

Production of Cellulosic Ethanol from Mixed Paper

CHE 4476

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Design Final Report

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1. Summary

The goal of this study was to determine the technical and economic feasibility of a large scale cellulosic ethanol production plant that incorporates recycled waste paper as the feedstock. Cellulosic ethanol is a promising alternative to current bio-ethanol production methods as it uses feedstocks that do not compete with food supplies (unlike conventional corn-based production) but suffers from the large additional costs associated with breaking down cellulose into the sugars necessary for glucose fermentation. It was theorized that through the potentially negative cost of the recycled feedstock for this product as well as current subsidies available in many areas, that a profitable and energy efficient method of producing biofuels could be designed. This project incorporates 6 primary operations to convert the paper into fuel grade ethanol: Pulping, Hydrolysis, Neutralization, Fermentation, Distillation, and Dehydration. Pulping, Hydrolysis, and Neutralization were used to convert the solid paper cellulose into a liquid stream of sugars that could be fermented into ethanol, incorporating low concentration sulfuric acid and high temperatures and pressures to break down cellulose. Fermentation uses yeast metabolism to convert the sugars into ethanol, while Distillation and Dehydration is used to purify the ethanol up to a usable standard through reboiling and molecular dehydration. Using our design, it was found that from the starting amount of 134 million kilograms of dry paper per year, 7.58 million gallons of fuel grade ethanol per year could be produced, at an energy cost of 1730 GJ/day or approximately 571000 GJ/year. The plant as designed in this paper would require a capital cost of 153 million dollars and an annual production cost of 59.8 million dollars per year. The current plant design would not be economically profitable as the annual production value, based on a current ethanol value of \$5.91 per gallon, is 50.4 million dollars per year, which is less than the annual production cost. The majority of this cost is incurred from the large fixed capital

investment, with the subsequent contributing factors being utility and labor costs. Areas for future developments on cellulosic ethanol processes include improvements on side product recovery, as well as more efficient cellulose breakdown processes and heat transfer processes that would all work towards bringing down the capital and utility costs that inhibit this process from being economically viable. In addition, future increases in the value of cellulosic ethanol either through higher market demand or increased subsidies could also allow for future economic viability.

2. Introduction

Society is currently searching for cleaner, sustainable alternatives to fossil fuels to meet the world's energy needs. A suitable alternative is needed since fossil fuels are in limited supply and release carbon dioxide to the atmosphere, contributing to adverse climate change. Many environmentalists support the adoption of electric vehicles coupled with making the power grid sourced from renewable energy as the way to reduce use of fossil fuels. However, issues associated with charging electric vehicles and the expense of their batteries are major barriers to widespread adoption. A better solution may be the use of biofuels as a replacement to gasoline in vehicles powered by internal combustion engines. One popular biofuel candidate is ethanol.

Life cycle emissions for ethanol are lower than those of gasoline because the ethanol's carbon source comes from plants that recently obtained their carbon from the atmosphere, whereas the carbon source for gasoline is crude oil made from carbon that has been sequestered for millennia. Since the source material for ethanol-based biofuels is grown within a lifetime, it's considered a sustainable, renewable energy source, unlike fossil fuels.

Currently, corn ethanol is used extensively as a blended add-in for gasoline, allowing for more complete combustion and lower emissions. Corn ethanol is cheap and easily fermented since corn kernels contain simple, fermentable sugars. However, production of corn ethanol competes with food production, effectively raising both the price of food and the price of ethanol production. Another common solution is using inedible, cellulosic sugar sources like corn stover, though corn stover is useful as fertilizer and animal feed. Moreover, the cost of the enzymes needed to break down cellulose and the price of feedstock make cellulosic ethanol more expensive to produce than gasoline. This project is an attempt to lower the cost of ethanol production by using a cheap and sustainable feedstock in the form of documents destroyed by government entities, businesses, and individuals. These documents were selected as a feedstock because companies typically pay a third party anywhere between \$120 and \$380 per ton to shred the documents in large quantities, or up to \$1 per pound (\$2000 per ton) for small quantities to ensure the information is securely destroyed (Thumbtack, 2020; Daciuk, 2017). In densely populated areas such as cities, these documents are available in large quantities and provide an estimated yield of 128.3 gallons of ethanol per dry ton; this yield is higher than corn stover, wood waste, and cardboard (Shi et al., 2009). Destroyed documents have no alternative use besides recycling, and currently, most shredded paper is incinerated or stored in landfills at cost. This allows us to acquire our feedstock at a negative cost. We estimate our overall feed cost will be negative \$50 per ton, after transportation costs (SafeSHRED, 2020).

3. Previous Work

Previous economic analysis of cellulosic ethanol estimates that ~35-50% of the cost of production is in the acquisition of the feedstock (Faost, 2007). This number is highly variable as

sources for cellulosic ethanol are highly variable, dependent on local geography, climate, economy, and other factors.

The separation of ethanol from water is typically the most energy intensive process in the production of bio-ethanol, and cellulosic ethanol production requires even more energy. Cellulosic ethanol yields are only about 50% that of grain-based ethanol, making the separation even more difficult (Koppram et al., 2004). As such, improvement in separation technologies and fermentation yield are major areas of focus for research in cellulosic ethanol.

There are currently two primary methods for conducting hydrolysis of cellulose; acid-based hydrolysis and enzymatic hydrolysis. Acid-based hydrolysis is largely considered to be effective for breaking down the cellulose polymer, but requires expensive, corrosive resistant stainless steel equipment. Additionally, the waste requires careful neutralization (Sievers et al., 2017). Enzymatic hydrolysis avoids these issues, but is currently quite expensive, due to the high cost of the cellulases that are known to hydrolyze cellulose (Bischof et al., 2016). Additionally, the rates of reaction for enzymatic hydrolysis tend to be slower than acid-based hydrolysis, often necessitating high concentrations of enzymes (Jeoh et al., 2017).

4. Discussion

Pulping

Prior to hydrolysis the incoming waste paper needs to be pulped and screened. Pulping is used to break up the cellulosic fibers contained in the feedstock and suspend them in a mixture with water in order to increase the surface area of the fibers allowing the cellulose to be converted to glucose more quickly and efficiently during hydrolysis. After the paper is converted

into a slurry it can then be screened separating the pulp from the non-pulp material. The non-pulp or rejects are discharged out the end of the screener onto a conveyor and carried to a screener rejects stockpile for recycling or disposal.

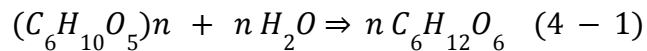
For our process we decided to use a drum pulper to pulp and screen our feedstock for multiple reasons. First drum pulpers only consume energy in the rotation of the drum offering energy savings up to 50% over other pulping methods. Also because the design of drum pulpers is relatively simple they have only a few wear parts contributing to a low maintenance cost. In addition the screen holes in the pulper are hard to plug allowing for longer continuous run times and fewer instances of required cleaning. Finally, by choosing a drum pulper we reduced our equipment cost because unlike other pulping methods drum pulpers also screen the slurry created eliminating the need for a separate piece of equipment for the removal of impurities (CNBM International). However, drum pulpers are large pieces of equipment which take up more room than other types of pulpers and because of the screening method used requires a low consistency pulp that uses more water than other high concentration pulpers.

Our streams were calculated using the design specifications for the ZG3000 drum pulper made by Leizhan. The pulping section of the drum can produce a slurry with a 14-18% pulp concentration and the following screening section requires the pulp concentration to be lowered to 3-4% (Leizhan). For our calculations, the concentration was assumed to be 16% in the pulping section and 4% in the screening section. Our feed supply was estimated by researching the amount of paper processed per year by a Los Angeles based document shredding service SAFESHRED. The amount of paper processed was over 134 million pounds per year or just over 184,000 kg/day (SafeSHRED). Using this number the two separate water streams required for the drum pulper were calculated (Appendix B). We chose to use warm water during pulping to

help facilitate the separation of fibers in the waste paper. To calculate energy requirements for pulping we first calculated the specific heat capacity of the slurry using paper using composition data to more precisely estimate its effect on the mixture (Ko, Leu, Chang, Chang, Wang, and Wang, 2015). Then using the average annual temperature in Los Angeles of 17.6°C as the initial temperature we then calculated the energy required to allow the slurry leaving the pulper to be at 60°C (Climate-Data). Because the paper is fed into the pulper at ambient temperature the water added must be heated to 60.6°C in order to allow the finished slurry to leave the pulper at 60°C.

