications ensure that our process is inherently safer when handling toxic substances. We also discuss the environmental considerations for this process and necessary controls for safe operation.

Additionally, economic feasibility based on selling n-butanol as a fuel or as a solvent are analyzed. Assuming the solvent market is large enough to support this plant, the process is highly profitable.

We highly recommend our continuous process, which has proved to be an economically stable investment. The net present worth of this project is $46 million over a 15-year project life and a return on investment of 41%.

INTRODUCTION AND PROBLEM STATEMENT

An important aspect of fuel production is to manufacture alcohols from renewable feedstock. Currently, several methods to produce biomass ethanol exist. As such, this design will focus primarily on extending the ethanol to longer chain alcohols via a catalytic reaction.

Long chain alcohols have a higher energy density than short chains. For example, butanol has an energy density of approximately 30 MJ/L versus ethanol with approximately 20 MJ/L [1]. Ethanol also has corrosive properties that prohibit piping. Ethanol with impurities of as little as 0.003 vol% of acetic acid in the presence of moisture is reactive to most metals [2]. Ethanol tends to absorb water and impurities typically found in fuel pipelines, hence making piping ethanol problematic [3]. Therefore, the benefits of increasing chain length are twofold: longer chains 1) have a higher energy value and 2) can be piped unlike their ethanol counterparts.

There are multiple potential mechanisms to increase the chain length using ethanol, including ethanol coupling (Guerbet reaction), direct dimerization, and organism modification. Considering the latter, current research has established the potential to genetically modify organisms to convert short chain alcohols to longer chains, but significant research and development is still needed before these organisms can be employed on an industrial scale [4]. When considering the first two methods, the exact pathway depends highly on the catalyst. For example, direct condensation pathways are thermodynamically feasible; however, the site requirements for the conversion of ethanol to butanol for several effective catalysts, such as hydroxyapatite, suggests that the process predominantly follows the Guerbet reaction pathway [5].

The Guerbet reaction is a multistep organic reaction mechanism that converts primary aliphatic alcohols to β-alkylated dimer alcohols. The reaction produces an alcohol with twice the chain length of the reactant alcohol plus a mole of water. The reaction proceeds in a series of four steps: 1) oxidation of alcohol to aldehyde, 2) aldol condensation, 3) dehydration, 4) hydrogenation [6]. The reaction mechanism is shown in Figure 1.

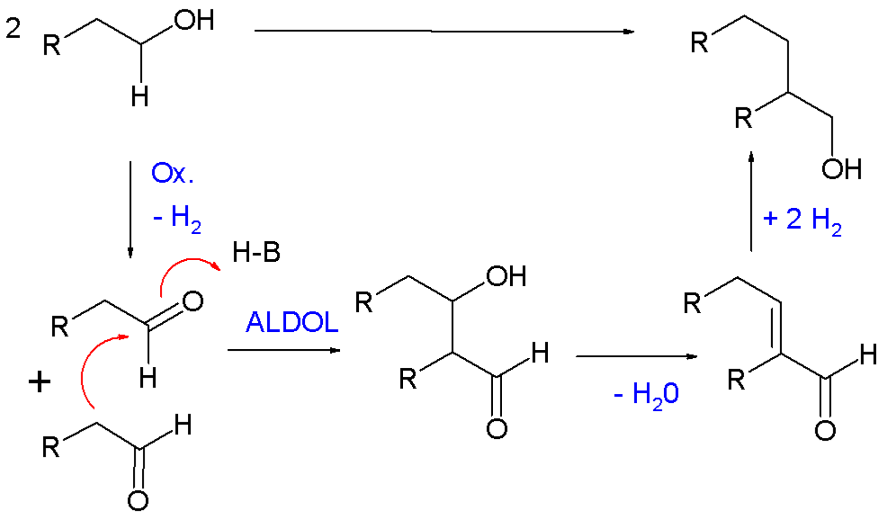

Figure 1: The Guerbet reaction mechanism.

The Guerbet reaction can take place without a catalyst, but a hydrogen transfer catalyst strongly catalyzes the reaction [7]. It must be noted that at temperatures greater than 180°C, other degradative reaction can occur.

Catalyst Selection

In the Guerbet reaction, catalyst selection is important. There are several hydrogen transfer catalysts that have been previously studied and are widely available for use in industrial systems. These include, but are not limited to, magnesium oxide, zinc oxide, and hydroxyapatites. A summary of catalyst yields is shown below. Hydroxyapatite outperforms the other catalysts with a yield of 19.8%, and is therefore selected for this design.

Table 1: Catalyst yields for the synthesis of n-butanol from ethanol.

Catalyst	Reaction Temperature (K)	n-butanol Yield (%)
MgO	773	4.9
$Mg(OH)_2$	723	9
CaO	723	1.2
$Ca(OH)_2$	723	2.2
CaF_2	773	5.2
$CaSiO_3$	723	2.1
Hydroxyapatite[1]	623	19.8
Hydrotalcite	623	12.2

Pairs of acid sites and base sites on the catalyst are crucial to the synthesis of n-butanol from ethanol. Hydroxyapatite with a calcium to phosphorous (Ca/P) ratio of 1.64 is optimal due to its large amount of acid and base sites and showed both the highest conversion of ethanol and selectivity to butanol (22.7% and 62.4% respectively) [8]. Figure 2 aids in visualization of the activation of ethanol over hydroxyapatite to produce butanol.

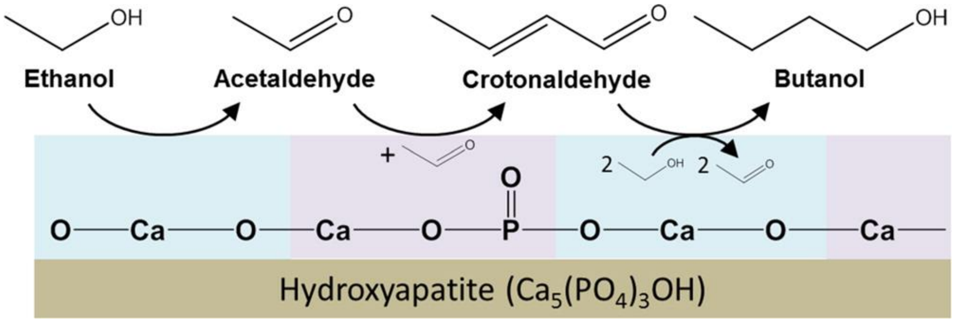

Figure 2: Catalysis of ethanol to butanol over a hydroxyapatite catalyst [5].

Tsuchida et al. examined the effect of different temperatures on the catalyst and results of interest are summarized in Table 2. With increased temperature, there is an increase in conversion, but a decrease of selectivity for the product. Giving consideration to recycling effluent from the

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[1] The hydroxyapatite has a Ca/P ratio of 1.61

reactor, lower temperature may prove to be optimal. Further discussion and optimization considerations can be found in Equipment List, Unit Descriptions/Specifications and Appendix 4: Reactor.

Table 2: Temperature effects on catalyst conversion and selectivity for n-butanol.

Reaction Temperature (K)	Contact Time (s)	Conversion (%)	Selectivity for n-butanol (C wt%)
573	1.78	14.7	76.3
623	1.78	26.1	68.8
723	1.78	57.4	44.8

Green Engineering Metrics

The green metrics are defined as follows [9]:

$$Effective\ mass\ yield\ (\%) = \frac{Mass\ of\ products\ x\ 100}{Mass\ of\ non-benign\ reagents} \tag{1}$$

$$E\ Factor = \frac{Total\ waste\ (kg)}{kg\ product} \tag{2}$$

$$Atom\ Economy = \frac{MW\ Desired\ Products}{MW\ Reactants} \tag{3}$$

$$Mass\ Intensity\ (MI) = \frac{Total\ mass\ used\ in\ process\ or\ process\ step\ (kg)}{Mass\ of\ product\ (kg)} \tag{4}$$

The green metrics and gross profit potential for the three reaction schemes have been compiled below.

Table 3: Green engineering metrics for the conversion of ethanol to butanol.

Effective Mass Yield (%)	E Factor	Atom Economy	Mass Intensity
50.4	0.60	1.61	6.64

Gross Profit Potential (GPP)

GPP is calculated using the monetary value of the chemicals and the molecular weight. The weights and market prices are tabulated below. All the dollar amounts are from or scaled to 2015 prices.

Table 4: Reaction metrics comparison [10] [11] [12] [13].

Chemical	**$/m.t.**	**Molecular Weight (g/mol)**
n-Butanol (as fuel)	2722	74.12
n-Butanol (as solvent)	1260	74.12
Ethanol	520	46.07

For example, the GPP for butanol as a solvent is estimated as follows:

$$\frac{\frac{\$2722}{m.t.} * 1746\ kg/hr - \frac{\$520}{m.t.} * 3467\ kg/hr}{1746\ kg/hr} = \$1.69/kg$$

The GPP for this reaction when selling butanol as a fuel is estimated to be $0.34/kg. This indicates that the reaction is potentially profitable; however, the small margin when selling as a fuel may not be sufficient to cover plant costs.

Catalyst Comparison and Selection

Two catalysts were examined in the reactor: hydroxyapatite and copper alumina. To compare, both were simulated in Aspen V9 with a plug flow reactor of the same dimensions. The reactor temperatures were optimized to produce the most n-butanol with the copper alumina operating at 220°C and the hydroxyapatite at 350°C [14] [15]. The table below gives a direct comparison of the effluents from the reactor with each catalyst.

Table 5: Reactor simulation with copper alumina and hydroxyapatite catalyst.

	Copper Alumina			Hydroxyapatite		
Compound	Moles Out (mol/hr)	Conversion (%)	Selectivity (%)	Moles Out (mol/hr)	Conversion (%)	Selectivity (%)
Ethanol	0	100	6.87	92.920	61.9	35.9
n-Butanol	10.302			20.471		

Since the copper alumina-catalyzed reaction has a much lower selectivity (6.87% versus 35.9%) and produces approximately half the amount of the hydroxyapatite-catalyzed reaction in a single pass, hydroxyapatite was selected as the catalyst for this process.

CONCLUSIONS

A design for the production of 13,800 metric tons/year of n-butanol from the reaction of ethanol over a hydroxyapatite catalyst is presented. The process results in 99% pure butanol. The return on investment for this project is 41%, with a payback period of 1.3 years. This process requires a significant level of control to ensure safe handling of flammable components including hydrocarbons and hydrogen gas. In addition, controls are needed to achieve proper separations and avoid overpressure situations throughout the process. Also, safeguards were put in place to prevent vapor explosions in the event of a process spill or overflow.

RECOMMENDATIONS

We strongly recommend the implementation of our process for the production of butanol. At 100% capacity, the process results in the production of 13,800 metric tons per year of n-butanol. For a 15-year project life, the net present worth of the project is approximately $46 million with all capital investment made in year zero. This project also achieves a profitable return on investment of 41%.

PROJECT PREMISES AND CONSTRAINTS

The process design and analysis follows from the assumption that ethanol comes from an existing process in a quantity similar to a medium sized ethanol plant. This allowed for our addition to produce 13,800 metric tons per year of butanol. Ethanol and butanol are highly flammable, therefore eliciting special considerations and controls schemes in our process design. We are not considering carbon emission and cost of incineration of certain byproducts. The cost analysis considers that the current amount of land is sufficient for the addition of this process. We also assumed that the butanol solvent market was large enough the plant production would have a small effect on the total market supply.

PROCESS FLOW DIAGRAM AND STREAM TABLE

We designed a continuous process for the conversion of ethanol to butanol over a hydroxyapatite catalyst. The process is designed to react ethanol in a single reactor, and then separate out the main product from other side products using a series of distillation columns. The process flow diagram (PFD) for the process with accompanying overall stream tables for the process is below. The process produces 99% pure butanol at 1746 kg/hr or 13,800 metric tons/year. Further details are discussed in the Process Description Section.

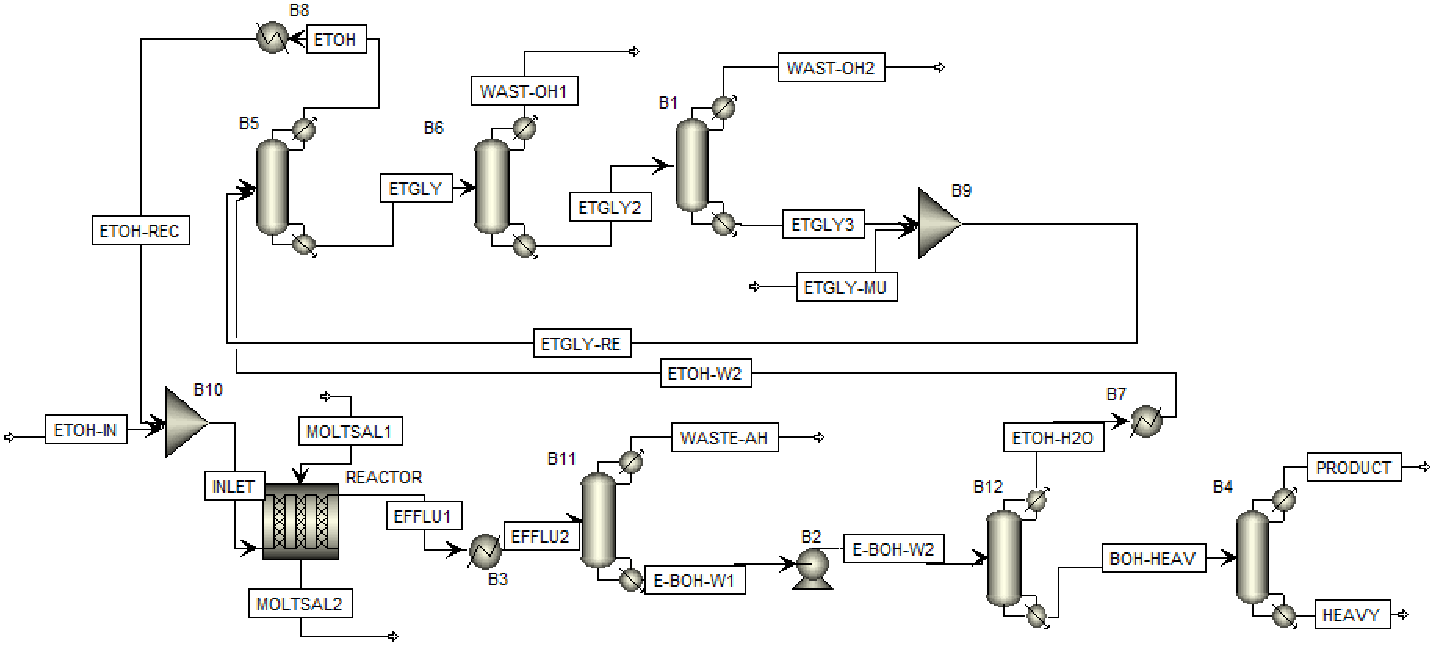
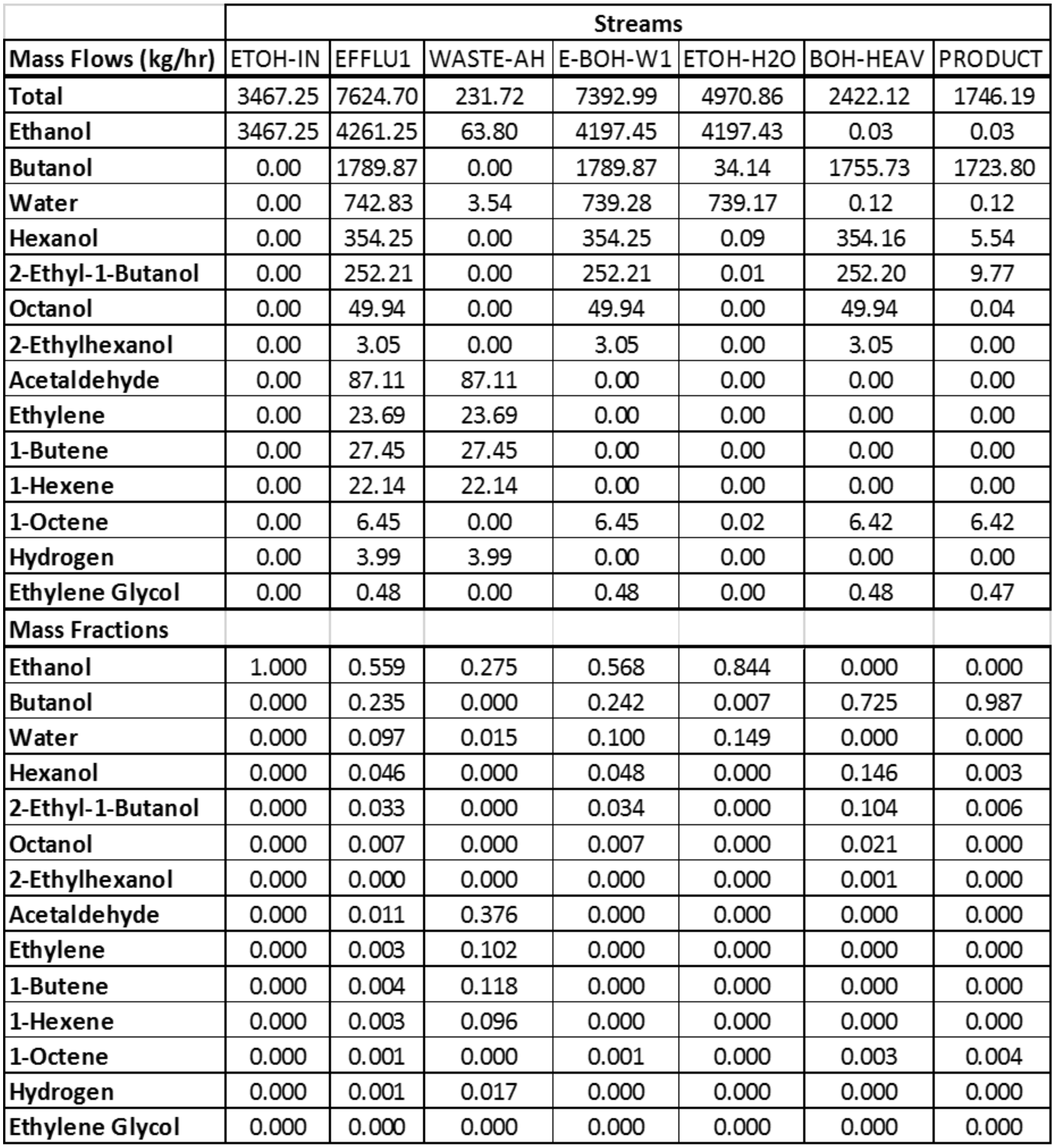


