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Comparison of Pretreatment Methods for Cellulosic Ethanol

Michael Eaton Western Michigan University, Michael.eaton2015@gmail.com

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Comparison of Pretreatment Methods for Cellulosic Ethanol

April 20th, 2020

Michael Eaton, Emily Schulte, Merlin Steffes, India Mclaurin, and Chad Sarquiz

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Introduction:

Bioethanol is a renewable energy source that offers an alternative to fossil fuels like petroleum. Mostly used as fuel for transportation, ethanol is commonly blended with gasoline in small proportions, such as E10 which contains 10% ethanol. In recent years, flex-fuel vehicles which accept E85 have become more prominent, somewhat due to government regulations and incentives. Ethanol use in the US increased from 6.2 B L/yr to over 50 B L/yr between 2000 and 2010, and in that time, the number of ethanol plants increased from 54 to 189 (Kumar 2). Traditional ethanol (1st generation) is mainly produced from corn, which means that there's a choice between producing food or fuel. There's a significant cost that comes with harvesting corn, and it's a very land and water intensive practice. Fortunately, some of these challenges are being overcome with the development of 2nd generation bioethanol, known as cellulosic ethanol. Cellulosic ethanol can use secondary substrates such as agricultural residues, grasses, wastepaper, and forestry wastes. These feedstocks are abundant, low cost, and are either a byproduct of other industries or nature.

In cellulosic ethanol production, the components of the biomass are separated so they can be processed more efficiently. The biomass components include cellulose, hemicellulose, and lignin. The cellulose and hemicellulose can be broken down through hydrolysis into sugar monomers (like glucose) to be turned into ethanol, and the lignin can be isolated and burned for on-site power generation. The main steps of cellulosic ethanol production are biomass preparation, pretreatment and separation, hydrolysis and fermentation, then the distillation of ethanol and separation of lignin, which can be seen in Figure 11 in the appendix. The biomass is prepared by mixing it with water, washing, and then finely shredding. The substrate then undergoes pretreatment to increase the susceptibility of the biomass to enzymes. Next, the cellulose and hemicellulose are treated with acid or enzymes to hydrolyze the sugar polymers into sugar monomers, which are then fermented. Enzymes use less energy and have higher yields than acid treatments, but are more vulnerable to impurities in the substrate. The mixture is then distilled to separate out the ethanol, then the lignin is isolated for heating or power generation.

Cellulosic ethanol has not been produced on an industrial scale yet due to uncertainty about its economic viability compared to other fuels. Numerous techno-economic models have been created to give a minimum selling price per liter of cellulosic ethanol, but there's significant variability in the results that the models produced. This is due to the wide variety of substrates available, as well as the many different pretreatment methods which are available. Pretreatment is necessary to open up the biomass structure to make it susceptible to enzymes. If not properly treated, the enzyme will bind to the lignin and will be restricted by the hemicellulose, rendering it ineffective. Some of the most common pretreatment methods include hot water, dilute acid, dilute alkali, and steam explosion. It's been found that some pretreatment methods have lower cost reactors, but that cost is counterbalanced with high recovery costs (Eggeman 3). All in all, from an economic perspective, the pretreatment methods are very similar. The goal of this report is to compare the most common methods, hot water and dilute acid, on the basis of cost, safety, efficiency, and overall feasibility.

This report includes a detailed table of contents, introduction, previous work history, proposed process flow diagrams, material and energy balances, project costs, financial analysis, general feasibility evaluation, conclusion, recommendations, references, and an appendix.

Previous Work / History:

For the purposes of the project, it was imperative to complete a market survey to understand the demand for a petroleum alternative such as cellulosic ethanol. There is currently a market in place for ethanol as an alternative transportation fuel, and the market survey found that the market share for the consumption of ethanol in this area has been steadily increasing over the years. The market share of ethanol as a replacement for traditional transportation fuels from 2000 to 2018 is depicted below in Figure 1.

Figure 1 - Market Share of Ethanol

Figure 1 shows that the market share of ethanol has grown from around 1% to just over 10% between 2000 and 2018. According to the U.S. Energy Information Association, biofuel consumption is projected to increase with the increase in demand for renewable diesels. This trend shows that there has been demand for ethanol as a replacement for traditional gasoline, and indicates that further optimization of the ethanol production process is necessary to make it more competitive. Figure 2, as pictured below, also supports this trend.

Figure 2 - Gasoline and Biofuel Consumption Trends

As seen in Figure 2, both gasoline and diesel use are expected to increase, as well as the share of fuel ethanol and biomass-based diesel in those blendstocks. US diesel fuel consumption, which includes biomass-based diesel, is expected to increase 3.8 million b/d to 3.9 million b/d between 2018 and 2020. The demand for renewable diesel and for stand-alone production facilities and petroleum refiners is expected to grow in 2020.

The pump price for gasoline and diesel varies across the US based on a number of factors, including transportation costs, demand, and taxes. Because of this variation, it's necessary to look at wholesale prices of the fuels. Figure 3 displays the wholesale truckload sales of gasoline and ethanol at terminals. The price of ethanol per gallon in December 2019 was \$1.32. The price of ethanol has gradually decreased since August 2011, where it cost \$2.94 per gallon. The price of ethanol closely follows the price of unleaded gasoline, also demonstrated in Figure 3. Future ethanol prices are difficult to project based on past price volatility.