Hydrolysis

This goal of the hydrolysis unit was to have the cellulose in the paper slurry undergo acid-catalyzed hydrolysis to get glucose sugar that can be fermented into ethanol as shown in Equation 4-1.



We initially modeled using a simple CSTR batch reactor, but found that it was not feasible to obtain a high conversion rate due to the large amount of acid necessary (Ebrik et al., 2009). Because of this, further research was done until it was determined to use a Bed-Shrinking Flow Through (BSFT) batch reactor, as shown in Appendix C, at high temperature and low acid concentration to obtain high conversion. This reactor maximizes conversion by shrinking the volume of fluid passing through the bed as the reaction proceeds. This reactor was initially designed by NREL and used in a study to determine if it could be used to maximize the conversion of cellulose to glucose with low acid concentration (Kim et al., 2001). By using this

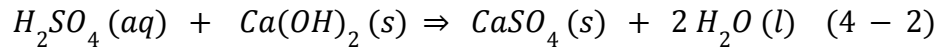
specialized flow reactor, we were able to reduce the acid concentration needed to hydrolyze to a mere 0.07 weight percent.

Our model was created by first taking the flow rates calculated from the drum pulper and separating the flow into the main categories that were relevant to this process; water, cellulose, solid waste, and acid. Using the assumption that we could get near the researched conversion rate at these conditions of 90% cellulose to glucose, material balances (Appendix D) were done to determine how much cellulose, glucose, and solid waste would come out of the reactor, accounting for the mass of the water molecules lost during hydrolysis. The acid flow rate was then back-calculated to reach the 0.07 weight percent as specified in the literature, and water flow was calculated assuming that the acid feedstock was 70% sulfuric acid. Using a lower purity acid stream (70% instead of our original 98% purity) is beneficial as so little acid is required for the process.

The heat capacity of the pulp was computed from the weighted average of the water and paper in the pulp mixture, and was then used to determine how much heat was needed to raise the temperature of the feed up to 220°C, including the mass of the acid that would be used but neglecting the slightly different heat capacity due to the very small fraction of the solution that would be acid. Kuniyama and Ogawa (1985) found that the heat of hydrolysis was about 23 J per gram of cellulose reacted, giving an almost insignificant increase in the enthalpy needed by the reactor of 3,250 kJ/day relative to the 3,000 GJ/day needed to heat the feed streams (Appendix E).

Neutralization

In the neutralization tank, the remaining sulfuric acid in the slurry is neutralized using calcium hydroxide (hydrated lime) via the reaction shown in Equation 4-2. The operation is a batch process, to more easily integrate with the hydrolysis tank.



The calcium sulfate (gypsum) produced is insoluble in water and precipitates, simplifying separations needed before the slurry is fermented. Before entering the neutralization tank, the slurry is cooled from 220°C to 35°C; Abdel-Banat et al. (2017) indicate that 35°C is within the optimal temperature range for yeast fermentation. Lewis et al. (n.d.) note a reaction time of 30 minutes at 35°C; no decrease in reaction time is expected at higher temperatures.

The amount of hydrated lime needed for neutralization is calculated stoichiometrically using the amount of sulfuric acid entering in the slurry feed (Appendix F). We expect to lose no glucose during neutralization. The hydrated lime used is 95% purity; any impurities from the lime addition are expected to precipitate as metal hydroxides during neutralization and are considered solid waste (Lewis et al., n.d.). Per day, 3250 kg of sulfuric acid will be neutralized in the tank, requiring 2455.05 kg of hydrated lime.

The material balances calculated in Appendix F assume complete neutralization of the acid present (a fractional conversion of 1) as both calcium hydroxide and sulfuric acid both dissociate completely in water. The amount of lime added to the tank is just enough to completely react with all acid to ensure the pH of the slurry does not exceed 7. Brewer's yeast prefers a neutral pH, but performs better in slightly acidic conditions than in slightly basic

conditions (FAO, n.d.). Slightly undershooting the amount of lime needed to neutralize the acid using a stoichiometric feed is better than adding calcium hydroxide in excess.

Our original plans featured the use of calcium oxide (quicklime) to neutralize the sulfuric acid as it is cheaper than hydrated lime. Quicklime must be slaked with water before use, a reaction involving large amounts of heat (it can be slaked in the reaction vessel, or using a slaking unit). By paying a slightly higher price for hydrated lime, we avoid the need for a slaking unit or additional cooling processes. Such an approach was suggested by Lewis et al., especially because the lime requirements of the process are very low.

The neutralization of sulfuric acid using hydrated lime is an exothermic reaction ($\Delta H_{R,25^{\circ}\text{C}} = -116.10 \text{ kJ/mol}$). The addition of hydrated lime at 18°C will remove some of the heat generated, and a cooling jacket or cooling coil will be used to remove the remaining heat generated during the reaction. After the lime has been heated to 35°C , the cooling coil must remove 3.90 GJ of heat per day. Keeping the neutralization tank as isothermal as possible eliminates the need for further heat removal before the slurry is fermented.

Filtration and Purging

Before fermentation, the gypsum precipitate and solid waste in the neutralized slurry were separated from the glucose and water using a filter. The solids removed were sent to a landfill without further processing as the components are not harmful to the environment or humans. The solid waste stream was assumed to be 50wt% solids and the balance water and dissolved glucose (present in the same fraction as the original stream). Due to this filtration step, 1,686.7 kg of glucose were lost to the landfill per day (see Appendix A for material balances). The remaining glucose, dissolved in water, was sent to a holding tank before being sent to

fermentation. Downtime during batches allows for maintenance and cleaning of the filter in the case of solid buildup or filter damage.

After fermentation, another filter is used to separate the yeast cells from the ethanol and water mixture. Again, it is assumed that the filter residue is 50wt% solids, and the balance ethanol and water, in the same fraction as the original stream. This filtration step removed 622.03 kg of ethanol from the fermentation slurry. The ethanol and water filtrate was sent to a storage tank before being distilled and dehydrated.

The yeast solids separated during filtration are recycled to the beginning of fermentation for reuse. To avoid accumulation of mass (due to the growth of the yeast cells), 15wt% of the recycle stream was purged before the yeast returned to the batch reactors. The purge stream removed 93.3 kg of ethanol from the recycle stream (Appendix A), which was then lost as the purge was landfilled. The remaining ethanol separated during filtration was added into the batch reactors; because the ethanol in the batch feed is so dilute (less than 1wt%), we do not expect that it would cause any adverse effects in the fermentation.

Fermentation

During fermentation, the glucose dissolved in the water is converted into ethanol using *Saccharomyces cerevisiae*, or brewer's yeast. Six batch tanks will be available for fermentation, but batch loading is staggered such that only three tanks are in use at any time (Fig. 4-1). This will allow time for maintenance, cleaning, or other operations without interfering with our production timeline. Each batch process, including filling and draining the tank, will take approximately 12 hours to complete.