Figure 3: Process flow diagram optimize for selling butanol as a solvent.

Table 6: Basic overall stream table (part 1).



	Streams						
Mass Flows (kg/hr)	ETOH-IN	EFFLU1	WASTE-AH	E-BOH-W1	ETOH-H2O	BOH-HEAV	PRODUCT
Total	3467.25	7624.70	231.72	7392.99	4970.86	2422.12	1746.19
Ethanol	3467.25	4261.25	63.80	4197.45	4197.43	0.03	0.03
Butanol	0.00	1789.87	0.00	1789.87	34.14	1755.73	1723.80
Water	0.00	742.83	3.54	739.28	739.17	0.12	0.12
Hexanol	0.00	354.25	0.00	354.25	0.09	354.16	5.54
2-Ethyl-1-Butanol	0.00	252.21	0.00	252.21	0.01	252.20	9.77
Octanol	0.00	49.94	0.00	49.94	0.00	49.94	0.04
2-Ethylhexanol	0.00	3.05	0.00	3.05	0.00	3.05	0.00
Acetaldehyde	0.00	87.11	87.11	0.00	0.00	0.00	0.00
Ethylene	0.00	23.69	23.69	0.00	0.00	0.00	0.00
1-Butene	0.00	27.45	27.45	0.00	0.00	0.00	0.00
1-Hexene	0.00	22.14	22.14	0.00	0.00	0.00	0.00
1-Octene	0.00	6.45	0.00	6.45	0.02	6.42	6.42
Hydrogen	0.00	3.99	3.99	0.00	0.00	0.00	0.00
Ethylene Glycol	0.00	0.48	0.00	0.48	0.00	0.48	0.47
Mass Fractions							
Ethanol	1.000	0.559	0.275	0.568	0.844	0.000	0.000
Butanol	0.000	0.235	0.000	0.242	0.007	0.725	0.987
Water	0.000	0.097	0.015	0.100	0.149	0.000	0.000
Hexanol	0.000	0.046	0.000	0.048	0.000	0.146	0.003
2-Ethyl-1-Butanol	0.000	0.033	0.000	0.034	0.000	0.104	0.006
Octanol	0.000	0.007	0.000	0.007	0.000	0.021	0.000
2-Ethylhexanol	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Acetaldehyde	0.000	0.011	0.376	0.000	0.000	0.000	0.000
Ethylene	0.000	0.003	0.102	0.000	0.000	0.000	0.000
1-Butene	0.000	0.004	0.118	0.000	0.000	0.000	0.000
1-Hexene	0.000	0.003	0.096	0.000	0.000	0.000	0.000
1-Octene	0.000	0.001	0.000	0.001	0.000	0.003	0.004
Hydrogen	0.000	0.001	0.017	0.000	0.000	0.000	0.000
Ethylene Glycol	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 7: Basic overall stream table (part 2).

	Streams							
Mass Flows (kg/hr)	HEAVY	ETOH	ETGLY	WAST-OH1	ETGLY2	WAST-OH2	ETGLY3	ETGLY-RE
Total	675.93	4157.46	8944.38	183.96	8760.41	632.83	8127.59	8130.97
Ethanol	0.00	4134.14	63.29	63.00	0.29	0.29	0.00	0.00
Butanol	31.93	1.67	32.48	27.92	4.55	4.55	0.00	0.00
Water	0.00	21.17	718.00	92.99	625.01	625.01	0.00	0.00
Hexanol	348.62	0.00	0.09	0.05	0.05	0.05	0.00	0.00
2-Ethyl-1-Butanol	242.42	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Octanol	49.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Ethylhexanol	3.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetaldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Octene	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethylene Glycol	0.01	0.48	8130.48	0.00	8130.48	2.90	8127.59	8130.97
Mass Fractions								
Ethanol	0.000	0.994	0.007	0.342	0.000	0.000	0.000	0.000
Butanol	0.047	0.000	0.004	0.152	0.001	0.007	0.000	0.000
Water	0.000	0.005	0.080	0.505	0.071	0.988	0.000	0.000
Hexanol	0.516	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl-1-Butanol	0.359	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Octanol	0.074	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethylhexanol	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Acetaldehyde	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Octene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylene Glycol	0.000	0.000	0.909	0.000	0.928	0.005	1.000	1.000

PROCESS DESCRIPTION

Process Description

Fresh ethanol enters the process from the adjoining plant and is combined in a mixer with an ethanol recycle stream from the process. This stream then enters a packed bed reactor temperature controlled by a co-current molten salt stream. The reactor catalyst is hydroxyapatite. The reactant enters at 350°C and the products exit at 384°C. Butanol is the desired product, although additional carbon chain side products are made as well. The effluent stream is cooled to 40°C and then enters distillation column (B11), which takes light waste gases including acetaldehyde, ethylene, and hydrogen off the top of the column. The bottoms, mainly composed of unreacted ethanol, butanol, water, and other heavy hydrocarbons is then pumped to another distillation column (B12) which separates the ethanol and water from the heavier hydrocarbons. The heavy stream is sent to a third distillation column (B4) which separates the main product (butanol) from heavy hydrocarbons such as hexanol and octanol. This column produces a product stream of 99% pure butanol.

The stream from the top of column B12 containing ethanol and water then needs to be separated. To do this, the stream enters a tertiary distillation column (B5) along with a 131 kmol/hr of ethylene glycol. This allows the ethanol to be separated off the top of the column and recycled back to the reactor. The ethylene glycol and water are then separated using two distillation columns (B1 and B6). The first column (B6) creates a water stream that needs to be sent to a wastewater treatment facility. The second column (B1) has a pure enough water stream (99.7%) that it can be pumped back into a natural water source. The ethylene glycol from the bottom of column B1 is then recycled back into the process.

Material Balances

To check the accuracy of our simulation, we conducted simple mass balance calculations around major units. Individual component mass flows were added together at the inlet and outlet of each equipment of interest. The overall process mass flows are small due to the large amount of recycle in the process. Table 8 summarizes the overall mass flow data and detailed tables can be found in Appendix 2: Material Balance Calculations.

Table 8: Mass flows around major units in the flash-based process

Unit	Mass In (kg/hr)	Mass Out (kg/hr)
Reactor	7625	7625
Distillation Column (B1)	7625	7625
Distillation Column (B4)	7393	7393
Distillation Column (B5)	2422	2422
Distillation Column (B6)	13102	13102
Distillation Column (B11)	8944	8944
Distillation Column (B12)	8760	8760
Overall	3471	3471

Energy Balances and Utility Requirements

Utilities are discussed in detail for each unit in the following section.

Equipment List, Unit Descriptions/Specifications

Overall design for the process was inspired by a patented process design for ethanol conversion to n-butanol, n-octanol, and n-decanol [16].

B10-MIXER

Ethanol flow rate into the process is approximately that of an average production of a medium sized ethanol plant [17]. B10-Mixer combines the fresh ethanol with recycled ethanol to make an ethanol stream of 165 kmol/hr.

REACTOR

The reactor is a packed bed of hydroxyapatite catalyst. Hydroxyapatite has a density of 3.2 g/cm^3 [18]. Selectivity for n-butanol over hydroxyapatite catalyst is known to be between 50-60 wt% although higher selectivity results in lower conversion of ethanol to product [8]. To optimize reactor kinetics and predict reaction products, a simulation was developed using Aspen Plus V9.

Reactor Simulation

Reaction schemes and kinetics have been outlined previously by Tsuchida et al. covering 13 gas phase reactions [8] [19]. For this simulation, reactions including alkene elimination or cyclization were not considered. Our model was based upon the reaction schemes and kinetic models shown in Appendix 4: Reactor [8].

A tubular reactor for this reaction was suggested by patent literature [20]. Bed voidage was taken to be 0.5. Design parameters for the tubular reactor were changed until selectivity to n-butanol was approximately 50-60 wt%. The reactor has 12,500 tubes with a diameter of 15 mm and a length of 2 m. The simulated model is shown below as a single block (Figure 4) and retains good prediction capability to experimental data.

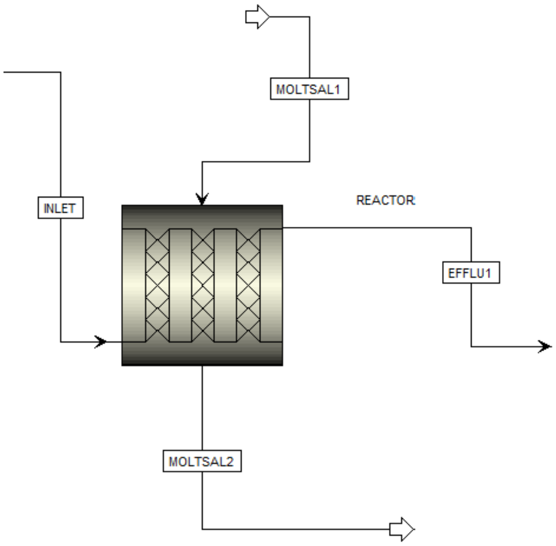


Figure 4: Aspen batch reactor block

Reaction temperature less than 250°C did not yield any product as shown in literature [8]. However, extremely high temperatures may cause sintering of the catalyst. For desired selectivity, reaction temperature should be maintained between 350°C and 400°C. Possible process fluids for heating the reactor include thermal oils such as mineral oil or molten salts [21] [22]. Thermal oils often contain a variety of different heavy organics, which is highly flammable [23]. Thus, sodium nitrite molten salt is utilized as the thermal heating flowrate. A high flowrate of 200 kmol/hr

(13,800 kg/hr) was chosen to remove heat quickly from the highly exothermic reaction. Temperature profile of the reactant mixture as a function of reactor length is shown in Figure 5.

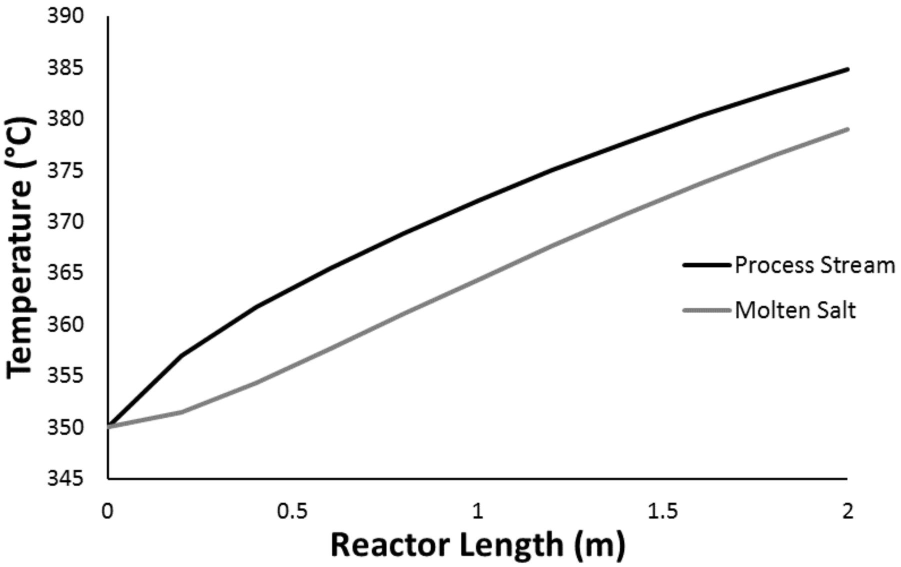


Figure 5: Aspen model reactor temperature profiles.

In the model, a heat transfer coefficient of 30 W/m^{2}K was used as suggested for gas to liquid heat transfer [24]. Outlet temperature of the molten stream is 379°C. The molten stream is then recycled which is outside the scope of this report.

Pressure drop across the reactor was simulated using frictional correlations. However, the pressure drop was minimal and less than 0.0001 bar. Further study of pressure drop is necessary.

The reactor is fed ethanol at 166.2 kmol/hr at over 99 mol% purity. The only impurity is water from the recycled ethanol stream. Composition of product in the reactor as a function of length is shown in Figure 6.