Figure 3 - Wholesale Prices of Gasoline and Ethanol

Discussion:

The discussion portion of this report is broken into a few key subsections, including general PFDs, material and energy balances, cost comparison and capital costs, economic analysis, and general feasibility.

Process Flow Diagrams

A process flow diagram was created for each process to further understand the flow of the materials and energy utilized in the two processes, as well as to identify proper sizing required for the equipment in the processes. A basis of 100,000 kg/hr of dry biomass into the reactor was used to compare each of the processes, with the composition shown in Table 8 in the appendix. The dilute acid pretreatment method has a couple different sub methods which deal with the acid neutralization differently. One method uses overliming and naturalization to bring the slurry within the desired pH range, while the other method uses ammonia. For the sake of comparison, the ammonia method was chosen because the LHW pretreatment method uses ammonia as well. That being said, the two process flow diagrams look very similar, the only difference being that the dilute acid pretreatment involves acid while the LHW pretreatment doesn't. There are significant differences in the material and energy balances and equipment costs though, which is discussed further in the Material and Energy Balances portion of the report.

The process flow diagram for the dilute acid pretreatment is shown in Figure 1 below.

Figure 4 - **Dilute Acid Pretreatment PFD**

The overall process begins with the addition of biomass, acid, water, and steam into the reactor. The contents of the reactor are heated using the steam to a target temperature of around 180 °C for a dwell time of about 3 minutes, allowing for the necessary reactions to occur. The reactions and conversions can be found in Table 9 in the Appendix. The contents of the reactor then exit to a blowdown tank, where some of the liquid is flashed to remove the undesired components in the form of an overhead vapor stream, which is utilized to power another part of the ethanol production process. The slurry from the blowdown tank is then pumped to a conditioning stage, where ammonia is added to increase the pH to a less acidic value. Once the desired pH is achieved after about 20 minutes of residence time, the product stream is pumped forward to the hydrolysis stage of the ethanol production process and the pretreatment process is complete.

The process for LHW is quite similar to that of dilute acid, and is shown below in Figure 5.

Figure 5 - Hot Water Pretreatment PFD

The biomass, water, and steam enter the pretreatment reactor, where the steam is used to increase the temperature of the components over 15 minutes to a temperature of around 200 $^{\circ}$ C (Zhou, 5). The water remains in the liquid form by running the reactor at a higher pressure. At such high temperatures and pressures, the water acts like an acid and allows for some of the reactions like in the dilute acid pretreatment, albeit significantly milder. The reactions and conversions for this process can be found in Table 10 in the appendix. From the reactor, the biomass slurry is pumped to a blowdown tank, where flash vapor is removed from the tank, increasing the solids of the slurry before it enters the ammonia conditioning stage. The ammonia is once again used to increase the pH of the slurry prior to the hydrolysis stage to improve the sugar yields for ethanol production. Once the pH of the slurry has been neutralized, the pretreatment process is complete, and the biomass slurry is sent on to the hydrolysis stage.

Material and Energy Balances

Material and energy balances were completed in Microsoft Excel for both of the pretreatment processes. This allows all the variables to be easily manipulated and controlled from one central location, and allows for assumptions to easily be changed. The overall process material and energy balance sheets can be found in Figure 13 and Figure 14 in the appendix. For the dilute acid pretreatment method, the process starts with a few different streams entering the pretreatment reactor. The biomass stream enters at a rate of around 133,000 kg/hr with 25 wt% moisture at 35 °C. The components of the selected biomass, corn stover, include cellulose, xylan and other hemi-sugars, lignin, ash, acetate, and trace amounts of various other components which were combined for the sake of simplicity as the respective compositions of each were negligible (Humbird, 12). Also entering the pretreatment reactor is sulfuric acid (H2SO4), water, and steam. The sulfuric acid is added at a rate of 0.04 kg acid per kg solids, which is calculated to be about 4,400 kg per hour (undiluted). The acid is diluted to around 1% with the addition of water before the mixture enters the reactor at 40 $^{\circ}$ C at a rate of about 167,000 kg/hr. High pressure steam enters the reactor at 250 °C at a rate of 70,000 kg/hr. The steam is used to heat the biomass, acid, and water to the desired temperature of around 180 °C. The components are left in the reactor for a target dwell time of 3 minutes (Humbird, 29). The dwell time was selected due to the desire to balance the desired and undesired reactions that occur in the reactor. Undesired reactions that occur in the reactor not only consume cellulose, but they also produce inhibitors such as furfural, which inhibit the fermentation of sugars to ethanol. After the dwell time is reached, the contents are sent to the blowdown tank. The composition of the stream entering the blowdown tank, following the reactions that occurred in the pretreatment reactor, are shown in Table 1 below. The stream has a solids percent of 13% and exits the reactor with a pH of 1.