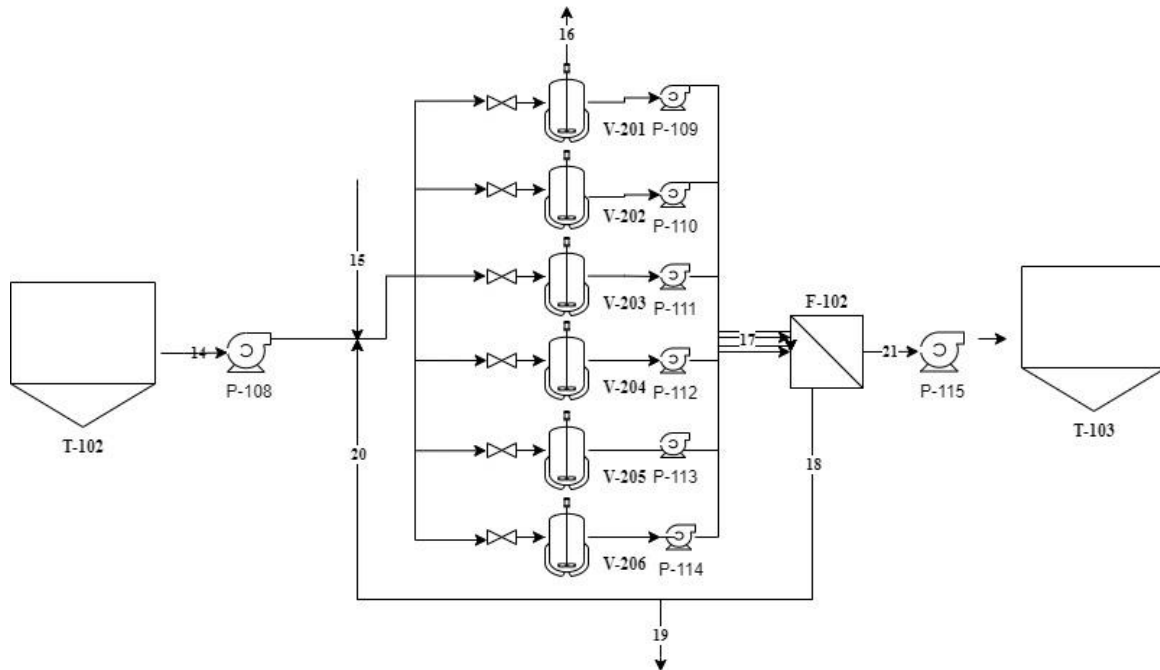


Figure 4-1. Diagram of Fermentation Reactor System

To begin fermentation, yeast nutrient is added to the sugar that was obtained from hydrolysis along with yeast cells. The reaction occurs in 3 batch reactor vessels, and gas is purged from the reactors containing the carbon dioxide produced to maintain pressure. This carbon dioxide could be isolated relatively easily with additional processes, and sold as an additional source of income as food-grade CO₂, but this analysis was determined to be out of scope for this project. Once the reaction is complete, a filter is used to separate the yeast cells from the ethanol produced; the ethanol is sent to the distillation feed tank, and the yeast cells are washed to a cell recycle stream where 15wt% of the slurry is removed to prevent dead yeast buildup.

In order to calculate the material and energy balances across these reactors, a complete conversion of sugar by the yeast was assumed due to the very low sugar content in the reactor (approximately 3wt%). Calculations were done by assuming linear kinetics akin to

stoichiometric calculations as they were found to be almost identical in these conditions due to the low possibility of inhibition due to low sugar concentrations and high residence times (Fonseca et al., 2017). Isothermal reactor operation was assumed; given that fermentation produces 555 kJ per kilogram of sugar fermented, the cooling requirement is 81.055 GJ per day. This design produced 74600 kg/day of ethanol, with a concentration of 1.68 wt% in water with minute amounts of other contaminants, mostly composed of nutrient salts. 122,299 kg per day of carbon dioxide needed to be purged from the fermentation reactors, and 10,987 kg per day of yeast waste needed to be removed to purge dead yeast cells. This ethanol concentration was lower than desired, and most likely contributed to the high energy requirement of the distillation and dehydration processes following. Further development of this process would most likely focus on lowering the amount of water needed for the pulping and neutralization earlier in the process, as this would increase the concentration of sugar in the fermentation and thus increase the concentration of ethanol being sent to distillation.

Distillation

The product from the filter is then sent as a feed into a 20 stage distillation column, with the feed stream entering above stage 10. The distillation was simulated in AspenPlus V11 using the NRTL-RK property method. The feed entering the column was at 35°C and 1.5 bara. The column was operated at 1.5 bara with a reflux ratio of 2.5 and a distillate rate of 80,000 kg/day. A total condenser and partial kettle reboiler were used to drive the separation.

The feed entering the distillation column was 1.68wt% ethanol and 98.32wt% water. In mass flow terms, this equates to 74,071 kg/day of ethanol and 4,323,750 kg/day of water being fed into the column. It is assumed that small levels of fermentation side products are present in

the feed such as unused yeast nutrient. The bottoms product consisted of spent water, which has approximately 0.05wt% ethanol, 99.95wt% water, and trace amounts of other components from fermentation. In mass flow terms, this equates to 2,219 kg/day of ethanol and 4,315,600 kg/day of water in the bottoms product as spent water. The temperature of the bottoms product stream was 111.3°C. The distillate leaving the top of the column consisted of 89.81wt% ethanol and 10.19wt% water. In mass flow terms, this equates to 71,852 kg/day of ethanol and 8,148.4 kg/day of water in the distillate product. The temperature of the distillate stream was 88.55°C. The distillate is not purified completely to fuel grade requirements because ethanol and water form an azeotrope that limits the purity achievable through simple distillation to just 95.6 percent, and molecular sieves can dehydrate ethanol with water concentrations up to 15wt%.

The heat duty on the total condenser was calculated to be -3,173 kW, which equates to -241.2 GJ/day of operation. The heat duty on the partial reboiler was calculated to be 19,830 kW, which equates to 1,713 GJ/day of operation. For sizing and costing purposes, the condenser and reboiler were modeled as heat exchangers using cooling water and medium pressure steam respectively as the heat transfer fluids, and had heat transfer areas of 580.9 m² and 312.7 m². Thus, the net heat duty on the distillation column is 16,660 kW, or 1,439 GJ/day of operation.

Dehydration

The distillate from the column is first sent to a pump to increase the pressure to 6 bar. Assuming a pump efficacy of 70% and a drive efficacy of 90% this pump requires 0.9 kW or 0.08 GJ/day of electricity for operation. Next the pressurized steam is heated to 160°C creating a superheated vapor that will prevent condensation from occurring inside the molecular sieves. This process requires 1016 kW or 87.8 GJ/day. The superheated vapor is then fed into the top of

one of the two molecular sieves where the water vapor is adsorbed by the bed of 3A zeolite beads contained in the vessel. The sieve is designed to adsorb for 8 hours before the feed is switched to the second molecular sieve and the first is regenerated. The heat of adsorption produces 32.45 GJ/day.

Both sieves contain 55 cubic meters of 3A zeolite beads which was calculated to have the required adsorption capacity to dehydrate the ethanol given that regeneration lowers the water concentration to 3-4% in the sieve. These beds are sized to last for 1.5 years or 820 cycles before the uptake capacity of the beads can no longer absorb the required amounts of water and the beads need to be replaced. The regeneration of the sieve is achieved by heating the bed to 230°C and feeding a small portion of the dehydrated product through the bed at a reduced pressure. This process removes the water from the beads and the vapor that has absorbed the water is then recycled back into the distillation column and is fed into the column above stage ten.

The molecular sieves are designed to recover 90-95% of the ethanol and create a product with a standard dryness: >99.5% (<5,000 ppm water). This results in the molecular sieves producing 74,243 kg/day of dried product and 11,258 kg/day of recyclable purge gas which is 35% ethanol by weight.

Economics and Profitability

The costs of construction of the ethanol production facility were calculated using CAPCOST (attached as a supplemental file in Appendix L), and the total Lang Factor equipment cost was calculated at \$153,000,000. A breakdown of the equipment cost and calculated fixed capital investment (with a Lang factor of 4.74) shows the equipment cost for the fermentation section of the process is the most expensive, accounting for about 70% of the FCI.