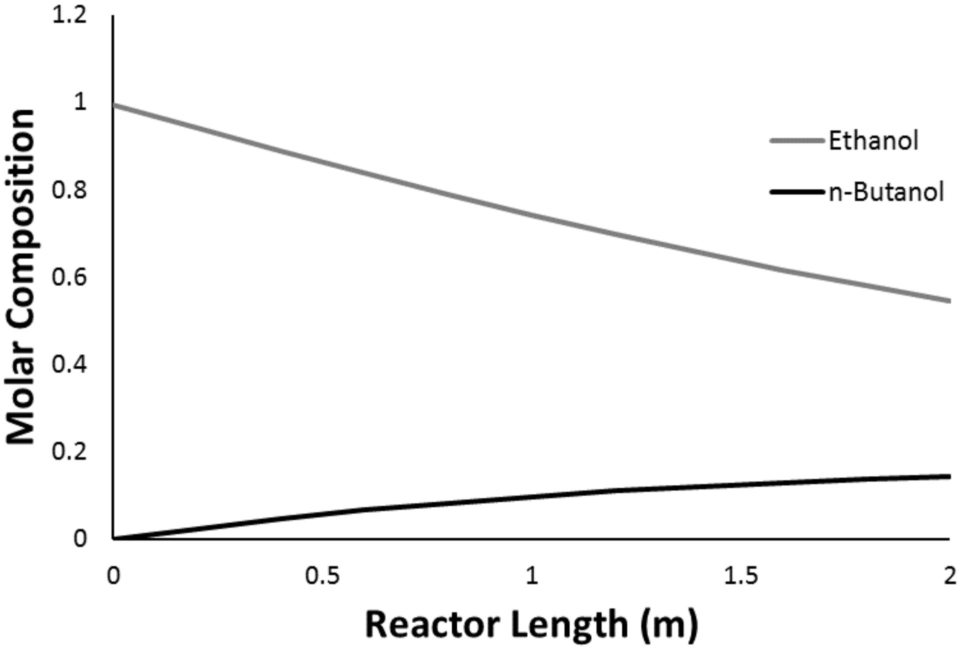


Figure 6: Simulated process stream composition

The simulation yields a conversion of 44% with a selectivity to n-butanol of 53 wt%. Other side products include water, hexanol, 2-ethyl-1-butanol, octanol, 2-ethylhexanol, octane, acetaldehyde, 1,3-butadiene, ethylene, butane, hexane, and octane. The largest side product is water at 22 wt% of all the products. In the presence of water and hydrogen at high temperatures, it is predicted that the unstable double bonded carbon chains will react further undergoing hydration or hydrogenation. However, simulation of these reactions are not considered in this report. Overall, simulation results accurately corresponded with experimental literature data [8].

B3 – COOLER

The B3-cooler cools reactant product from 384°C to 40°C before entering column B11. Utility for the cooler is cooling water at a flowrate of 611,000 kg/hr for a duty of -12.8 GJ/hr.

B11 – SEPARATOR

The B11-Separator is a distillation column which removes acetaldehyde and hydrogen from the other reaction products. This column was optimized based on a column described by

Rajendran et al. [25] Additionally, hydrogen removed should be within the combustible limits, since the distillate stream is to be sent to the flare. The column is 21.33 m tall with a diameter of 0.762 m with sieve trays. There are 30 stages with a partial-vapor condenser and kettle reboiler. Feed enters above stage 14. Optimally, the column is operated with a reflux ratio of 6 and distillate to feed ratio of 0.042 on a molar basis. Pressure of the column is maintained at atmospheric pressure. Utility for the condenser is cooling water at a rate of 87,000 kg/hr removing heat at a rate of -1.82 GJ/hr. The reboiler utilizes low pressure steam at a rate of 1,300 kg/hr for a duty of 2.99 GJ/hr. A description of process control for this column is presented in Process Controllability and Instrumentation.

B2 – PUMP

B2-Pump is a centrifugal pump which increases pressure in the liquid process stream from 1 bar to 20 bar. Efficiency of the pump was taken to be 45% as given by heuristics for pumps with liquid flow rates of 6×10^{-3} m/s [24]. Driver efficiency for centrifugal pumps is approximately 80% [26]. Electrical duty on the pump is 14.98 kW.

B12 – SEPARATOR

B12-Separator is a distillation column to remove ethanol and water from the butanol and heavy hydrocarbon stream. The column has sieve trays, a partial-vapor condenser, a kettle reboiler and is 12.19 m in height and 1.83 m in diameter. There are 15 stages and the feed enters above stage 4. Operating conditions are a reflux ratio of 4 and a distillate to feed ratio of 0.815 on a molar basis. Pressure within the column is maintained at 20 bar. Cooling water is used as the condenser utility with a flowrate of 770,000 kg/hr to remove heat at a rate of -16.1 GJ/hr. The reboiler is powered by natural gas fired heat for a duty of 23.7 GJ/hr at a rate of 263,000 kg/hr. Some of the fuel used is obtained by burning of the heavy waste stream.

B4 – SEPARATOR

The B4-Separator is the last purification step for butanol product achieving 99 mol% purity and a fuel stream containing heavycarbons. The column has 20 stages with a partial-vapor condenser, kettle reboiler, and sieve trays. Height of the column is 15.25 m, and the diameter is 1.22 m. Feed enters the column above stage 3. The reflux ratio is 6 and the distillate to feed ratio is 0.78 on a molar basis. Pressure in the column is kept at 20 bar. The condenser utility is cooling water at a flowrate of 168,000 kg/hr to remove heat at a rate of -3.50 GJ/hr. Fired heat is used to power the reboiler at a rate of 6,900 kg/hr to provide a duty of 4.14 GJ/hr.

B7 – COOLER

The cooler takes the ethanol and water stream from B12-Separator and cools and partially condenses it from 180°C to 78.2°C. Cooling water is used as the heat transfer fluid at a rate of 297,000 kg/hr to remove heat at a rate of -6.2 GJ/hr. Before the ethanol and water stream is sent to B5-Separator, pressure is dropped from 20 bar to 1 bar.

B5 – SEPARATOR

Separations of ethanol from water are difficult due to the presence of an azeotrope [27]. In order to improve separations, ethyl glycol is added making a tertiary system. In B5-Separator, ethyl glycol is added at a 1:1 molar ratio as suggested by literature [28] [29]. Ethyl glycol and water exit in the bottom of the column, and purified ethanol distillate is sent to B8-heater and recycled. The column is 16.46 m tall and has a diameter of 1.22 m. The column has 22 stages including a partial-vapor condenser and a kettle reboiler. Ethanol and water feed enters above stage 12, and ethyl glycol enters above stage 3. The column is operated at 1 bar with a reflux ratio of 1 and a distillate to feed ratio of 0.345 on a molar basis. Cooling water is used as the condenser utility at a rate of 172,000 kg/hr to remove heat at a rate of -3.58 GJ/hr. Reboiler utility requirement is high pressure steam at 3,400 kg/hr at a duty of 5.88 GJ/hr.

B6 – SEPARATOR

The B6-separator removes waste water WAST-OH1 in the distillate from the ethyl glycol stream. WAST-OH1 has residual amounts of ethanol and butanol. This allows for waste water disposal without further purification. The column has 10 stages including a partial-vapor condenser and a kettle reboiler. The column is operated with a reflux ratio of 2 and a distillate to feed ratio of 0.04 on a molar basis. Feed enters above stage 5, and pressure in the column is maintained at 1 bar. Condensor utility is cooling water at a rate of 27,000 kg/hr to remove heat at a rate of 0.57 GJ/hr. Reboiler utility usage is high pressure steam at 620 kg/hr with a duty of 1.06 GJ/hr.

B1 – SEPARATOR

Finally, all remaining impurities in the ethyl glycol stream are removed as distillate in the WAST-OH2 stream. The bottoms stream contains over 99.99 mol% ethyl glycol which is recycled to B5-Separator. The column has 10 stages, and the feed enters above stage 4. The column has a reflux ratio of 2 and distillate to feed ratio of 0.21 on a molar basis. Pressure is kept at 1 bar. Cooling water drives the partial-vapor condenser at a rate of 144,000 kg/hr for a duty of 3.02 GJ/hr. The kettle reboiler utilizes high pressure steam at a rate of 3,200 kg/hr for a duty of 5.56 GJ/hr.

B9 – MIXER

The ethyl glycol recycle stream is combined with a make-up ETGLY-MU stream. The combined stream is sent back to the B5-Separator.

B8 – HEATER

After ethanol is taken off the B5-Separator column, the recycle stream is sent to the B8-heater. The stream is heated from 78°C to 350°C. The heater is powered by natural gas at a rate of 3,800 kg/hr for a duty of 2.29 GJ/hr. Ethanol exiting the heater is sent back to the reactor.

Other Important Factors

Green Engineering Metrics

Quantifying environmental hazards is often difficult; however, a few green engineering metrics have been developed to determine the mass efficiency of the process. These metrics include effective mass yield, mass intensity, and E-factor, which are defined below [30].

$$Effective\ Mass\ Yield = \frac{Mass\ Products}{Mass\ of\ non\text{-}benign\ Reagents} * 100\% \tag{5}$$

$$Mass\ Intensity = \frac{Mass\ used\ in\ Process}{Mass\ of\ Product} \tag{6}$$

$$E - factor = \frac{Total\ Waste}{Mass\ of\ Product} * 100\% \tag{7}$$

In general, a high effective mass yield and low mass intensity and E-factor is desirable. For this process, n-butanol is considered the only desirable product, so the effective mass yield is 50.4%. It should be noted that the heavy hydrocarbon steam can be used or sold for fuel value. The mass intensity of the process is 6.64, which is large due the ethyl glycol necessary to separate ethanol from water. Molten salt mass flow was not considered in the mass intensity calculation. The E-factor is 0.60, which accounts for excess water and light hydrocarbons.

Ethanol

Ethanol is generally recognized as a safe chemical. Aside from water, people have the most exposure to ethanol than any other solvent due to alcoholic beverage consumption [31]. At 25°C, ethanol has a vapor pressure of 59.3 mmHg and therefore exists solely as vapor in the atmosphere [32]. Estimated half-life when degraded in the atmosphere is 36 hours [33]. In the case of an aquatic spill, ethanol is biodegradable under aerobic and anaerobic conditions and has a low aquatic toxicity [32]. The threshold limit value 8 hour time weighted average (TLV-TWA) for workers is 1000 ppm [34]. At concentrations of 3300 ppm or higher, ethanol is immediately dangerous to life or health [35].

n-Butanol

N-butanol is classified as a hazardous substance and any spills must be reported [36]. In the ambient atmosphere, n-butanol is semi-volatile and is expected to exist in the vapor phase due to the vapor pressure of 7 mm Hg at 25°C [37]. N-butanol is considered readably biodegradable [38]. The TLV-TWA is 20 ppm, and worker exposure levels may not exceed more than 3 times the TLV-TWA for 30 minutes during a day of work [39]. Recommended exposure limit for a 15-minute ceiling is 50 ppm and immediate dangers to life or health occur at 1400 ppm [35].

Ethylene Glycol

Ethylene glycol is commonly found in antifreeze, brake fluid, and cosmetics [35]. However, large spills greater than 5,000 lbs must be reported as ethylene glycol is considered a hazardous substance [36]. If released into the air, ethylene glycol will exist as a vapor at atmospheric pressure due to the vapor pressure of 0.0979 mm Hg at 25°C [40]. Biodegradation in activated sludge, sewage, and soil inocula was essentially complete in less than 1 to 4 days, and risk of bioaccumulation is low [41]. Ethylene glycol is not classifiable as a human carcinogen, and in aerosol form, the ceiling threshold limit is 100 mg/m^3 [35] [39].

Safety and Health Concerns

There are several health and safety concerns associated with this process. Significant hazards associated with flammable hydrocarbons and hydrogen gas will require constant monitoring and inherently safer design of equipment. Additional safety hazards and design choices are also discussed in the following sections.

Reactor Control

In order to better control the reactor, several design aspects were considered. Most importantly, the reaction temperature needs to be controlled and maintained by a molten salt stream. Temperature can also be controlled by changing feed flowrate. Since the reaction is exothermic, there is potential for a runaway reaction if not properly controlled. At higher temperatures, pressure inside the reactor will increase. If abnormally high pressure is obtained, a high pressure alarm will sound, and the relief valve will open. Additionally, at higher temperatures, conversion of ethanol to product will increase releasing more gaseous products including hydrogen. Combustible gas concerns relating to hydrogen are discussed below. The major concern at low temperatures is reduced conversion and selectivity.

Flammable Liquids

This process handles many organic flammable liquids and gases. The primary safeguard to reduce flammability risks is to reduce risk of a leak. However, if a leak occurs, all units are surrounded by a containment dike. A smaller dike diameter is desirable to reduce surface area lowering the evaporation rate. The area around all process units is be monitored using combustible gas detectors. In the presence of an alarm, all personnel should evacuate the area. Many of the chemicals in the process would be within the lower and upper explosive limits if released [42]. Therefore, electrical equipment is classified as Class I Division II and follows regulated standards outlined by OSHA and NFPA [43] [44]. Also, a sprinkler system and foam system are used for fire and vapor suppression respectively as suggested by NFPA [45].

Hydrogen

Handling of hydrogen requires additional safety measures as outlined by NFPA [46]. If oxygen enters the process at any point, the hydrogen has the possibility to ignite or explode. Lower and upper explosion limits in air are 15% and 59 vol% [47]. The lower and upper flammability limits in air are 4% and 74 vol% respectively [48]. To prevent these hazards, the process should always be purged of oxygen before start-up. Additionally, hydrogen sent to the flare should be monitored.

Process Controllability and Instrumentation

Control considerations and a Process Hazards Analysis (PHA) study were conducted over distillation column B11 for this process.

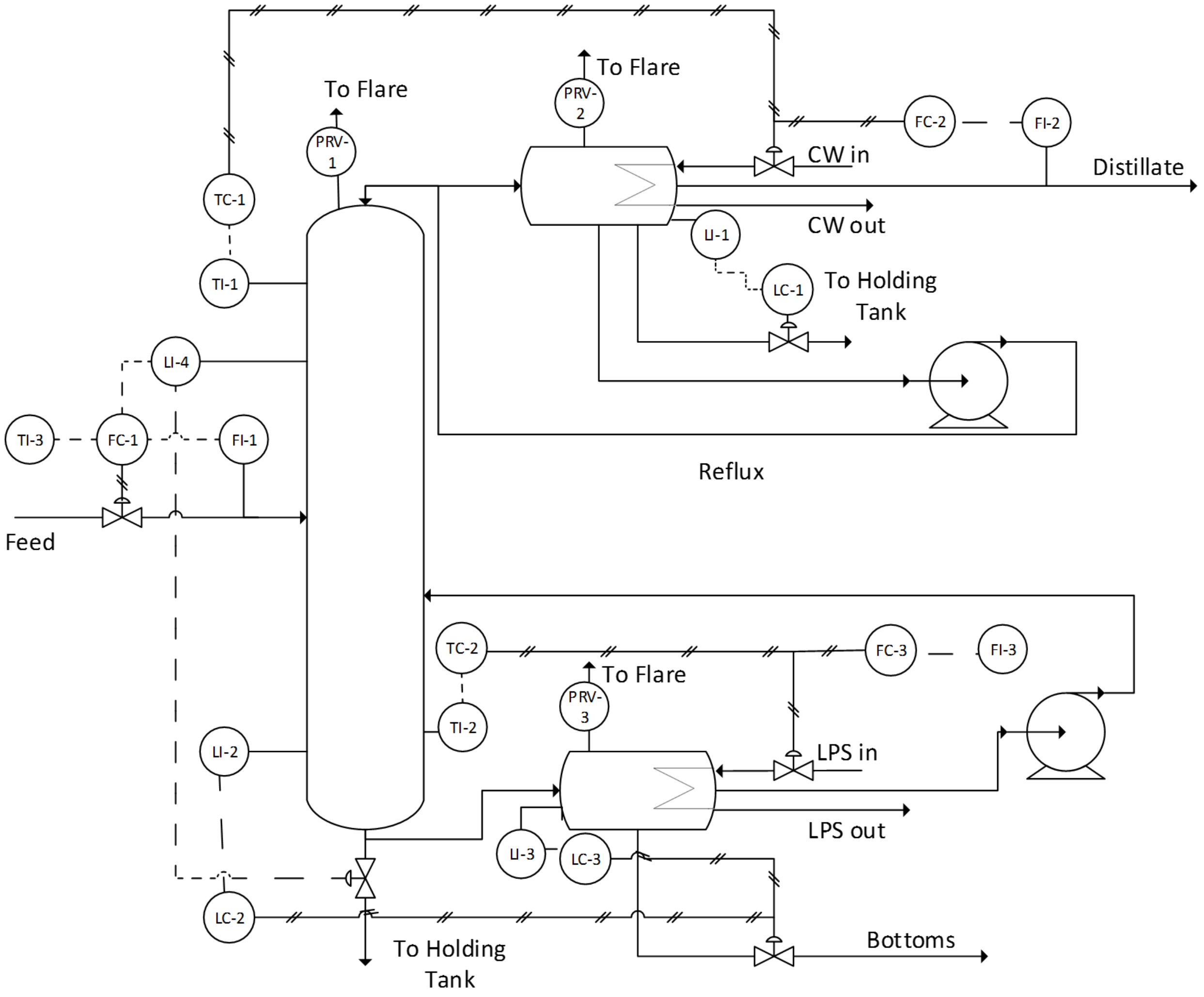


Figure 7: Distillation Column B11 P&ID

The considerations for the controls around the distillation column are shown in the piping and instrumentation diagram (P&ID) in Figure 7 and described in the ensuing sections. A PHA study was conducted to determine and evaluate hazards and establish a basis for necessary instrumentation and controls for this system.

Table 9: Codes for utility table.

Kansas State University

Senior Design Project
Process Hazard Analysis Exercise

Project Name: Conversion of Ethanol to Liquid Fuels

Facilitator: Chris Aiken

Team Members: Martha Floy, Diane Collard, Matthew Webb

Node: Distillation

Scenario	Guidewords	Initiating Event	Consequences	Safeguards	Recommendation
Example	High Pressure	Low pressure steam valve (1302/81A-LPS) fails open when deaerator tank (1302) is isolated pressurizing the tank to 3 bar	Deaerator tank rated for 1 bar fails resulting is a sudden release of pressure, steam and shrapnel with the potential to cause a fatality	Pressure transmitter (PT1302/81A) alarms to operator when pressure > 10 mmbarg	Add if the number of safeguards are not sufficient
1.0	High Temperature	Low Pressure Steam (10psig) supply valve to reboiler malfunctions opening to 100%	Column temperature increases to 90C increasing the pressure to xxpsig potentially over pressuring the column causing the column to rupture releasing flammable liquid and vapor. The vapor ignites resulting in a flash fire with the potential to cause an injury or possible fatality	PRD 1 TI-2 gives an alarm to an operator at 85C	Need to determine vapor pressure at 90C Consider designing the column to withstand pressure at 90C
2.0	High Temperature	Low Pressure Steam (10psig) supply valve to reboiler malfunctions opening to 100%	Column temperature increases to 90C increasing the pressure to xxpsig potentially over pressuring the condenser causing the column to rupture releasing flammable liquid and vapor. The vapor ignites resulting in a flash fire with the potential to cause an injury or possible fatality	PRD 3 TI-2 gives an alarm to an operator at 85C	Need to determine vapor pressure at 90C Consider designing the condenser to withstand pressure at 90C
3.0	High Temperature	Loss of cooling of reactor discharge feeds column with gas at 300C	Column liquid level drops closing column discharge valve increasing column pressure. Pressure causes column to rupture releasing flammable liquid and vapor. The vapor ignites resulting in a flash fire with the potential to cause an injury or possible	PRD-1	Add a temperature transmitter to column feed to shut FC1 control valve at high temperature
4.0	High Level	Column bottoms discharge valve malfunctions and closes	Column fills with liquid and floods overloading structural support causing the column to collapse	Structural steel designed for a fully flooded column	
5.0	High Level	Column bottoms discharge valve malfunctions and closes	Column fills with liquid and floods sending high volume of liquid to distillate possibly overflowing distillate tank	High level (LC1) in condenser opens valve to the condensate	Consider impact of overflowing distillate storage tank Consider adding a high level switch to column and to the condenser to shut FC-1 with high level Design downstream process for condenser condensate for full liquid flow from column
6.0	High Level	Column bottoms discharge valve malfunctions and closes	Column fills with liquid and floods sending high volume of liquid to distillate possibly overflowing distillate tank	None identified	Consider impact of overflowing distillate storage tank Consider adding a high level switch to column to shut FC-1 with high level
7.0	High Level	Column bottoms discharge valve malfunctions and closes	Column fills with liquid and floods causing the PRD-1 to open releasing liquid to the flare	None identified	Consider adding a high level switch to column and to the condenser to shut FC-1 with high level Consider liquid deviation from column in the flare design requirement
8.0	High Level	Column bottoms discharge valve malfunctions and closes	Column fills with liquid and pressurizes causing the column to rupture releasing flammable liquid and vapor	The column is designed above the deadhead pressure of the reactor condenser discharge pump	Consider adding a high level switch to column and to the condenser to shut FC-1 with high level Consider liquid deviation from column in the flare design requirement
9.0		H2 feeds column and discharges top via the distillate.	Team discovered distillate not designed for H_2 containment		Modify design to manage H_2 and associated risk in the distillate
10.0	High Flow	Cooling water control valve to distillate condenser malfunctions and opens to 100% causing high cooling water flow	Condensing more hydrocarbon vapor increases the concentration of H_2 gas in the condenser and in the distillate.	Low temperature (TI-1) gives an alarm at XXC to the operator	Evaluate the risk associate with higher concentrations of H2 in the distillate. Consider inerting gases/O_2 removal from the process including downstream equipment
11.0	High Flow	Cooling water control valve to distillate condenser malfunctions and opens to 100% causing high cooling water flow	Column temperature drops increasing the level of impurities in the bottoms affecting product quality.	Low temperature (TI-1) gives an alarm at XXC to the operator	Determine the minimum operating temperature required to meet product specifications
12.0		Piping or column develops a leak from lack of maintenance or error installing gasket	The release of flammable liquid causes a vapor cloud and ignites resulting in a flash fire with the potential to cause an injury or possible fatality	Combustible gas detector providing a plant wide alarm initiating an evacuation Sprinkler system in the event of a fire Foam system for the dike area Area/buildings are electrically classified as Class I Div II	

Process control of each distillation column is very detailed. First, the feed flow and temperature are both monitored (FI-1, TI-3). This allows for control of the flow rate to the column, as well as a safeguard preventing the column from overheating in the event that a process upset occurs upstream of the column. There is also a high-level switch (LI-4) on the column that will shut off the feed to the column in the case that the column is flooded. At the same time, LI-4 will open a valve at the bottom of the column which will drain the liquid volume to a holding tank. In addition, the column has a pressure relief valve (PRV-1) that will open if the column is pressurized above standard operating conditions.

The column is heated by a kettle reboiler at the bottom of the column. The heat is supplied by low pressure stream. The stream control valve (FC-3) is controlled by both the temperature at the bottom of the column (TI-2) and the recycle of the bottoms back to the column (FI-3). For example, if the bottoms were to decrease in temperature, the stream valve would open, thus increasing the temperature of bottoms being recycled back to the column. In addition, the reboiler is equipped with a pressure relief valve (PRV-3) that acts a safeguard in an overpressure situation. The liquid level in the reboiler is also monitored by LI-3. If flooding were to occur in the reboiler, additional liquid would be taken off in the bottoms stream by a control valve. This same valve can also be controlled by the level controller on the bottom of the column (LI-2).

At the top of the column is a partial condenser. The condenser is equipped with a pressure relief valve (PRV-2) as a safeguard in an overpressure situation. The temperature at the top of the column (TI-1) is maintained by increasing or decreasing the cooling water flow to the condenser. The liquid level in the condenser is monitored by LI-1, which will drain the condenser to a holding tank in the event that the condenser is flooded. The distillate flow rate is also monitored by FI-2 and can be adjusted via the cooling water flow rate which will change the amount of distillate that is condensed.

PROCESS ECONOMICS AND PROFITABILITY

Initially, a process for making butanol as a fuel and as a solvent were considered. For the fuel process, the product did not require the same level of purity, but had a much lower sale price. This process was found to not be profitable based on several measures. Based on the current price of ethanol ($0.50/kg), and sale price of butanol fuel ($1.26/kg), the return on investment for this process would be negative. In order to achieve a positive return on investment, the price ethanol would need to be $0.18/kg. Even if the purchase price of ethanol was free, the ROI would only be 18%, which is not a large enough return to consider this process feasible. Therefore, the focus of the economics section will be on the process for making high purity butanol and selling it as a solvent.

The utility costs of the process are tabulated and discussed below. Various utilities were used, including cooling water, steam, and natural gas. Table 10 correlates the code in the utility table to descriptions.

Table 10: Codes for utility table.

Utility Code Key	
CW	Cold Water
RW	Refrigerated Water
HPS	High Pressure Steam
LPS	Low Pressure Steam
Molten	Molten Stream
CD	Condenser
RB	Reboiler

Table 11 below shows the total utility costs for this process. These costs are approximately $5 million per year. A majority of this cost comes from the B12 reboiler which requires natural gas. Costs of utilities were estimated using Aspen simulator.

Table 11: Utility costs.

Equipment	**Utility**	**Amount**		**Cost of Utility**			**Total Cost (per year)**	
Cooler (B3)	CW	12.801	GJ/hr	$	0.35	/GJ	$	35,889.91
B11 Condensor	CW	1.82	GJ/hr	$	0.35	/GJ	$	5,102.70
B11 Reboiler	LPS	2.99	GJ/hr	$	13.28	/GJ	$	314,481.02
Pump (B2)	Electric	15	kW	$	0.06	/kWh	$	7,128.00
B12 Condensor	CW	16.1	GJ/hr	$	0.35	/GJ	$	45,139.25
B12 Reboiler	Natural Gas	23.7	GJ/hr	$	11.00	/GJ	$	2,064,744.00
B4 Condensor	CW	3.51	GJ/hr	$	0.35	/GJ	$	9,840.92
B4 Reboiler	Natural Gas	4.14	GJ/hr	$	11.00	/GJ	$	360,676.80
Cooler (B7)	CW	6.18	GJ/hr	$	0.35	/GJ	$	17,326.74
B5 Condensor	CW	3.59	GJ/hr	$	0.35	/GJ	$	10,065.21
B5 Reboiler	HPS	5.88	GJ/hr	$	17.70	/GJ	$	824,281.92
B6 Condensor	CW	0.57	GJ/hr	$	0.35	/GJ	$	1,598.10
B6 Reboiler	HPS	1.06	GJ/hr	$	17.70	/GJ	$	148,595.04
Heater (B8)	Natural Gas	2.33	GJ/hr	$	11.00	/GJ	$	202,989.60
B1 Condensor	CW	3.02	GJ/hr	$	0.35	/GJ	$	8,467.11
B1 Reboiler	HPS	5.56	GJ/hr	$	17.70	/GJ	$	779,423.04
						TOTAL	**$**	**4,835,749.36**

In addition to utilities, the total production cost was calculated for this process. This calculation can be seen in Appendix 3: Economic Analysis and Calculations. The total production cost was found to be approximately $24.7 million/year. Similar to the Fixed Capital Investment (FCI) estimation, we utilized several suggested factors by Peters et al. for each of the operating costs. In addition, we did not include depreciation in this calculation, as it will be considered in the profitability measurements.

The largest contributor to the operating costs was the reagent, ethanol. It makes up over half of the production costs and was largely the reason the butanol fuel process was not profitable. A deeper discussion on the profitability of the butanol solvent process can be found in Appendix 3: Economic Analysis and Calculations section.

Equipment Cost Summary

Using the process flow diagram for this process, each piece of equipment was costed in 2016 dollars using a CEP Index of 226.8. For most equipment, two sources were used for finding the information necessary to cost the equipment. These sources can be seen in the Equation section of the table below. In addition, Aspen simulator was used to cost certain pieces of equipment. The total equipment cost for this project is approximately $2.8 million.

Table 12: Equipment cost.

Equipment	Additional Info	Equipment Specs	Equation	Cost	CP Index	Equipment Cost In 2010
REACTOR	Costed as Shell & Tube	S.S., 12500 tubes, D=15mm, L=2 ft, A=1178 m2	(Seider et al., Eq 16.43, p.523)	$ 423,105	394	$ 597,931
Cooler (B3)	Q=3.56E6 Watts, U=425 W/m2*K (P&T)	A=24.35 m2, S.S. shell and tube-fixed head	(Peters et al, p. 682)	$ 7,500	390.4	$ 10,697
Pump (B2)	Size based on capacity = 0.0027 m3/s and kPa=2000	S.S., centrifugal pump	(Peters et al, pg. 519)	$ 5,900	390.4	$ 8,415
Cooler (B7)	Q=1.72e6 Watts, U=560 W/m2*K (P&T)	A=30.72 m2, S.S. shell and tube-fixed head	(Peters et al, p. 682)	$ 8,500	390.4	$ 12,123
Heater (B8)	Q=647093 Watts	Fired Heater	C=0.512*Q^0.81 (Seider et al.)	$ 70,500	394	$ 99,630
Column(B11)	Tower Cost	H=21.33 m, D=0.762 m, S.S. Sieve trays	(Peters et al, p. 793-794)	$ 156,000	390.4	$ 222,492
	Condensor		Aspen	$ 26,400	550.8	$ 26,688
	Reboiler		Aspen	$ 17,700	550.8	$ 17,893
	Reflux Pump		Aspen	$ 4,500	550.8	$ 4,549
Column(B12)	Tower Cost	H=12.19 m, D=1.83 m, S.S. Sieve Trays	(Peters et al, p. 793-794)	$ 143,000	390.4	$ 203,951
	Condensor		Aspen	$ 37,400	550.8	$ 37,807
	Reboiler	Fired Heater Reboiler	C=0.512*Q^0.81 (Seider et al.)	$ 461,000	394	$ 651,484
	Reflux Pump		Aspen	$ 6,400	550.8	$ 6,470
Column(B5)	Tower Cost	H=16.46 m, D=1.22 m, S.S. Sieve Trays	(Peters et al, p. 793-794)	$ 139,000	390.4	$ 198,246
	Condensor		Aspen	$ 28,500	550.8	$ 28,810
	Reboiler		Aspen	$ 19,500	550.8	$ 19,712
	Reflux Pump		Aspen	$ 5,200	550.8	$ 5,257
Column(B4)	Tower Cost	H=15.25 m, D=0.762 m, S.S. Sieve Trays	(Peters et al, p. 793-794)	$ 110,850	390.4	$ 158,098
	Condensor		Aspen	$ 27,900	550.8	$ 28,204
	Reboiler	Fired Heater Reboiler	C=0.512*Q^0.81 (Seider et al.)	$ 112,260	394	$ 158,646
	Reflux Pump		Aspen	$ 5,600	550.8	$ 5,661
Column(B6)	Tower Cost	H=9.14 m, D=0.61 m, S.S. Sieve Trays	(Peters et al, p. 793-794)	$ 67,000	390.4	$ 95,557
	Condensor		Aspen	$ 24,100	550.8	$ 24,363
	Reboiler		Aspen	$ 12,400	550.8	$ 12,535
	Reflux Pump		Aspen	$ 4,500	550.8	$ 4,549
Column (B1)	Tower Cost	H=9.14 m, D=1.07 m, S.S. Sieve Trays	(Peters et al, p. 793-794)	$ 78,500	390.4	$ 111,959
	Condensor		Aspen	$ 26,500	550.8	$ 26,789
	Reboiler		Aspen	$ 37,000	550.8	$ 37,403
	Reflux Pump		Aspen	$ 4,500	550.8	$ 4,549
					TOTAL	**$ 2,820,467**

Fixed Capital Investment Summary

Based on the purchased equipment cost, the fixed capital investment (FCI) can be calculated. A delivery cost of 10% of the equipment cost was assumed. Then, the direct and indirect cost could be calculated from the purchased delivered equipment cost. Peters et al. offers suggested percentages to use for a fluids plant, are often given as a range. Each of these ranges was evaluated for our specific purposes. For example, a fluids plant requires a large amount of piping, so we used a larger percentage for this cost. Following this, the FCI was calculated to be approximately $14 million and the Total Capital Investment (TCI) was found to be approximately $17 million. The working capital was assumed to be 15% of the TCI.