Table 4-1: Equipment Cost Breakdown by Process

Process Section:	Equipment Cost (\$)	FCI (With Lang Factor)
Upstream	8,209,200	38,900,000
Fermentation	22,618,400	107,000,000
Downstream	1,482,300	7,030,000
Total	32,309,900	153,000,000

In addition to the initial fixed capital investment, the annual production costs were calculated using the following equation from “Analysis, Synthesis, and Design of Chemical Processes” by Turton:

$$COM = 0.280FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \quad (4 - 3)$$

Where FCI is the fixed capital investment, C_{OL} is the operating labor cost, C_{UT} is the cost of utilities, C_{WT} is the waste treatment cost, and C_{RM} is the cost of raw materials. Operating labor was determined using the following equation with a P value of 1 and a N_{np} value of 13, where P is the number of particulate processing steps and N_{np} is the number of nonparticulate processing steps:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad (4 - 4)$$

This equation gave us a total of 6.4 positions to be filled, and using the analysis in Turton that about 4.5 operators must be hired per position gave us a requirement of 29 operators for the

plant. Using an average annual salary of \$77,614 per year, the annual labor cost was determined to be \$2,250,814 per year. Using a factor of 2.73 as defined by Turton to account for other labor costs such as supervisory costs and other factors, this comes out to a total COM factor of \$6,144,700 per year, 10.1% of the total COM.

The total utility cost for the facility was calculated per utility by determining the power requirement for each type of utility, and using the standard utility cost as given in Turton table 8.3. The breakdown of utility costs can be seen in table 4-2, which shows that the high pressure steam used for heating in hydrolysis and dehydration is the greatest contributor to the total utility cost, accounting for about two-thirds of the roughly \$8.65 million annual cost.

Table 4-2: Utility Cost Breakdown

Utility	Process Components	Power Cost (\$/GJ)	Power Required (GJ/day)	Utility Cost (\$/year)
Low Pressure Steam	Pulper, Heat exchangers	4.54	787	1,180,000
Medium Pressure Steam	Distillation reboiler	4.77	190	300,000
High Pressure Steam	Hydrolysis, Dehydration	5.66	3057	5,710,000
Cooling Water	Neutralization, Fermentation, Distillation Condenser	0.38	3826	477,000
Electricity	Pulping, mixing, pumping	18.72	159	984,000
Total	-----	-----	-----	8,651,000

The costs associated with landfilling solid waste streams from the neutralization and fermentation units as well as treating the spent water from distillation are enumerated in Table 4-3 below. Treating the spent water from the distillation column is responsible for 97.5% of our daily waste treatment costs, due to the amount of water that must be treated per day.

Table 4-3: Waste Treatment Cost Breakdown

Waste Type	Amount of Waste (kg/day)	Cost of Disposal (\$/day)	Annual Cost of Disposal (\$/year)
Filtered Solids	96,206	5	1,800
Yeast Purge	10,987	1	200
Distillation Bottoms	4,323,575	242	79,900
Total	-----	-----	81,900

The raw material cost was determined to be \$970,000 per year. A full breakdown of these can be seen in table 4-4 below. This is a relatively small proportion of the total cost of manufacturing, accounting for 1.6% of the total cost after the 1.23 factor used by Turton.

Table 4-4: Raw Material Cost Breakdown

Material	Amount Used (kg/day)	Cost (\$/kg)	Annual Cost (\$/year)
Mixed Paper	184,186	-0.05	-3,040,000
Water	4,420,465	0.00018	263,000
Sulfuric Acid	3,250	0.11	123,000
Hydrated Lime	2,455	0.15	122,000

Urea	7,684	0.19	2,890,000
Magnesium Sulfate	117	0.40	94,000
Calcium Chloride	58	0.27	31,000
Gasoline	2,296	0.41	311,000
Total			794,000

The total annual production cost was calculated at \$60.7 million, with the individual components contributing to the cost as follows:

Table 4-5: Total Cost of Manufacturing Breakdown

Component of COM	Cost (\$/year)	Portion of Total Cost (%)
Fixed Capital Investment	42,900,000	70.6
Operating Labor	6,100,000	10.1
Utilities	10,600,000	17.5
Waste Treatment	100,000	0.2
Raw Materials	970,000	1.6
Total	60.7 million	100

The current market price of ethanol as of April 2021 is \$2.01 per gallon (Trading Economics, n.d.). Additionally, the average LCSF credit for ethanol when sold in California is approximately \$0.50 per gallon (Noda, 2019) and the second generation biofuel producer tax credit is \$1.01 per gallon (U.S Department of Energy, n.d.). Finally D3 RIN credits have a value

of \$2.39 as of march 2021 (EPA, 2021). Therefore, the product produced by this plant has a value of \$5.91 per gallon and a total production value of 50.4 million dollars per year. The Cost of Manufacturing for this plant was calculated at 59.8 million dollars per year when including depreciation. Therefore this plant is not profitable as designed in this paper.

While the current design of the plant is not profitable there are multiple changes that could be made to increase the profit of the plant. First the carbon dioxide produced by fermentation can be captured and sold for approximately 1.1 million dollars per year which would provide the plant with an additional source of revenue (Doty Energy, 2011). Also designing an anaerobic digester that could treat the wastewater produced by the plant would allow for the capturing of biogas which could be burned to reduce the amount of natural gas needed to create steam and lower the utility cost of the plant. The utility cost of the plant could be lowered even further if the heat was recycled in the plant. For example the water being fed to the drum pulper could first be used to condense the vapor in the distillation columns reboiler and reduce the steam needed to heat the water before it enters the pulper. Another example would be to use the heat removed from the slurry after hydrolysis to reduce the steam needed to heat the reboiler or to heat the feed entering hydrolysis. Finally water could be removed from the slurry after pulping and screening and the slurry being fed to hydrolysis can have its concentration increased from 4 percent to 10 percent paper. This change would reduce the amount of energy required to heat and cool the slurry as it continues moving through the process and reduce the utilities cost throughout the plant.

Changes to the price of ethanol could also affect the profitability of the plant. Since the beginning of 2021 the price of ethanol has risen by \$0.58 per gallon (Trading Economics, n.d.). Also the price of LCFS credits has increased from 95 dollars per ton in january 2017 to 200

dollars per ton in January of 2021 (NESTE, n.d.). Finally the price of D3 rin credits has risen significantly in the last year from less than a dollar per credit in January of 2020 to \$2.39 per credit in March of 2021 (EPA, 2021). If the combination of credits and ethanol rose another \$1.09 per gallon the process would break even and if they rose by a combined \$2.00 per gallon the process would produce a profit of 7.75 million dollars per year. In conclusion if further work is done to recycle heat, capture and sell carbon dioxide, and produce biogas the process has the potential to make a significant profit so long as the push for renewable and environmentally friendly fuel continues to drive the price of ethanol and the associated credits higher.

5. Final Design

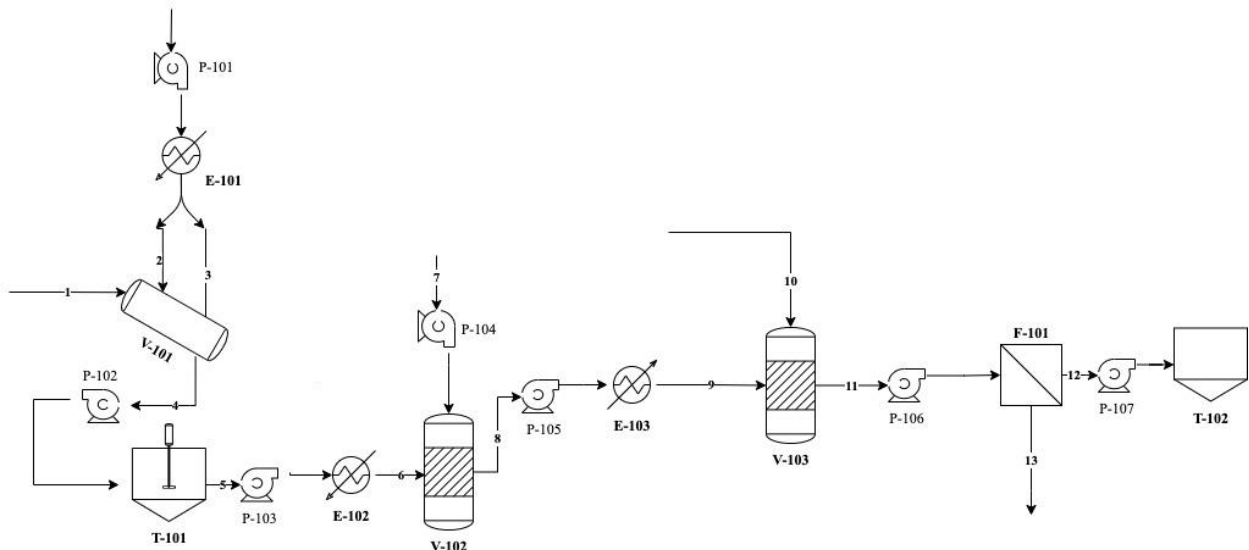


Fig. 5-1. Upstream Process Flow Diagram

The conversion of mixed paper into ethanol has six main steps: pulping, hydrolysis, neutralization, fermentation, distillation, and dehydration (see Fig. 5-1, Fig. 5-2, and Fig. 5-3; see Appendix K for stream composition tables). The first unit in the operation is the pulping