Table 13: Capital investment.

Costs	% of Delivered Eq.	Justification	Cost
Direct Costs			
Purchased Equipment Delivered	100	Calculated Previously	$ 3,102,513
Purchased Equipment Installation	47	Installation varies from 25-55 %, higher for fluids plant	$ 1,458,181
Instramentation & Controls	36	This process will require a significant amount of control. Range from 8-50%	$ 1,116,905
Piping	68	Fluids processesing requires a larger amout of required piping. Max=80%	$ 2,109,709
Electrical Systems	11	Suggested percentage from for fluids process plant (Table 6-9)	$ 341,276
Buildings	6	This is the percent given for an expansion to an existing site	$ 186,151
Yard Improvements	10	ranges 10-20%	$ 310,251
Service Facilities	40	Ranges 30-80%, for single product, continuous process will be lower	$ 1,241,005
		Total	$ 9,865,992
Indirect Costs			
Engineering & Supervision	30	Approximately 30%	$ 930,754
Construction Expenses	41	Suggested percentage	$ 1,272,030
Legal Expenses	4	Mostly from equipment purchases, and environmental & safety complience	$ 124,101
Contractor's Fee	22	Suggested percentage	$ 682,553
Contingency	40	A value slightly smaller than suggested due to this only being an addition.	$ 1,241,005
		Total	$ 4,250,443
		Fixed Capital Investment	**$ 14,116,436**
		Working Capital	**$ 2,761,237**
		Total Capital Investment	**$ 16,877,673**

Economic Analysis

The first profitability measurements calculated for the butanol solvent process are return on investment (ROI) and payback period (PBP). Both measurements were calculated in the third year of production, as it was assumed that the process would be at full capacity by this point. The project was estimated to have a 50% capacity in year 1, and a 90% capacity in year 2. The table for calculating these measurements can also be found in Appendix 4. Return on Investment is defined as:

$$ROI\ (year\ 3) = \frac{Annual\ Net\ Profit}{Total\ Capital\ Investment}$$

$$= \frac{(Sales - Costs - Depreciation)(1 - tax\ rate)}{Total\ Capital\ Investment}$$

For these calculations, a tax rate of 35% was assumed. The ROI was found to be 0.41 for this process. Additionally, the payback period was calculated in year 3; the equation is as follows:

$$PBP(year\ 3) = \frac{Total\ Depreciable\ Capital}{Annual\ Cash\ Flow} = \frac{TDC}{(S - C)(1 - t) + D}$$

The payback period was found to be 1.3 years. Both the ROI and PBR show that this process stands to be very profitable.

Profitability

Net Present Worth

The next profitability measure we calculated is net present worth. We calculated the net present worth (NPW) for two scenarios. One in which all the total investment is all payed at year 0, and the other when the total investment is done in several payments prior to the plant start up. Net present worth is defined as:

$$NPW = Present\ Worth\ of\ Cash\ Flows - Present\ Worth\ of\ Capital\ Investments$$

The calculations of NPW can be found in Appendix 3: Economic Analysis and Calculations, and can also be seen in the graphs below. Figure 8 is a cash flow diagram over the 15-year project life, showing the initial capital investment paid in year zero, and the profits made following that year.

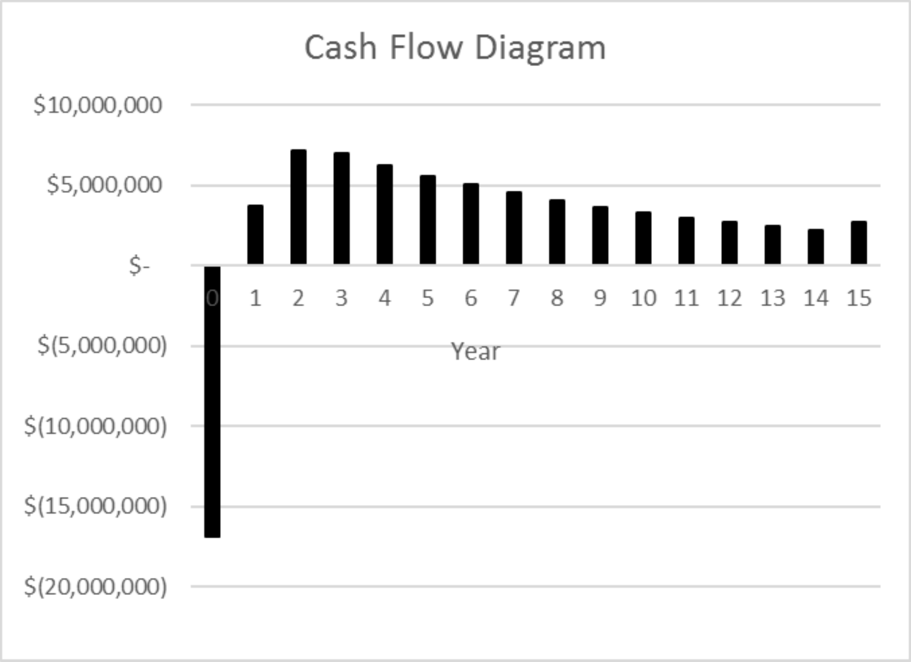


Figure 8: Annual cash flow diagram considering all investment at year zero.

Figure 9 shows the net present worth over the 15-year project life. This chart shows that the process will start to be profitable in year 3 following the start-up of the plant. The total NPW at the end of the 15-year period is approximately $46 million. This shows that the butanol solvent process stands to be extremely profitable.

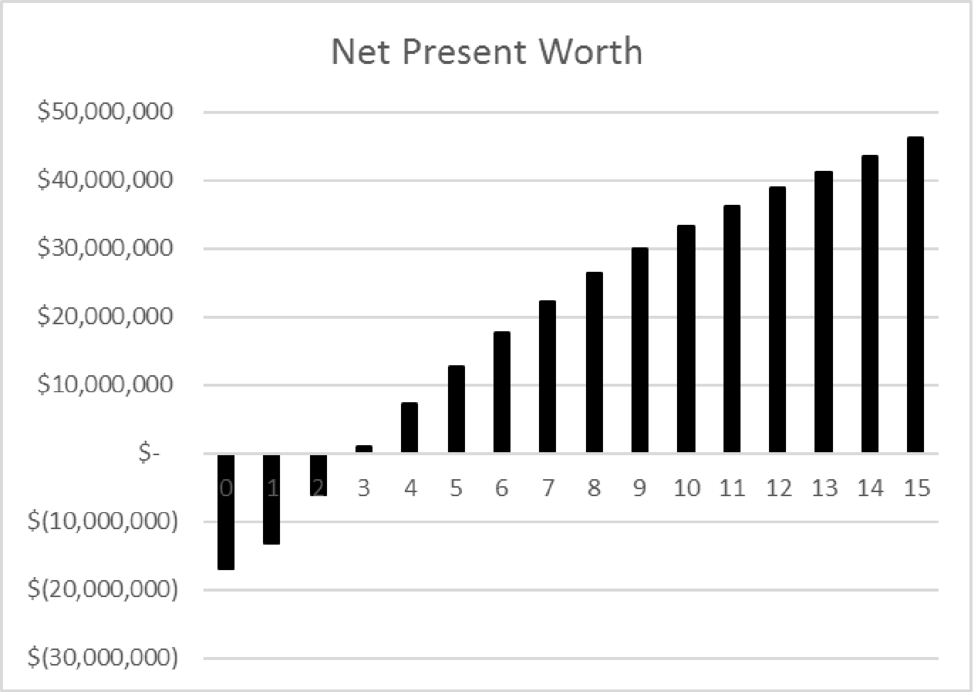


Figure 9: Annual net present worth considering all investment at year zero.

In contrast, we looked at the situation in which the total capital investment is made in a series of payments prior to start up. 70% would be paid two years before start-up, and the other 30% paid one year before start up. The corresponding charts (Figure 10 and Figure 11) can be seen below for the annual cash flow and NPW. Both the cash flow diagram and net present worth chart have similar trends to that of the single total capital investment payment.

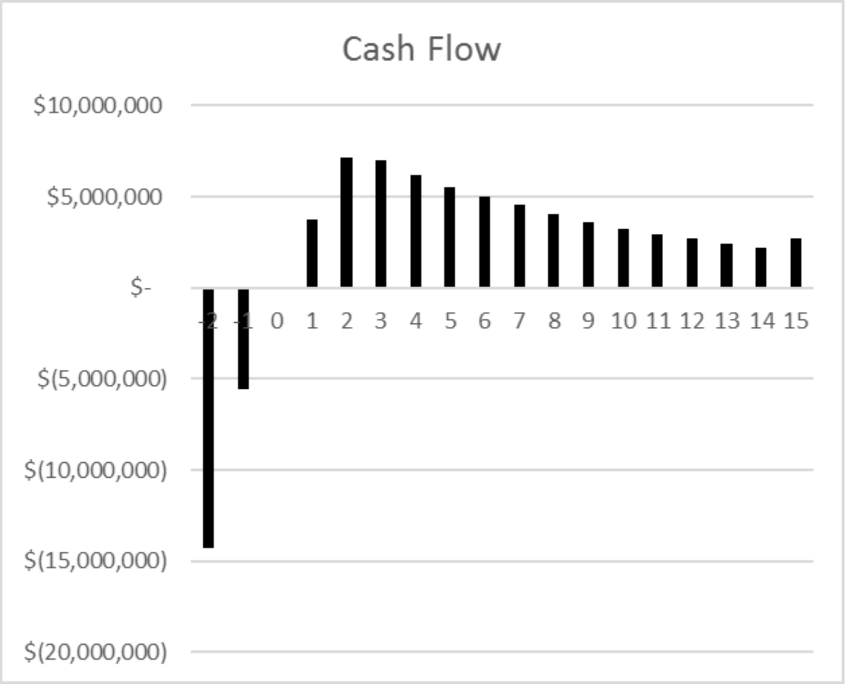


Figure 10: Annual cash flow diagram considering all investment two years before year zero.

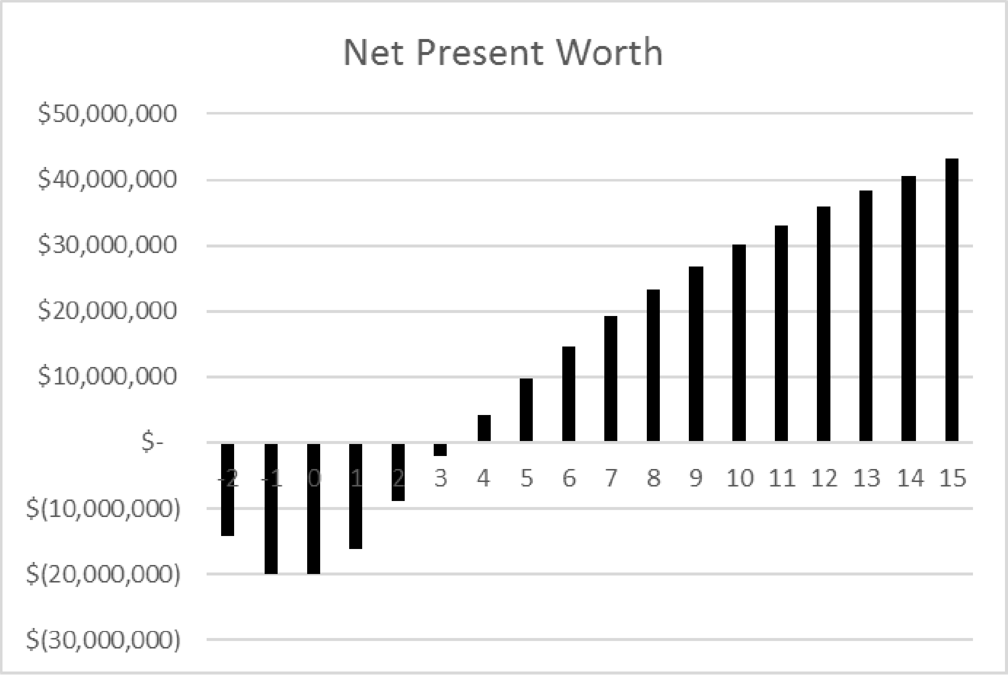


Figure 11: Annual net present worth considering all investment two years before year zero.

Figure 12 shows the net present worth of both scenarios compared to one another. It can be seen from this chart that the NPW at year 15 will be slightly lower at approximately $43 million. Both methods will be extremely profitable for this process.

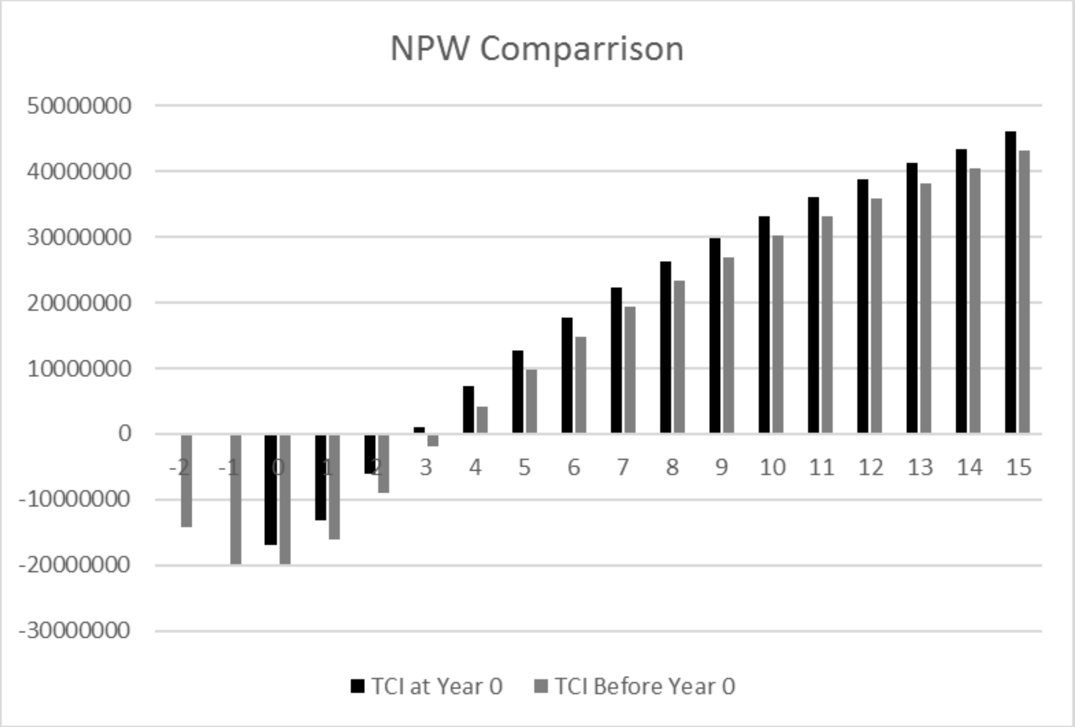


Figure 12: Comparison of annual net present worth considering all investment at year zero and two years before year zero.

Discounted Cash Flow Rate of Return

Finally, we calculated the discounted cash flow rate of return (DCFR). Due to the similarities in NPW regardless of year of investment, we only performed this calculation for the scenario in which all of the total capital investment is paid in year zero, prior to start up. The table below shows that for our presented process, the DCFR is 0.44 or 44%. This far exceeds the desired rate of return of 30%, thus making our recommended process a viable option.

Table 14: Discounted cash flow rate summary.

FCI	Tax Rate	DCFR
$14,116,436	0.35	0.44

Table 15: Discounted cash flow rate of return considering all capital investment at year zero.

Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
0					$16,877,673		1.000	$ -	$ 16,877,673
1	$ 18,820,000	$ 13,600,000	14.29	$ 2,017,239	$ -	$ -	0.695	$ 2,849,904	$ -
2	$ 33,880,000	$ 22,440,000	24.49	$ 3,457,115	$ -	$ -	0.483	$ 4,179,383	$ -
3	$ 37,640,000	$ 24,630,000	17.49	$ 2,468,965	$ -	$ -	0.336	$ 3,132,505	$ -
4	$ 37,640,000	$ 24,650,000	12.49	$ 1,763,143	$ -	$ -	0.234	$ 2,117,151	$ -
5	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.162	$ 1,443,400	$ -
6	$ 37,640,000	$ 24,650,000	8.92	$ 1,259,186	$ -	$ -	0.113	$ 1,003,486	$ -
7	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.079	$ 697,725	$ -
8	$ 37,640,000	$ 24,650,000	4.46	$ 629,593	$ -	$ -	0.055	$ 473,043	$ -
9	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.038	$ 320,524	$ -
10	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.026	$ 222,848	$ -
11	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.018	$ 154,938	$ -
12	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.013	$ 107,723	$ -
13	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.009	$ 74,896	$ -
14	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.006	$ 52,072	$ -
15	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$2,761,237	0.004	$ 48,043	$ -
							SUM	$ 16,877,642	
							NPW (~0)	**$**	**(30.48)**

ACKNOWLEDGEMENTS

We would like to acknowledge Dr. Jennifer Anthony and Dr. John Schlup for guiding us through the project and providing us with a strong foundation from which to begin the design. A special thanks to Cargill representatives Chris Aikens and Luke Hirschler for guidance on process safety.

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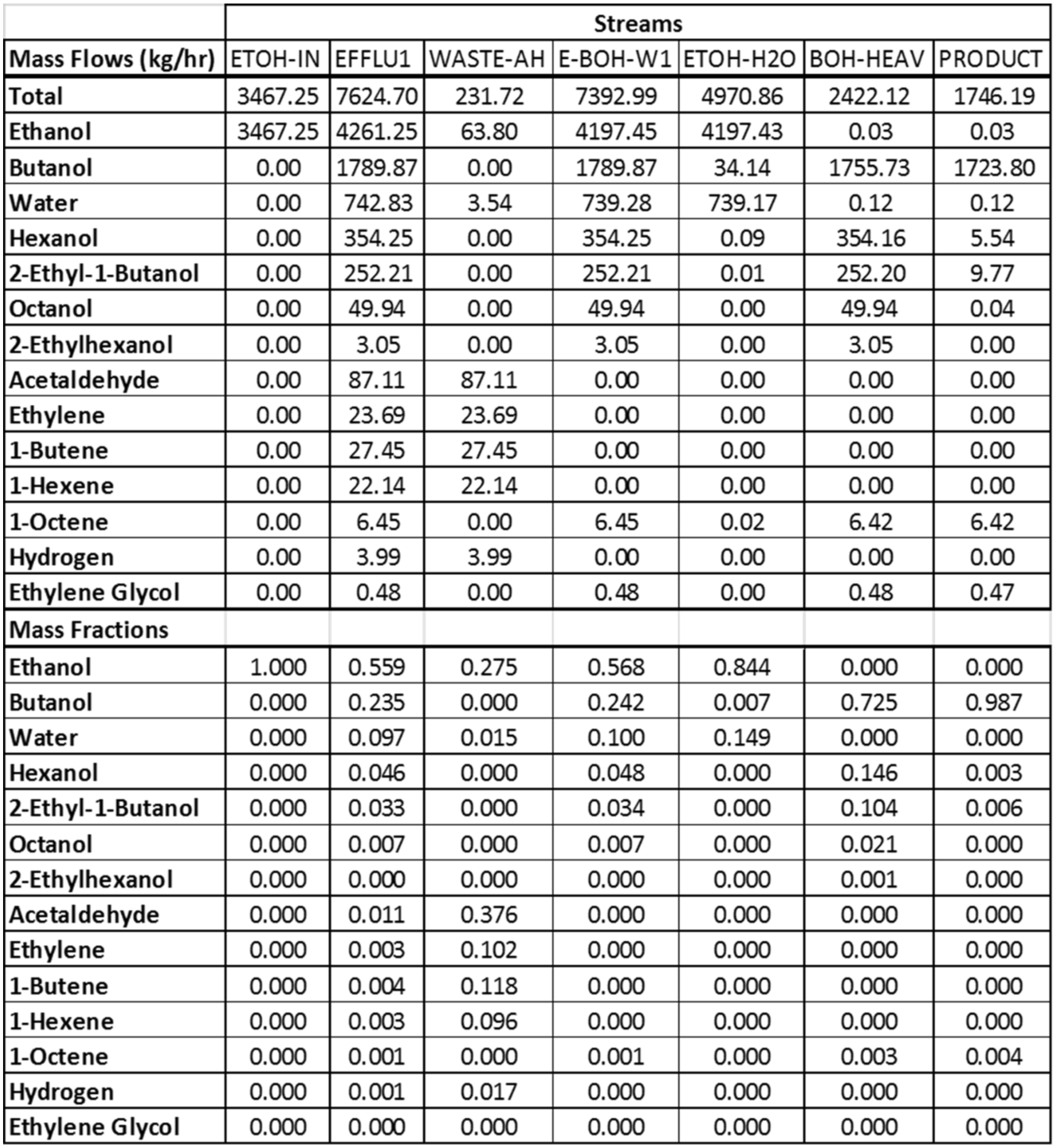
APPENDICES

Appendix 1: Stream Tables

Appendix Table 1: Complete stream table (Part 1).



	Streams						
Mass Flows (kg/hr)	ETOH-IN	EFFLU1	WASTE-AH	E-BOH-W1	ETOH-H2O	BOH-HEAV	PRODUCT
Total	3467.25	7624.70	231.72	7392.99	4970.86	2422.12	1746.19
Ethanol	3467.25	4261.25	63.80	4197.45	4197.43	0.03	0.03
Butanol	0.00	1789.87	0.00	1789.87	34.14	1755.73	1723.80
Water	0.00	742.83	3.54	739.28	739.17	0.12	0.12
Hexanol	0.00	354.25	0.00	354.25	0.09	354.16	5.54
2-Ethyl-1-Butanol	0.00	252.21	0.00	252.21	0.01	252.20	9.77
Octanol	0.00	49.94	0.00	49.94	0.00	49.94	0.04
2-Ethylhexanol	0.00	3.05	0.00	3.05	0.00	3.05	0.00
Acetaldehyde	0.00	87.11	87.11	0.00	0.00	0.00	0.00
Ethylene	0.00	23.69	23.69	0.00	0.00	0.00	0.00
1-Butene	0.00	27.45	27.45	0.00	0.00	0.00	0.00
1-Hexene	0.00	22.14	22.14	0.00	0.00	0.00	0.00
1-Octene	0.00	6.45	0.00	6.45	0.02	6.42	6.42
Hydrogen	0.00	3.99	3.99	0.00	0.00	0.00	0.00
Ethylene Glycol	0.00	0.48	0.00	0.48	0.00	0.48	0.47
Mass Fractions							
Ethanol	1.000	0.559	0.275	0.568	0.844	0.000	0.000
Butanol	0.000	0.235	0.000	0.242	0.007	0.725	0.987
Water	0.000	0.097	0.015	0.100	0.149	0.000	0.000
Hexanol	0.000	0.046	0.000	0.048	0.000	0.146	0.003
2-Ethyl-1-Butanol	0.000	0.033	0.000	0.034	0.000	0.104	0.006
Octanol	0.000	0.007	0.000	0.007	0.000	0.021	0.000
2-Ethylhexanol	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Acetaldehyde	0.000	0.011	0.376	0.000	0.000	0.000	0.000
Ethylene	0.000	0.003	0.102	0.000	0.000	0.000	0.000
1-Butene	0.000	0.004	0.118	0.000	0.000	0.000	0.000
1-Hexene	0.000	0.003	0.096	0.000	0.000	0.000	0.000
1-Octene	0.000	0.001	0.000	0.001	0.000	0.003	0.004
Hydrogen	0.000	0.001	0.017	0.000	0.000	0.000	0.000
Ethylene Glycol	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Appendix Table 2: Complete stream table (Part 2).

	Streams							
Mass Flows (kg/hr)	HEAVY	ETOH	ETGLY	WAST-OH1	ETGLY2	WAST-OH2	ETGLY3	ETGLY-RE
Total	675.93	4157.46	8944.38	183.96	8760.41	632.83	8127.59	8130.97
Ethanol	0.00	4134.14	63.29	63.00	0.29	0.29	0.00	0.00
Butanol	31.93	1.67	32.48	27.92	4.55	4.55	0.00	0.00
Water	0.00	21.17	718.00	92.99	625.01	625.01	0.00	0.00
Hexanol	348.62	0.00	0.09	0.05	0.05	0.05	0.00	0.00
2-Ethyl-1-Butanol	242.42	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Octanol	49.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Ethylhexanol	3.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetaldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Octene	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethylene Glycol	0.01	0.48	8130.48	0.00	8130.48	2.90	8127.59	8130.97
Mass Fractions								
Ethanol	0.000	0.994	0.007	0.342	0.000	0.000	0.000	0.000
Butanol	0.047	0.000	0.004	0.152	0.001	0.007	0.000	0.000
Water	0.000	0.005	0.080	0.505	0.071	0.988	0.000	0.000
Hexanol	0.516	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl-1-Butanol	0.359	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Octanol	0.074	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethylhexanol	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Acetaldehyde	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Octene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylene Glycol	0.000	0.000	0.909	0.000	0.928	0.005	1.000	1.000

Appendix 2: Material Balance Calculations

Material Balance Over Individual Units

Appendix Table 3: Reactor material balance.

Reactor		
Component	**Inlet (kg/hr)**	**Outlet (kg/hr)**
Ethanol	7601.39	4261.25
n-Butanol	1.67	1789.87
Water	21.17	742.83
1-Hexanol	0.00	354.25
2-Ethyl-1-But	0.00	252.21
1-Octanol	0.00	49.94
2-Ethylhexanol	0.00	3.05
Acetaldehyde	0.00	87.11
Ethylene	0.00	23.69
1-Butene	0.00	27.45
1-Hexene	0.00	22.14
1-Octene	0.00	6.45
Hydogen	0.00	3.99
Ethylene Glycol	0.48	0.48
TOTAL	**7624.70**	**7624.70**

Appendix Table 4: Distillation column (B1) material balance.

Distillation Column (B1)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	0.29	0.29	0.00
n-Butanol	4.55	4.55	0.00
Water	625.01	625.01	0.00
1-Hexanol	0.05	0.05	0.00
1-Octene	0.02	0.02	0.00
Ethylene Glycol	8130.48	2.90	8127.59
TOTAL MASS IN:	**8760.40**	**TOTAL MASS OUT:**	**8760.40**

Appendix Table 5: Distillation column (B4) material balance.

Distillation Column (B4)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	0.03	0.03	0.00
n-Butanol	1755.73	1723.80	31.93
Water	0.12	0.12	0.00
1-Hexanol	354.16	5.54	348.62
2-Ethyl-1-But	252.20	9.77	242.42
1-Octanol	49.94	0.04	49.90
2-Ethylhexanol	3.05	0.00	3.05
1-Octene	6.42	6.42	0.00
Ethylene Glycol	0.48	0.47	0.01
TOTAL MASS IN:	**2422.12**	**TOTAL MASS OUT:**	**2422.12**

Appendix Table 6: Distillation column (B5) material balance.

Distillation Column (B5)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	4197.43	4134.14	63.29
n-Butanol	34.14	1.67	32.48
Water	739.17	21.17	718.00
1-Hexanol	0.09	0.00	0.09
1-Octene	0.02	0.00	0.02
Ethylene Glycol	8130.97	0.48	8130.48
TOTAL MASS IN:	**13101.82**	**TOTAL MASS OUT:**	**13101.82**

Appendix Table 7: Distillation column (B6) material balance.

Distillation Column (B6)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	63.29	63.00	0.29
n-Butanol	32.48	27.92	4.55
Water	718.00	92.99	625.01
1-Hexanol	0.09	0.05	0.05
1-Octene	0.02	0.00	0.02
Ethylene Glycol	8130.48	0.00	8130.48
TOTAL MASS IN:	**8944.37**	**TOTAL MASS OUT:**	**8944.37**

Appendix Table 8: Distillation column (B11) material balance.

Distillation Column (B11)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	4261.25	63.80	4197.45
n-Butanol	1789.87	0.00	1789.87
Water	742.83	3.54	739.28
1-Hexanol	354.25	0.00	354.25
2-Ethyl-1-But	252.21	0.00	252.21
1-Octanol	49.94	0.00	49.94
2-Ethylhexanol	3.05	0.00	3.05
Acetaldehyde	87.11	87.11	0.00
Ethylene	23.69	23.69	0.00
1-Butene	27.45	27.45	0.00
1-Hexene	22.14	22.14	0.00
1-Octene	6.45	0.00	6.45
Hydogen	3.99	3.99	0.00
Ethylene Glycol	0.48	0.00	0.48
TOTAL MASS IN:	**7624.70**	**TOTAL MASS OUT:**	**7624.70**

Appendix Table 9: Distillation column (B12) material balance.

Distillation Column (B12)			
Component	**Inlet (kg/hr)**	**Distillate (kg/hr)**	**Bottoms (kg/hr)**
Ethanol	4197.45	4197.43	0.03
n-Butanol	1789.87	34.14	1755.73
Water	739.28	739.17	0.12
1-Hexanol	354.25	0.09	354.16
2-Ethyl-1-But	252.21	0.01	252.20
1-Octanol	49.94	0.00	49.94
2-Ethylhexanol	3.05	0.00	3.05
1-Octene	6.45	0.02	6.42
Ethylene Glycol	0.48	0.00	0.48
TOTAL MASS IN:	**7392.99**	**TOTAL MASS OUT:**	**7392.99**

Appendix 3: Economic Analysis and Calculations

Operating Costs

Appendix Table 10: Full tabulated calculations of operating costs.