drum (V-101). Water and shredded paper are added to the first section of the drum, where high shear is used to break the shredded paper into a pulp. After the paper is broken down, it moves to the second part of the pulper where it is mixed with more water to create a looser slurry, which aids in piping slurry through the process. After pulping, the slurry is sent to a heat exchanger (E-101), where it is heated to 220C, and then to the hydrolysis batch reactor (V-102). E-101 operates using high pressure steam at a shell pressure of 41.4 barg and a calculated heat transfer area of 4580 m². During hydrolysis, the cellulose in the pulp slurry is broken down into glucose using sulfuric acid in a 6.66 meter diameter reactor. After hydrolysis, the glucose slurry is sent to heat exchanger E-102, where it is cooled to 35C using cooling water and a heat transfer area of 9910 m². The slurry is then sent to the neutralization tank, V-103, where it is mixed with hydrated lime to neutralize the sulfuric acid. The slurry is sent to a filter after neutralization, where the solid precipitate of neutralization, unreacted cellulose, and other solid waste is removed from the slurry. The filtrate is sent to storage tank T-102 to await

fermentation, while the solids are landfilled.

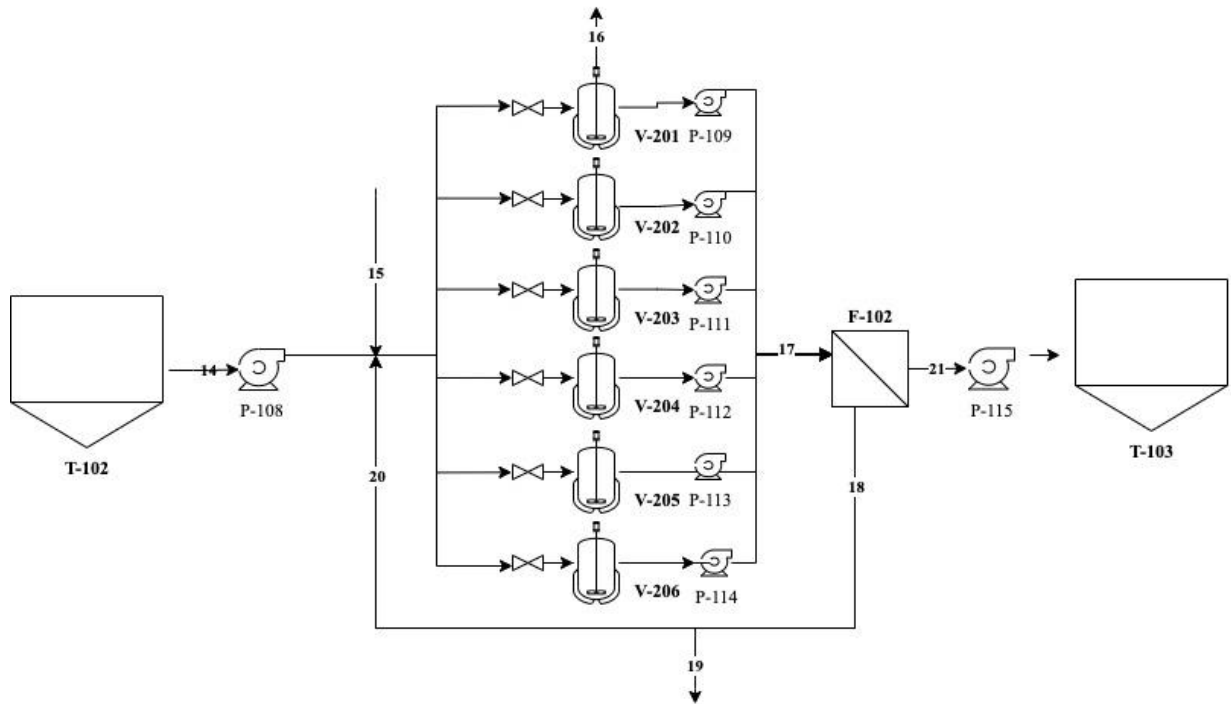


Fig. 5-2. Fermentation Process Flow Diagram

The slurry is pumped into one of six batch reactors (V-201 through V-206) for fermentation. Each batch reactor has a size of 11.4 meters diameter. At any time, three batch reactors are in use, allowing for more efficient filling, emptying and cleaning of the reactors between batches. Yeast and yeast nutrient (containing urea, calcium chloride, and magnesium sulfate) is added to the reactor. The slurry remains in the reactor for 12 hours, after which it is sent to filter F-102. The filtrate (a mixture of water, ethanol, and some dissolved yeast nutrient) is sent to a storage tank (T-103) before being fed to distillation. The solids separated during filtration are yeast biomass, which is recycled and fed to another batch fermenter. To avoid the buildup of dead yeast biomass, 15 wt% of the recycle stream is purged and landfilled.