Operating Cost	Factor	Rate		Cost		Total Cost
Ethanol		3413	kg/hr	0.502	$/kg	$ 13,569,541.92
Ethylene Glycol		136.5	kg/hr	1.43	$/kg	$ 1,545,944.40
Operating Labor	27700 operating hours per year	6925	hours skilled	33.67	$/hour	$ 764,589.25
		20775	hours common	25.58	$/hour	
Operating Supervision	15% operating labor	`				$ 114,688.39
Utilities	Previously calculated					$ 4,835,749.36
Maintenance and Repair	7% of FCI					$ 988,150.50
Operating Supplies	15% of maintenance and repairs					$ 148,222.58
Laboratory Charges	15% of operating labor					$ 114,688.39
Royalties	NONE					$ -
Catalyst	Hydroxyapatite	2250	kg	12	$/kg	$ 27,000.00
				Variable Production Cost		**$ 22,108,574.78**
Taxes(property)	2% FCI					$ 282,328.71
Insurance	1% of FCI					$ 141,164.36
				Fixed Charges		**$ 423,493.07**
Plant Overhead Costs	60% of operating labor, supervision and maintenance					$ 1,120,456.88
Adminsitrative Costs	20% of operating labor					$ 152,917.85
Distribution and Marketing	5% of total production cost					$ 425,000.00
R& D	5% of total production cost					$ 425,000.00
				General Expenses		**$ 2,123,374.73**
				Total Product Costs (without depreciation) per year		**$ 24,655,442.59**

Profitability

Appendix Table 11: Full, tabulated annual profitability calculations for 15-year project life.

	Year															
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**SUM**
Percent of Operating Time	50	90	100	100	100	100	100	100	100	100	100	100	100	100	100	
Product rate, 10^6 kg/year	6.92	12.456	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	13.84	199.30
Sales revenue ($2.72/kg) $10^6/yr	18.82	33.88	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	37.64	542.09
Variable Costs, $10^6 / year	11.05	19.90	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	22.11	318.36
Fixed Costs (except depreciation)	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	38.20
Total Costs(except depreciation)	13.60	22.44	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	24.66	356.57
Depreciation Rate % (7yr MACRS)	14.29	24.49	17.49	12.49	8.93	8.92	8.93	4.46	0	0	0	0	0	0	0	100
Deprecaition, $10^6/year	2.02	3.46	2.47	1.76	1.26	1.26	1.26	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.12

Net Present Worth

Appendix Table 12: Annual present worth considering all investment at year zero.

Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
0					$ 16,877,673		1.000	$ -	$ 16,877,673
1	$ 18,820,000	$ 13,600,000	14.29	$ 2,017,239	$ -	$ -	0.909	$ 3,726,394	$ -
2	$ 33,880,000	$ 22,440,000	24.49	$ 3,457,115	$ -	$ -	0.826	$ 7,145,447	$ -
3	$ 37,640,000	$ 24,630,000	17.49	$ 2,468,965	$ -	$ -	0.751	$ 7,002,733	$ -
4	$ 37,640,000	$ 24,650,000	12.49	$ 1,763,143	$ -	$ -	0.683	$ 6,188,512	$ -
5	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.621	$ 5,516,705	$ -
6	$ 37,640,000	$ 24,650,000	8.92	$ 1,259,186	$ -	$ -	0.564	$ 5,014,908	$ -
7	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.513	$ 4,559,261	$ -
8	$ 37,640,000	$ 24,650,000	4.46	$ 629,593	$ -	$ -	0.467	$ 4,041,753	$ -
9	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.424	$ 3,580,868	$ -
10	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.386	$ 3,255,335	$ -
11	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.350	$ 2,959,395	$ -
12	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.319	$ 2,690,359	$ -
13	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.290	$ 2,445,781	$ -
14	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.263	$ 2,223,437	$ -
15	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ 2,761,237	0.239	$ 2,682,325	$ -
							SUM	$ 63,033,214	
							NPW	**$ 46,155,541**	

Appendix Table 13: Net present worth considering all investment at year zero.

Year	Cash Flow	Net Present Worth
0	$ (16,877,673)	$ (16,877,673)
1	$ 3,726,394.12	$ (13,151,278.50)
2	$ 7,145,446.52	$ (6,005,831.98)
3	$ 7,002,732.99	$ 996,901.01
4	$ 6,188,511.71	$ 7,185,412.72
5	$ 5,516,705.39	$ 12,702,118.11
6	$ 5,014,907.83	$ 17,717,025.94
7	$ 4,559,260.65	$ 22,276,286.59
8	$ 4,041,753.49	$ 26,318,040.08
9	$ 3,580,868.24	$ 29,898,908.33
10	$ 3,255,334.76	$ 33,154,243.09
11	$ 2,959,395.24	$ 36,113,638.33
12	$ 2,690,359.31	$ 38,803,997.64
13	$ 2,445,781.19	$ 41,249,778.83
14	$ 2,223,437.45	$ 43,473,216.28
15	$ 2,682,324.92	$ 46,155,541.20

Appendix Table 14: Net present worth considering all investment two years before year zero.

Year	Cash Flow	Net Present Worth
-2	$ (14,295,389)	$ (14,295,389)
-1	$ (5,569,632)	$ (19,865,021)
0	$ -	$ (19,865,021)
1	$ 3,726,394	$ (16,138,627)
2	$ 7,145,447	$ (8,993,180)
3	$ 7,002,733	$ (1,990,447)
4	$ 6,188,512	$ 4,198,065
5	$ 5,516,705	$ 9,714,770
6	$ 5,014,908	$ 14,729,678
7	$ 4,559,261	$ 19,288,939
8	$ 4,041,753	$ 23,330,692
9	$ 3,580,868	$ 26,911,560
10	$ 3,255,335	$ 30,166,895
11	$ 2,959,395	$ 33,126,290
12	$ 2,690,359	$ 35,816,650
13	$ 2,445,781	$ 38,262,431
14	$ 2,223,437	$ 40,485,868
15	$ 2,682,325	$ 43,168,193

Appendix Table 15: Annual present worth considering all investment two years before year zero.

Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
-2					$11,814,371		1.210	$ -	$ 14,295,389
-1					$ 5,063,302		1.100	$ -	$ 5,569,632
0							1.000	$ -	$ -
1	$ 18,820,000	$ 13,600,000	14.29	$ 2,017,239	$ -	$ -	0.909	$ 3,726,394	$ -
2	$ 33,880,000	$ 22,440,000	24.49	$ 3,457,115	$ -	$ -	0.826	$ 7,145,447	$ -
3	$ 37,640,000	$ 24,630,000	17.49	$ 2,468,965	$ -	$ -	0.751	$ 7,002,733	$ -
4	$ 37,640,000	$ 24,650,000	12.49	$ 1,763,143	$ -	$ -	0.683	$ 6,188,512	$ -
5	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.621	$ 5,516,705	$ -
6	$ 37,640,000	$ 24,650,000	8.92	$ 1,259,186	$ -	$ -	0.564	$ 5,014,908	$ -
7	$ 37,640,000	$ 24,650,000	8.93	$ 1,260,598	$ -	$ -	0.513	$ 4,559,261	$ -
8	$ 37,640,000	$ 24,650,000	4.46	$ 629,593	$ -	$ -	0.467	$ 4,041,753	$ -
9	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.424	$ 3,580,868	$ -
10	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.386	$ 3,255,335	$ -
11	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.350	$ 2,959,395	$ -
12	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.319	$ 2,690,359	$ -
13	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.290	$ 2,445,781	$ -
14	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$ -	0.263	$ 2,223,437	$ -
15	$ 37,640,000	$ 24,650,000	0.00	$ -	$ -	$2,761,237	0.239	$ 2,682,325	$ -
							SUM	$ 63,033,214	
							NPW	**$ 43,168,193.15**	

Appendix 4: Reactor

Introduction

The purpose of the reactor design is to convert ethanol, from an existing plant, to n-butanol. The reactions and kinetics were taken from experimental work by Tsuchida et. Al. covering 13 gas phase reactions [8] [19]. However, for this simulation, reactions involving alkene elimination or cyclization were not considered. Thus, some reactor products include alkenes which would likely not be present. A tubular reactor was suggested by patent literature [20]. Combining the following reactions and kinetic equations, a packed bed reactor simulation was developed in Aspen Plus V9.

Primary Reaction

$$2C_2H_5OH \rightarrow n - C_4H_9OH + H_2O \tag{1}$$

Secondary Reactions

$$C_2H_5OH + 1 - C_4H_9OH \rightarrow 1 - C_6H_9OH + H_2O \tag{2}$$

$$C_2H_5OH + 1 - C_4H_9OH \rightarrow C_2H_5CH(C_2H_5)CH_2OH + H_2O \tag{3}$$

$$C_2H_5OH + 1 - C_6H_{13}OH \rightarrow 1 - C_8H_{17}OH + H_2O \tag{4}$$

$$C_2H_5OH + 1 - C_6H_{13}OH \rightarrow C_4H_9CH(C_2H_5)CH_2OH + H_2O \tag{5}$$

$$C_2H_5OH \rightarrow CH_2 = CH_2 + H_2O \tag{6}$$

$$1 - C_4H_9OH \rightarrow 1 - C_4H_8 + H_2O \tag{7}$$

$$1 - C_6H_{13}OH \rightarrow 1 - C_6H_{12} + H_2O \tag{8}$$

$$1 - C_8H_{17}OH \rightarrow 1 - C_8H_{16} + H_2O \tag{9}$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \tag{10}$$

Rate Laws

$$r_1 = 33\frac{L}{mol * s} \times [C_2H_5OH]^2 \times e^{\frac{-61\frac{kJ}{mol}}{RT}} \tag{11}$$

$$r_2 = 41\frac{L}{mol * s} \times [C_2H_5OH] \times [1 - C_4H_9OH] \times e^{\frac{-70\frac{kJ}{mol}}{RT}} \tag{12}$$

$$r_3 = 21\frac{L}{mol * s} \times [C_2H_5OH] \times [1 - C_4H_9OH] \times e^{\frac{-50\frac{kJ}{mol}}{RT}} \tag{13}$$

$$r_4 = 54\frac{L}{mol * s} \times [C_2H_5OH] \times [1 - C_6H_{13}OH] \times e^{\frac{-92\frac{kJ}{mol}}{RT}} \tag{14}$$

$$r_5 = 79\frac{L}{mol * s} \times [C_2H_5OH] \times [1 - C_6H_{13}OH] \times e^{\frac{-21\frac{kJ}{mol}}{RT}} \tag{15}$$

$$r_6 = 0.02\frac{1}{s} \times [C_2H_5OH] \times e^{\frac{-119\frac{kJ}{mol}}{RT}} \tag{16}$$

$$r_7 = 0.069\frac{1}{s} \times [1 - C_4H_9OH] \times e^{\frac{-91\frac{kJ}{mol}}{RT}} \tag{17}$$

$$r_8 = 0.28\frac{1}{s} \times [1 - C_6H_{13}OH] \times e^{\frac{-40\frac{kJ}{mol}}{RT}} \tag{18}$$

$$r_9 = 0.72\frac{1}{s} \times [1 - C_8H_{17}OH] \times e^{\frac{-30\frac{kJ}{mol}}{RT}} \tag{19}$$

$$r_{10} = 0.041\frac{1}{s} \times [C_2H_5OH] \times e^{\frac{-102\frac{kJ}{mol}}{RT}} \tag{20}$$

The units of concentration are mol/(L·s) (gas), and temperature is in Kelvin.

Catalyst

Literature suggests several catalysts for conversion of ethanol to n-butanol as discussed in Catalyst Selection. Hydroxyapatite is the ideal catalyst for this reaction with the highest conversion of ethanol and selectivity to butanol [8]. A second catalyst, copper alumina, was examined as a comparison. Optimal conditions were simulated for each catalyst, utilizing data presented by Riittonen et al. and Tsuchida et al. [8] [14]. As expected, the hydroxyapatite catalyst outperformed copper alumina, and was therefore selected for this process.

Hydroxyapatite is derived from bone or can be chemically synthesized at various calcium to phosphorous (Ca/P) ratios [8]. Tsuchida et al. showed that a Ca/P ratio of 1.64 was optimal, however differences in Ca/P ratios were not investigated in this report. Hydroxyapatite has a density of 3.2 g/cm^3. Hydroxyapatite can also be synthesized to have different size crystals [55]. For this study, bed voidage was taken to be 0.5.

Constraints and Parameters

Patent literature for a gas-phase reaction over a packed bed suggests a tube diameter of 25 mm and length of 1.5-3 m [56] [57]. The selected final length of the reactor tubes was optimized through reactor design to be 12,500 tubes with a dimeter of 15 mm and a length of 2 m.

The suggested reaction temperature was from 300-400°C. These were used as starting points for a simulation study investigating the optimal temperature for reactor operation. Ideally, the pressure range of the reactor is low for safety reasons [8].

Simulation Study

First, the simulated reactor at a constant temperature was compared to literature data. The reactor effluent is similar between the model predictions and experimental results as shown below. The model reactor was designed to have 10,000 tubes, a diameter of 15 mm, and a length of 2 m which correlated to the literature contact time of 1.78 s. For comparison, hexene and octene in the model were assumed to react to form octanol and hexanol which is likely due to the presence of water.

Appendix Table 16: Comparison of model with literature values [8].

	Literature	Model
Temperature (°C)	300	300
Conversion (%)	14.7	14.9
Compound	(C wt%)	
Ethylene	0.6	0.15
Acetaldehyde	1.7	0.82
Butene	0.4	0.1
Butanol	76.3	71.4
Hexanol	8.6	3.67
Octanol	1	0.074
Decanol	0.2	-

Furthermore, literature shows that increasing contact time in the reactor increases conversion of ethanol, however, at a point, n-butanol selectivity decreases. The table below shows the effect of increasing the number of tubes. Increasing the number of tubes in the reactor increases reactor costs and increased conversion of ethanol but decreased selectivity to n-butanol. Therefore, the optimal number of tubes was selected to be 12,500.

Appendix Table 17: Optimization of contact area

	Trial 1	Trial 2	Trial 3
Number of Tubes	10,000	12,500	15,000
Temperature (°C)	300	300	300
Conversion (%)	14.9	18.1	21.1
Compound	(C wt%)		
Ethylene	0.15	0.19	0.15
Acetaldehyde	0.82	1.03	0.83
Butene	0.1	0.15	0.14
Butanol	71.4	87.5	68.1
Hexanol	3.67	5.5	0.19
Octanol	0.074	0.139	0.151

Reaction temperature should be maintained between 300°C and 400°C as suggested by literature [8]. Several commercial process fluids are on the market including thermal oils or molten salts [21] [22]. Thermal oils contain a variety of heavy organics which are be highly flammable [23]. Specialty non-flammable thermal oils are available; however, another industry alternative is molten salt. Thus, sodium nitrite molten salt was utilized as the thermal heating flowrate at 200 kmol/hr (13,800 kg/hr) to quickly remove heat from the exothermic reaction.

A reactor can be cooled via either countercurrent and co-current heat transfer methods. However, co-current cooling is generally used to avoid hot spots and optimize conversion [58]. One method of measuring reaction selectivity is through conversion of ethanol as given in Equation (21) and selectivity to n-butanol (assumed to be the only desirable product) Equation (22). A heat transfer coefficient of 30 W/m^{2}K was used as suggested for gas to liquid heat transfer [24]. By applying the developed Aspen model for countercurrent and co-current systems, we confirmed that co-current cooling is preferred for optimal selectivity as shown in Appendix Table 18.

$$Conversion = 1 - \frac{Flow\ rate\ of\ Ethanol\ in\ Product\ Stream}{Flow\ rate\ of\ Ethanol\ Reactant} \tag{21}$$

$$Selectivity = \frac{Flow\ rate\ of\ Butanol\ in\ Product\ Stream}{Flow\ rate\ Products} \tag{22}$$

Appendix Table 18: Comparison of conversions of countercurrent vs. co-current at two different temperatures.

Reactants Inlet Temperature (°C)	Coolant Inlet Temperature (°C)	Counter Current Conversion	Counter Current Selectivity	Co-current conversion	Co-current Selectivity
300	350	51%	48%	34%	60%
350	350	58%	44%	44%	53%

The co-current design was further optimized by varying molten salt coolant inlet temperature and reactant inlet temperature. At higher temperatures, conversion of ethanol increases, but selectivity to n-butanol decreases. For safety reasons, it would be preferable to operate at lower temperatures. Therefore, coolant inlet temperature and reaction inlet temperature were optimized to be 350°C. Reactor profiles for the optimized case are shown below.

Appendix Table 19: Co-current reactor conversion and selectivity of coolant inlet temperature vs reactor inlet temperature.

Co-current Reactor							
		Reactor Inlet Temperature (°C)					
		300		350		400	
		Conversion	Selectivity	Conversion	Selectivity	Conversion	Selectivity
Coolant Inlet Temperature (°C)	300	21%	68%	31%	62%	42%	55%
	350	34%	60%	**44%**	**53%**	55%	46%
	400	48%	51%	58%	44%	66%	38%

Pressure drop across the reactor was simulated using Beggs-Brill friction correlation. However, reaction simulation predicted a pressure drop of less than 0.0001 bar. This seems highly unrealistic for pressure drop across a packed bed. Thus, further study of pressure drop is necessary.

Conclusion

The ideal reactor design is a packed bed reactor with a co-current heat exchanger for the catalytic conversion of ethanol to n-butanol. The reactor has a length of 2 m with 12,500 15 mm diameter tubes. The catalyst selected is hydroxyapatite. Ideal inlet reactant temperature is 350°C with a coolant inlet temperature of 350°C. Heat transfer fluid is molten sodium nitrite at 13,800 kg/hr.

Appendix 5: Separations

Introduction

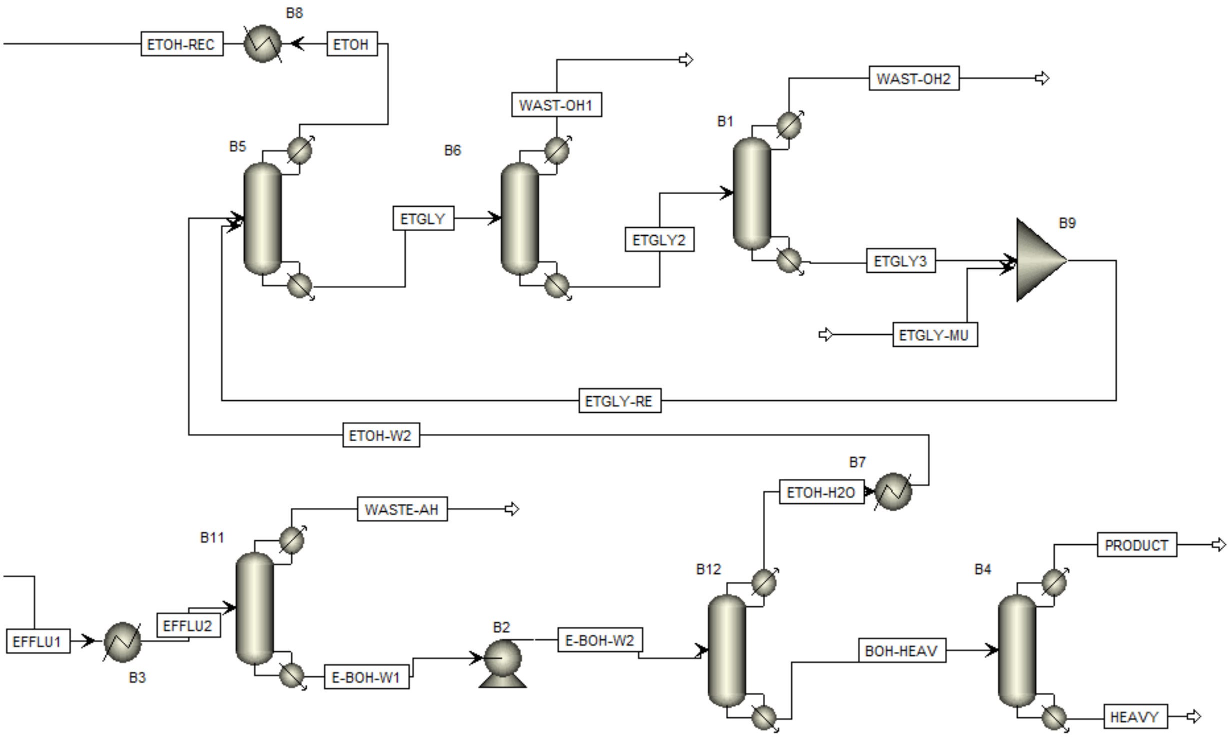
This report includes optimization of the separations units in the production of n-butanol from ethanol. This design employs a series of six trayed distillation columns. Optimization led to final n-butanol product with a purity of over 99 mol%. Unreacted ethanol is also recycled back to the reactor.

Flash distillation units utilize one of the simplest separations processes. A liquid stream is partially vaporized in a flash drum at a particular temperature and pressure resulting in two phases: a vapor phase with the mover volatile components and a liquid phase with the less [59]. Distillation columns are essentially a series of flash drums that separate compounds via their relative volatilities [60]. The higher the relative volatility, the better the separations [61]. When the volatility differences between two or more species is small as to necessitate 100 or more stages for adequate separations, then "extractive distillation" is considered [62].

A major concern for any design considering the combining hydrocarbons to produce longer chains is the amount of water produced. Firstly, water separations with an organic phase are difficult and require a lot of heat due to large heat capacities [63]. Secondly, ethanol and water are known to have an azeotrope which cannot be easily overcome [27]. A few methods to overcome the azeotrope include introducing an additional species to create a ternary system, liquid-liquid extraction, use of molecular sieves, and pressure swing adsorption [27].

The general separations process is shown in Appendix Figure 1. Reactor effluent is cooled to 40°C, mostly liquid, before entering column B11. Waste-AH includes acetaldehyde, hydrogen, 1-butene, 1-hexene, and minimal amounts of water and ethanol.

E-BOH-W1 is pumped to 20 bar and sent to column B12. At column B12, distillate ETOH-H2O contains ethanol and water, and the bottoms stream, BOH-HEAV, contains heavy hydrocarbons and butanol. Column B4 is the last purification step achieving more than 99 mol% purity butanol as distillate. The impurities present in the n-butanol product stream include 1-hexanol, 2-ethyl-1-butanol, 1-octene, and residual water, ethanol, and 1-octanol. The HEAVY bottoms stream contains 1-hexanol, 2-ethyl-1-butanol, 1-octanol, 2-ethylhexanol, and minimal amounts of n-butanol. ETOH-W2 stream from column B12 is cooled to 78.2°C and separated in a series of 3 columns. The first combines ethyl glycol and ETOH-W2 to removing ethanol for recycle back to the reactor. Water is removed from ethyl glycol in columns B6 and B1. Two columns are used so that WAST-OH1, distillate product from column B6, does not need further water treatment. WAST-OH2, distillate product from column B1, contains water and small quantities of n-butanol, ethanol, 1-hexanol, 1-octene, and ethylene glycol. Ethylene glycol in the bottoms stream has over 99 mol% and is recycled back to column B5. ETGLY-MU stream adds make-up ethyl glycol to the system.



Appendix Figure 1: Separations process PFD.

Models presented in this work use Non-Random Two Liquid (NRTL) equilibrium method. Generally, NRTL is an activity coefficient model and recognized as a good method for low pressure systems of an organic liquid mixture and water [64]. NRTL is generally not a good method for gas phase interactions. Thus, originally we looked at using equation of state models such as Suave-Redlich-Kwong (SRK) and Peng-Robinson (PR) which are good for gas and liquid hydrocarbon mixtures. These models accurately predicted reaction products, as compared with literature data, but did not predict the ethanol-water azeotrope [65]. Turning to activity coefficient models, we compared UNIFAC, UNIQUAC, and NRTL. All three methods correctly predicted the ethanol-water azeotrope. NRTL was selected, because it most accurately predicted reaction products compared to reaction literature data and equation of state models.

Conclusion

The method of optimization described in this appendix was applied to all columns in the process to optimize the n-butanol product purity and flowrate with regards to operation costs and sizing.

Distillation Column Design Optimization

Each separation unit was optimized by varying number of trays, feed location, and reflux ratio. Below is a description of optimization of column B11.

Optimization Example (Column B11)

Distillation column B11 removes acetaldehyde, hydrogen, 1-butene, 1-hexene, and minimal amounts of water and ethanol as distillate in stream WASTE-AH from the reactor effluent. In order to optimize the column, we changed variables such as feed stage, tray type, number of stages, etc., and analyzed the outputs given in Aspen. The optimal results are as shown in Appendix Table 20.

Appendix Table 20: B11 column design specifications.

B11 Column Design Specifications		
Reflux Ratio (Molar)	6	
Condensor	Partial-Vapor	
Condensor Utility	Cooling Water	
Reboiler	Kettle	
Reboiler Utility	Low Pressure Steam	
Tray Type	Sieve Tray	
Feed Above Stage	14	
Number of Stages	30	
Diameter	0.762	m
Height	21.33	m
Distillate/Feed Ratio (Molar)	0.042	
Pressure	1	bar

For a column diameter larger than 0.5 m, heuristics recommends a trayed column [24]. Since there were no issues with flooding in the column, sieve trays were chosen due to being the least expensive and having the smallest pressure drop [66].

The value for reflux ratio, number of trays, and feed location were initially set based on a literature study and then optimized [4]. For the distillation column, the table below shows that 30 trays are optimal to remove all acetaldehyde in the distillate.

Appendix Table 21: Tray optimization data from Aspen simulations.

		40 Trays		30 Trays		20 Trays	
Mass Flow (kg/hr)	Inlet	Distillate	Bottoms	Distillate	Bottoms	Distillate	Bottoms
Ethanol	4261.25	63.79	4197.46	63.80	4197.45	64.33	4196.92
n-Butanol	1789.87	0.00	1789.87	0.00	1789.87	0.00	1789.87
Water	742.83	3.55	739.28	3.54	739.28	3.57	739.26
1-Hexanol	354.25	0.00	354.25	0.00	354.25	0.00	354.25
2-Ethyl-1-But	252.21	0.00	252.21	0.00	252.21	0.00	252.21
1-Octanol	49.94	0.00	49.94	0.00	49.94	0.00	49.94
2-Ethylhexanol	3.05	0.00	3.05	0.00	3.05	0.00	3.05
Acetaldehyde	87.11	87.11	0.00	87.11	0.00	86.55	0.57
Ethylene	23.69	23.69	0.00	23.69	0.00	23.69	0.00
1-Butene	27.45	27.45	0.00	27.45	0.00	27.44	0.00
1-Hexene	22.14	22.14	0.00	22.14	0.00	22.14	0.00
1-Octene	6.45	6.45	6.45	0.00	6.45	0.00	6.45
Hydogen	3.99	3.99	0.00	3.99	0.00	3.99	0.00
Ethylene Glycol	0.48	0.00	0.48	0.00	0.48	0.00	0.48

The feed stage was found to be optimal above stage 14 when considering a 30-trayed system. The ideal separation removes all the acetaldehyde in the distillate and the least amount of ethanol. Using this criterion, optimal feed location is above stage 14.

Appendix Table 22: Effect of feed stage on trayed distillation.

Feed Above Stage	14		18		22	
Mass Flow (kg/hr)	Distillate	Bottoms	Distillate	Bottoms	Distillate	Bottoms
Ethanol	63.80	4197.45	64.38	4196.88	64.88	4196.38
n-Butanol	0.00	1789.87	0.00	1789.87	0.00	1789.87
Water	3.54	739.28	3.32	739.51	3.18	739.65
1-Hexanol	0.00	354.25	0.00	354.25	0.00	354.25
2-Ethyl-1-But	0.00	252.21	0.00	252.21	0.00	252.21
1-Octanol	0.00	49.94	0.00	49.94	0.00	49.94
2-Ethylhexanol	0.00	3.05	0.00	3.05	0.00	3.05
Acetaldehyde	87.11	0.00	87.11	0.01	86.97	0.15
Ethylene	23.69	0.00	23.69	0.00	23.69	0.00
1-Butene	27.45	0.00	27.45	0.00	27.45	0.00
1-Hexene	22.14	0.00	22.14	0.00	22.14	0.00
1-Octene	0.00	6.45	0.00	6.45	0.00	6.45
Hydogen	3.99	0.00	3.99	0.00	3.99	0.00
Ethylene Glycol	0.00	0.48	0.00	0.48	0.00	0.48

The reflux ratio was found to be optimal at 6 (on a molar basis) when considering a 30-trayed system. The ideal separation removes all the acetaldehyde in the distillate and the least amount of ethanol. Using this criterion, increasing the reflux ratio from 6 to 12 had no effect on the separation. A reflux of 6 is preferred for the best separation and lowest operating cost [67].

Appendix Table 23: Effect of reflux ratio on trayed distillation.

Reflux Ratio	1		6		12	
Mass Flow (kg/hr)	Distillate	Bottoms	Distillate	Bottoms	Distillate	Bottoms
Ethanol	74.66	4186.59	63.80	4197.45	63.79	4197.47
n-Butanol	0.00	1789.87	0.00	1789.87	0.00	1789.87
Water	4.80	738.03	3.54	739.28	3.55	739.28
1-Hexanol	0.00	354.25	0.00	354.25	0.00	354.25
2-Ethyl-1-But	0.00	252.21	0.00	252.21	0.00	252.21
1-Octanol	0.00	49.94	0.00	49.94	0.00	49.94
2-Ethylhexanol	0.00	3.05	0.00	3.05	0.00	3.05
Acetaldehyde	73.66	13.45	87.11	0.00	87.11	0.00
Ethylene	23.69	0.00	23.69	0.00	23.69	0.00
1-Butene	27.44	0.00	27.45	0.00	27.45	0.00
1-Hexene	22.14	0.00	22.14	0.00	22.14	0.00
1-Octene	0.00	6.45	0.00	6.45	0.00	6.45
Hydogen	3.99	0.00	3.99	0.00	3.99	0.00
Ethylene Glycol	0.00	0.48	0.00	0.48	0.00	0.48

Optimization of Process

Optimization of the other columns was performed in a similar manner. To achieve maximum purity of n-butanol in the product stream, maximum amounts of ethanol and water must be removed in column B12. Then, column B4 removes all remaining heavy components from the n-butanol stream. Ethanol-water separations are costly due to the azeotrope. However, literature has shown that addition of ethyl glycol in a 1:1 molar ratio allows for removal of ethanol from the tertiary system [28] [29]. Column B5 was optimized to remove the maximum amount of ethanol at the maximum purity. Column B6 was optimized to remove the most water possible while keeping within requirements for waste water without treatment. Column B1 removes all remaining impurities from the ethyl glycol stream to avoid accumulation within the ethanol-water separations.