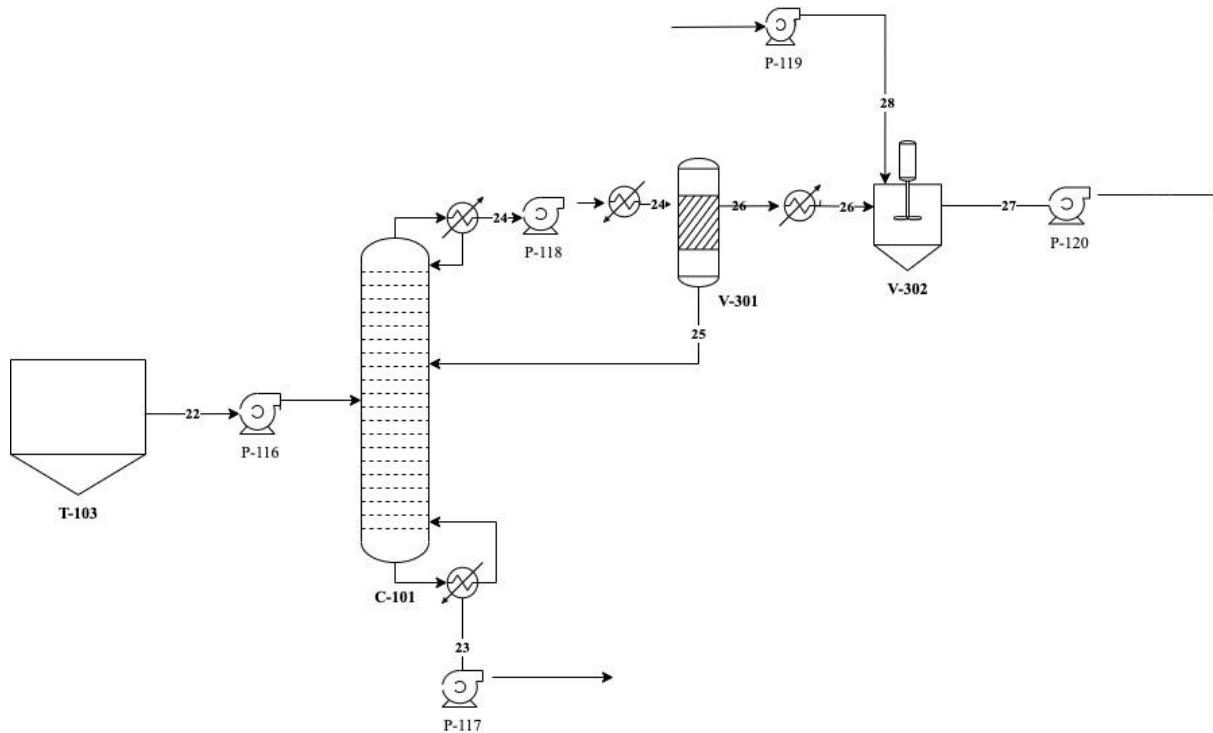


Fig. 5-3. Downstream Process Flow Diagram

The ethanol and water mixture is continuously fed to a distillation column (C-101), where the concentration of ethanol in the mixture is increased. This distillation column was determined to have a height of 15 meters and a diameter of 2.5 meters, and uses 24 stainless steel sieve trays. As previously stated, the condenser and reboiler were modeled as heat exchangers using cooling water and medium pressure steam with heat transfer areas of 580.9 m² and 312.7 m² respectively. The bottoms product of the column is 4323575 kg/day of spent water (containing dissolved yeast nutrient, a very small amount of ethanol, and any other impurities). It is sent to a wastewater treatment plant before reintroduction into the water supply. The distillate is sent to a molecular sieve (V-301), where excess water is removed to meet fuel ethanol specifications. The superheater for this process operates as a heat exchanger using high pressure steam with a heat duty of 55.35 GJ/day, requiring an area of 62.2 m². After dehydration, the ethanol is mixed

with gasoline (a denaturant added to avoid food taxes), in a mixing tank (V-302) to create the final product of the process. This amounts to 76,550 kg of product per day, with the final product being 96.6% ethanol, 3% gasoline, and the remainder water. More detailed equipment information can be found in the supplemental files located in Appendix G such as pump specifications, heat exchanger temperatures, and more.

6. Safety Review

The chemicals required to convert cellulosic material into ethanol pose various safety risks to plant personnel. Other safety hazards may arise from the inadvertent mixing of process chemicals due to abnormal operating conditions. Machinery failures or hot work (welding, soldering, etc.) and other maintenance procedures can ignite or detonate flammable materials within the plant as well. Analysis of these safety hazards and subsequent installation of necessary safeguards can mitigate the risk of worker injury or death in the event of an incident. Note that the hazards discussed refer to those that threaten human health and safety; some situations deemed non-hazardous may still result in a loss of revenue for the plant or may shut down production for cleaning and machinery repair.

Chemical Hazards

The chemicals used during plant operation each pose a unique set of hazards; the most hazardous chemicals used include sulfuric acid, hydrated lime, urea, calcium chloride, and gasoline. Sulfuric acid can cause skin corrosion, serious eye damage, and can corrode metal (AquaPheonix, 2015). Hydrated lime, or calcium hydroxide, can cause severe eye damage and may be carcinogenic when inhaled; inhaling small amounts of hydrated lime can irritate

respiratory pathways (Pete Lien & Sons, Inc, 2019). Urea can irritate respiratory pathways, eyes, and skin; those manipulating the substance should avoid breathing urea dust and wear long clothing to protect the skin (PCS Sales, Inc, 2017). Calcium chloride can burn the skin and eyes, and will burn the respiratory tract if inhaled. If ingested, calcium chloride can cause cardiovascular disturbances and seizures (LabChem, Inc, 2006). Gasoline vapor is toxic when inhaled and poses a serious fire and explosion threat if ignited (Marathon Petroleum Company, 2018).

Loss of primary containment (LOPC), human error, or machinery failure will inevitably occur over the operating lifetime of the plant and may lead to unintended chemical interactions. Using the CAMEO Chemicals software suite, a chemical compatibility chart was generated to predict any hazards due to mixing process chemicals (see Appendix J for complete compatibility chart). Several chemical combinations do not result in safety hazards; accidental mixing of urea with gasoline or ethanol does not generate chemicals that would threaten personnel safety. Sulfuric acid poses the most hazards as its mixing with every other chemical in the plant is incompatible or generates heat. Other incompatible mixtures include calcium hydroxide with calcium chloride and calcium hydroxide with urea. When deciding plant layout, it is best if chemicals that will generate undesirable products are stored far away from each other to prevent possible mixing in the event of an LOPC.

Other Hazards

The flammable nature of paper, ethanol and gasoline make it important to understand the risk of fire in the plant and install safety measures to mitigate damage and injury. The waste paper feedstock can autoignite when stored in damp or wet conditions; bacteria thriving in the

anaerobic environment in the middle of the shredded paper pile increase the temperature such that it exceeds the flammability limit of the paper. Sparks or other ignition sources can also ignite ethanol or gasoline vapors present around the plant. Fire prevention begins with correct storage of these products, but it is important to also install extensive fire mitigation equipment, including flame arresting devices, water deluge cooling systems on storage tanks, and up-to-date fire alarm systems to alert plant workers in the event of a fire.

Other non-chemical hazards, including machinery failure or injury due to process machinery also exist in this plant. The pulping drum used to break down paper into pulp poses such a hazard; plant operators unfamiliar with the pulper may not understand the danger of the drum and can injure themselves by reaching into the operating pulper or getting their fingers and clothes caught in the drum's rotating inner shell. Also, the large tank size necessary to store process chemicals can pose a drowning hazard; even if the tanks are holding benign chemicals, operators working at the top of the tank or on the roof are at risk of falling into the tank and drowning or being consumed by the chemicals inside. Such risks can be mitigated by developing and enforcing proper protocol for tank maintenance and installing other barriers like metal cages (which can contain any debris and prevent workers from inadvertently getting caught in machinery).

Proposed Safeguards

The hazards outlined above can be mitigated using a variety of safeguards. For example, to prevent the serious hazards of sulfuric acid mixing with other process chemicals, the sulfuric acid storage tank will be situated away from other storage vessels, the pipe connection used for acid delivery will be clearly labeled and situated away from other pipe connections to prevent

inadvertent mixing during delivery. The sulfuric acid storage tank is also designed to hold less inventory than other tanks in the plant, which reduces the amount that may be released during an incident. Though the smaller tank size means more acid deliveries must be made, the danger posed to operators is greatly reduced. Regular inspections of the storage tank's integrity will be scheduled to avoid an LOPC from tank corrosion. A dike will be used as secondary containment in case of an LOPC; to avoid possible interactions with other chemicals, the dike around the sulfuric acid tank will not be shared with other storage tanks.

Due to the hazards posed from solids used during production (hydrated lime, urea, and calcium chloride) operators working with the chemicals will have comprehensive PPE including respirators, long sleeves and pants, gloves, and goggles. The plant is designed such that operators will manually add solid chemicals to the reactors; future designs will include screw conveyors to move solid chemicals from dry storage to the reactors, which will mitigate dust dispersion and isolate operators from the chemicals. Other design options to mitigate the risks posed include adding water to create aqueous solutions of the solid chemicals, which eliminates dust concerns and allows the use of piping to move the chemicals through the plant.

The gasoline storage tank will be grounded and bonded to nearby tanks to eliminate the possibility of a static charge buildup (which may lead to ignition of any gasoline vapors present), and a floating roof tank will be used to reduce the amount of gasoline vapor present. Another possible solution to reduce the gasoline storage tank's fire hazard is to inert the tank using nitrogen, but the first option was chosen to reduce operating costs. To prevent spontaneous combustion, the paper feedstock will be stored in a closed structure with a crushed rock floor to maintain low moisture levels and prevent bacteria growth. Automatic fire suppression systems will be installed throughout the plant, including automatic deluge systems around tanks

containing flammable materials (the ethanol product tank and gasoline storage tank). In the event of a fire at the plant, these deluge systems will prevent overpressurization and subsequent explosion or rupture of the tanks. Plant operators will be trained on how to respond to fires or explosions within the plant. Plant management will work closely with nearby first responders to communicate the hazards of the plant, should they have to respond in an emergency.

As mentioned above, safety shields will be installed around machinery that may unexpectedly fling debris (including pumps and the drum pulper). These shields will protect nearby workers and prevent workers from getting caught in process machinery. Rigorous maintenance standards will be developed to ensure no operators are harmed during routine maintenance tasks. To monitor the presence of flammable vapors around the plant, gas detectors will be installed at various locations and checked regularly to ensure they are operating correctly.

7. Environmental Considerations

Environmental hazards are also present due to the chemicals used in this plant. Chemicals spilled due to an LOPC or other process upset can leach into groundwater or nearby water bodies, damaging local ecosystems. Some provisions have been made in plant design, including preliminary wastewater neutralization on site. Factors including plant location, secondary containment systems, and operating procedures will be carefully chosen to protect the environment from process chemicals. The CO₂ produced during fermentation can be captured (not vented to the atmosphere) to prevent unnecessary greenhouse gas emissions.

Containment dikes are primarily installed to protect operators in the event of an LOPC; these dikes can also prevent spilled chemicals from leaching through the ground into nearby water sources. The dikes installed in the plant will have drainage valves that can be used to easily

remove chemicals after an incident without draining them directly into the environment. Solid chemicals will not be stored in direct contact with the ground; moisture from the ground can dissolve the chemicals and carry them to nearby water sources. In addition to the measures enumerated above, nearby water sources will be routinely tested to ensure no chemicals are polluting the environment. Routine water tests will ensure safety devices are working properly and the plant is not causing unnecessary damage. Tank cleaning or other maintenance procedures that prioritize environmental safety will be implemented.

The CO₂ produced during fermentation poses another environmental hazard. Current plant design indicates that the gas will be vented from the fermenters directly to the atmosphere. In future designs, CO₂ will be collected instead of being vented; the gas can either be sold or sequestered. Carbon sequestration is a costly process, but it is much easier to remove the carbon at the plant than it is once it has been released into the atmosphere. Other options include capturing the CO₂ and selling it to a refinery for further processing, where it is purified and resold for drink carbonation or use in other food applications. Current CO₂ production (40.4 tons per year) is much less than production in a typical oil refinery (0.8 to 4.2 million tons per year); the amount vented to the atmosphere is not of immediate concern (van Straelen et al., 2009). The above options should be used if the plant grows or starts producing more ethanol than this design does, but the amount of CO₂ produced in this design is not large enough to warrant the cost needed to capture it.

8. Conclusions/Recommendations

We conclude that the production of fuel-grade ethanol is both technically achievable and energetically positive with the design described in this paper. The process scheme designed in this report will produce 76,539 kg/day of denatured ethanol. That equates to 25868 gallons of

ethanol produced per day. For the 330-day operating year, the plant designed in this report would be capable of producing 25.26 million kg/year of denatured ethanol, which equates to 8.54 million gallons per year. The total heat duty of the plant is 1,730 GJ per day. This is 76% of the heat of combustion of -2,271 GJ per day (OpenStax, 2016). Therefore, the process scheme described in this report is energetically favorable since less energy is consumed to produce the ethanol than can be obtained from burning the finished product.

Given the current market price of ethanol, the plant as designed in this paper would not operate profitably, as the annual cost of manufacturing is about 18.5% greater than the total annual production value. Several possibilities could be explored in an attempt to make the plant profitable, either through increasing the value of the products or through decreasing the cost of production. The value of products could be increased by utilizing side products, such as carbon dioxide produced during fermentation, that are currently not designed for capture, or through the potential increase in the value of the ethanol product. The greatest contributor to the high production cost is the fixed capital investment, accounting for about 71.7% of the annual production cost, followed by the costs of utilities and labor, accounting for 17.8% and 10.3%, respectively. This indicates that future efforts to reduce production costs should be focused on these components, and should largely ignore the costs of raw materials and waste treatment, as they account collectively for only about 0.2% of the annual production cost.

9. Acknowledgements

We would like to acknowledge Professor Eric W. Anderson of the University of Virginia's Chemical Engineering Department for being the advisor for our capstone project.

We would also like to thank the professors of the University of Virginia's Chemical Engineering Department for their tireless efforts to help us successfully learn and apply essential chemical engineering concepts.

Table of Nomenclature

Saccharomyces cerevisiae - commonly known as Brewer's yeast, is a single-celled organism that convert glucose to ethanol via fermentation

Fermentation - process of yeast converting glucose to ethanol and side products through metabolism

Fermentor - bioreactor used to convert glucose into ethanol

Distillation column - separation apparatus using a reboiler to drive separation of two or more components on trays

Distillation trays - The individual stages of a distillation column

Cellulosic Ethanol - Bio-ethanol sourced from the cellulose of a plant, rather than the fruit, seeds, or other plant materials

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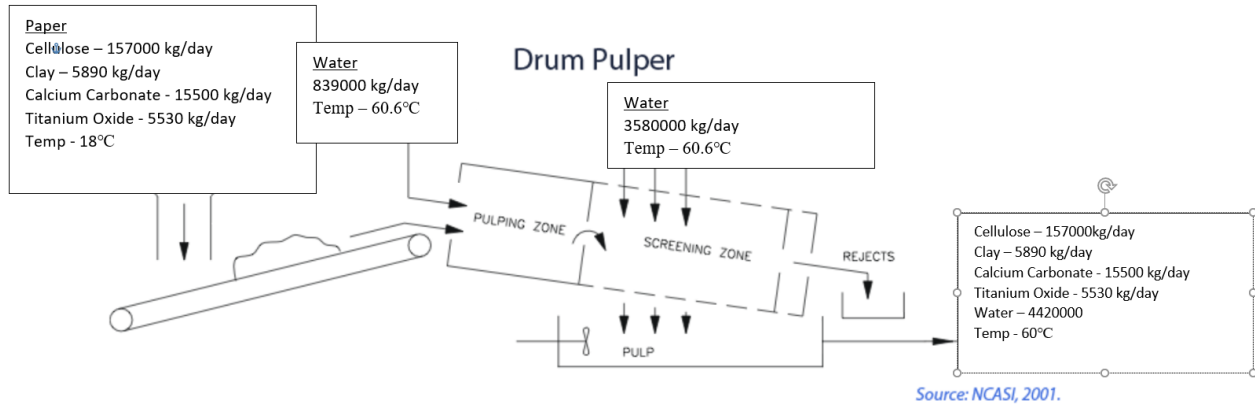
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Appendix

Appendix A: Drum Pulper Diagram



Appendix B: Bed-Shrinking Flow Through Reactor Lab-Scale Design (Kim et al., 2001)

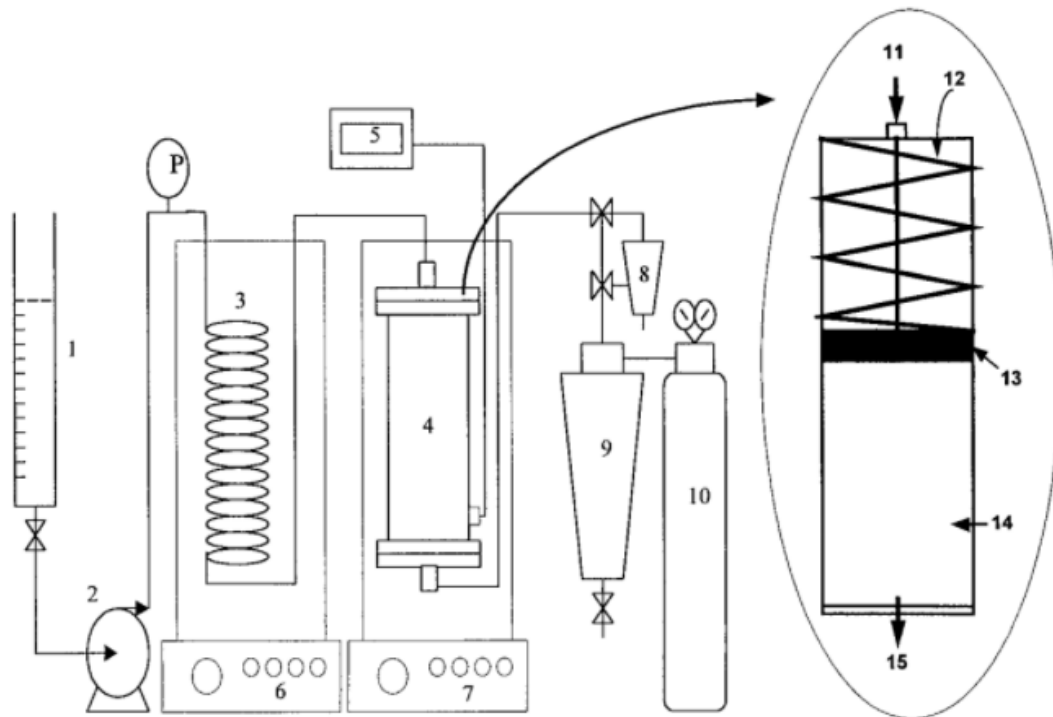


Fig. 1. Laboratory setup for BSFT reactor system: 1, liquid tank; 2, metering pump; 3, preheating coil; 4, bed-shrinking reactor; 5, thermometer; 6 and 7, temperature programmable sand bath; 8, sampling port; 9, pressure holding tank; 10, N₂ gas; 11, acid fluid inlet; 12, spring; 13, movable end; 14, compressed solid biomass; 15, liquid outlet.

Appendix C: Enthalpy Calculation for Hydrolysis & Neutralization Reactor Feeds

	Hydrolysis	Neutralization
Specific Heat (J/(kg*K))	4071	4071
Initial T (°C)	60	220
Final T (°C)	220	35
Enthalpy Needed (kJ/day)	3,000,000,000	-3,470,000,000

Appendix D: Enthalpy Calculations for Neutralization Tank

Table D-1: Heat of Neutralization Reaction

Species	Heat of Formation @25C (kcal/mol)
Sulfuric Acid	-212.03
Hydrated Lime	-235.58
Water	-68.31
Gypsum	-338.73
Heat of Reaction (kcal/mol)	-27.75
Heat of Reaction (kJ/mol)	-116.10

Table D-2: Enthalpy Needed to Heat Lime Feed

Specific Heat (j/kg*K)	1214
Mass (kg)	2455
Change in Temperature (C)	17
Enthalpy Needed (J)	50,674,000
Enthalpy Needed (kJ)	50,674

Table D-3: Enthalpy to be Removed

Moles Reacted (mol)	33,136
Heat of Reaction (kJ/mol)	-116
Enthalpy Needed to Heat Lime (kJ)	50,674
Enthalpy Removed (kJ)	-3,897,685

Enthalpy Removed (GJ)	-3.897
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Appendix E: Chemical Compatibility Chart

1. CALCIUM CHLORIDE	1. CALCIUM CHLORIDE						
2. CALCIUM HYDROXIDE	Incompatible: Generates heat	2. CALCIUM HYDROXIDE					
3. ETHANOL	Compatible:	Compatible:	3. ETHANOL				
4. GASOLINE	Compatible:	Compatible:	Compatible:	4. GASOLINE			
5. SULFURIC ACID	Caution: Generates heat	Incompatible: Generates gas,Generates heat,Intense or explosive reaction	Incompatible: Explosive,Flammable, Generates gas,Intense or explosive reaction,Toxic	Incompatible: Generates gas,Generates heat,Toxic	5. SULFURIC ACID		
6. UREA	Incompatible: Flammable,Generates gas,Toxic	Caution: Generates gas	Compatible:	Compatible:	Caution: Generates gas,Generates heat	6. UREA	
7. WATER	Caution: Corrosive,Generates gas,Generates heat	Caution: Generates heat	Compatible:	Compatible:	Caution: Corrosive,Generates gas,Generates heat,Toxic	Caution: Generates gas	7. WATER

Appendix F: Stream Tables, Separated by Operation

Table F-1: Pulper Stream Table

Stream	1	2	3	4
From	Input	Input	Input	Pulper
To	Pulper	Pulper	Pulper	Slurry Tank
Temperature (°C)	18.0	60.0	60.0	60.0
Pressure (bar)	1.0	1.0	1.0	1.0
Phase	S	L	L	L
Paper	184186.0			
H₂O		966976.7	3453488.4	4420465.1
Cellulose				157294.9
Solid Waste				26891.2
Total (kg/day)	184186.0	966976.7	3453488.4	4604651.1

Table F-2: Hydrolysis Stream Table

Stream	5	6	7	8
From	Slurry Tank	Heater 1	Input	Hydrolysis
To	Heater 1	Hydrolysis	Hydrolysis	Cooler 1
Temperature (°C)	60.0	220.0	18.0	220.0
Pressure (bar)	1.0	1.0	1.0	1.0
Phase	L	L	L	L
H₂O	7873953.4	4420465.1	1392.9	4406124.7
Cellulose	157294.9	157294.9		15729.5
Glucose				157298.7
H₂SO₄			3250.0	3250.0
Solid Waste	26891.2	26891.2		26891.2
Total (kg/day)	8058139.5	4604651.1	4642.9	4609294.0

Table F-3: Neutralization & Pre-fermentation Filtration Stream Table

Stream	9	10	11	12	13
From	Cooler 1	Input	Neutralization	Filter	Filter
To	Neutralization	Neutralization	Filter	Preferment Tank	Landfill
Temperature (°C)	35.0	18.0	35.0	35.0	35.0
Pressure (bar)	1.0	1.0	1.0	1.0	1.0
Phase	L	S	L	L	L
H₂O	4406124.7		4407318.2	4360057.2	47261.0
Cellulose	15729.5		15729.5		15729.5
Glucose	157298.7		157298.7	155611.9	1686.8
H₂SO₄	3250.0				
Ca(OH)₂		2455.0			
Solid Waste		129.2	27020.4		27020.4
CaSO₄			4511.1		4511.1

Total (kg/day)	4582402.8	2584.3	4611877.9	4515669.1	96208.8
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Table F-4: Fermentation Stream Table

Stream	14	15	16	17
From	Preferment Tank	Yeast Storage	Batch Fermenter	Batch Fermenter
To	Batch Fermenter	Batch Fermenter	Gas Purge	Filter
Temperature (°C)	35.0	18.0	35.0	35.0
Pressure (bar)	1.0	1.0	1.0	1.0
Phase	L	S	G	L
H₂O	4360057.2			4390920.3
Glucose	155611.9			
Ethanol				75222.4
CO₂			122298.8	
Yeast				36309.4
Yeast Nutrient		47158.5		
Total (kg/day)	4515669.1	47158.5	122298.8	4502452.2

Table F-5: Post-Fermentation Filtration Stream Table

Stream	18	19	20	21
From	Filter	Purge	Purge	Filter
To	Purge	Waste	Batch Fermenter	Postferment Tank
Temperature (°C)	35.0	35.0	35.0	35.0
Pressure (bar)	1.0	1.0	1.0	1.0
Phase	L	G	L	L
H₂O	36309.4	5446.4	30863.0	4323750.0
Ethanol	622.0	93.3	528.7	74071.0
Yeast	36309.4	5446.4	30863.0	
Yeast Nutrient	3.9	0.6	3.3	

Total (kg/day)	73244.8	10986.7	62258.1	4397821.0
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Table F-6: Distillation Stream Table

Stream	22	23	24
From	Postferment Tank	Distillation (Bottoms)	Distillation (Distillate)
To	Distillation		Molecular Sieve
Temperature	35.0	120.3	96.5
Pressure (bar)	1.5	1.5	1.5
Phase	L	L	L
H₂O	4323750.0	4323440.0	7673.1
Ethanol	74071.0	135.3	77826.9
Total (kg/day)	4397821.0	4323575.3	85500.0

Table F-7: Dehydration & Denaturing Stream Table

Stream	25	26	27	28
From	Molecular Sieve	Molecular Sieve	Input	Denaturing Tank
To	Denaturing Tank	Distillation	Denaturing Tank	Product Tank
Temperature (°C)	150	150	18	18
Pressure (bar)	3.5	3.5	1.0	1.0
Phase	L	L	L	L
H₂O	306.9	7366.3		306.9
Ethanol	73935.6	3891.4		73935.6
Gasoline			2307.7	2307.7
Total (kg/day)	74242.5	11257.7	2307.7	76550.2

Appendix G: Supplemental Links

[CAPCOST 2017 ETHANOL PLANT.xlsm - Google Sheets](#)
[Equipment Spreadsheet Ethanol Plant - Google Sheets](#)