Composition (kg/hr)						
Cellulose		28,446 Glucose	3.310			
Xylan		3,368 Xylose	13,296			
Sugars		6,020 Oligomers	11,677			
Ash		5,930 Acetic Acid	5,440			
Lignin		9,621 Sol Liginin	1,069			
Other Comp	18.994	Water	268,278			

Table 1 – Dilute Acid: Composition of Stream Exiting Reactor

In the blowdown tank, the pressure is decreased, and flash vapor is removed from the process at a rate of about 34,000 kg/hr, thus increasing the percentage of solids in the outgoing stream from 13% to 14%. From the blowdown tank, the pretreated biomass slurry is conditioned with ammonia to increase the pH from 1 to around 5.5. This is necessary, as the slurry cannot enter the hydrolysis stage with a very acidic pH as it hinders the ability of the enzymes to work on the cellulose (Kumar, 9). The slurry is conditioned with ammonia for a dwell time of 20 minutes, allowing for enough time to neutralize the acid and increase the pH before the hydrolysis stage.

For the hot water pretreatment method, the biomass enters the reactor at 35° C at a rate of 133,000 kg/hr, with a moisture of 25 wt%. Water enters the reactor at 40 °C with a flowrate of 367,000 kg/hr, where the dilution ratio of the water to solids in the reactor is 4 kg water/kg solids. Additionally, steam is added to the reactor at a rate of 120,000 kg/hr to heat the contents to a final temperature of 190 °C over the course of 15 minutes. During this time, reactions occur with the water and the components of the lignocellulosic biomass, including the cellulose, hemicellulose, and lignin. The cellulose and hemicellulose such as xylan react with the water to produce glucose and xylose, sugars which are a desired product for the fermentation of the final product, ethanol. The lignin is broken down into soluble lignin, where it can be removed and used to power other parts of the ethanol production process (Zhou, 3). Once the 15-minute dwell time has been reached, the slurry enters a blowdown tank with a solids percentage of 9%. The composition of the slurry can be found in Table 2.

Table 2 – LHW: Composition of Stream Exiting Reactor

The blowdown tank is used to increase the solids content to 11% by the removal of 111,000 kg/hr of flash vapor. The slurry is then pumped to the ammonia conditioning tank, where ammonia is added to the slurry at a rate of 1,200 kg/hr to increase the pH. This rate is equivalent to about 0.0047 kg NH³ per kg slurry.

Overall, the dilute acid and LHW pretreatment processes are very similar. Both processes include the biomass, water, and steam entering a pretreatment reactor, where the reactions break down the lignin, increase the accessibility of cellulose, and form sugars. The difference with the dilute acid is the presence of the sulfuric acid, which allows for less time spent in the reactor by assisting with the decreasing the crystallinity of the cellulose and breaking down the lignin. However, unlike the LHW process, it has the potential to form more inhibitors, such as furfural. Dilute acid also produces a higher solids content upon leaving the reactor due to its lower dilution ratio. Both processes utilize the blowdown tank as well as ammonia conditioning. Dilute acid requires the addition of about 400 kg/hr more of ammonia as it enters the conditioning stage at a slightly more acidic pH value than that of the LHW pretreatment process.

When comparing the material balances for the two processes, the overall inputs and outputs of the processes were surprisingly different. Table 3 shows the comparison of the inputs between the dilute acid pretreatment process and the liquid hot water process.

Input Variable	Dilute Acid Process	Hot Water Process
Biomass	133,000 kg/hr	133,000 kg/hr
Water	167,000 kg/hr	367,000 kg/hr
Steam	70,000 kg/hr	122,000 kg/hr
Sulfuric Acid	4,400 kg/hr	0 kg/hr
Ammonia	1,600 kg/hr	1,200 kg/hr

Table 3 – Comparison of Input Variables

From Table 3, it is clear that the dilute acid process requires the addition of the acid, while the hot water requires no addition of acid to the process. However, the LHW process requires 200,000 kg/hr more water, as well as around 50,000 kg/hr more steam than the dilute acid. It is also important to compare the difference in the outputs of the two processes, especially with respect to the components of the biomass in the product stream. Table 4 shows the overall process outputs of both pretreatment processes.

Output Variable	Dilute Acid Process	Hot Water Process
Water	236,000 kg/hr	411,000 kg/hr
Vapor	34,000 kg/hr	112,000 kg/hr
Total Sugars	60,000 kg/hr	62,000 kg/hr
Lignin	10,000 kg/hr	10,000 kg/hr
Acetic Acid	5,400 kg/hr	5,400 kg/hr

Table 4 – Comparison of Output Variables

The term "total sugars" includes the total amount of cellulose, glucose, xylan, and xylose and glucose oligomers in the product stream. As shown in Table 4, there are some differences in the amount of each component that makes up the final product stream. The LHW process has more water in the final product stream, which is understandable as it begins with a higher input as well. It is important to compare the difference in the total sugars between the two processes. The sugars are the desired product from the pretreatment process, and therefore the process with the higher yield in sugars is more desirable. According to Table 4, the LHW process has a slightly higher fraction of sugars in the final stream than the dilute acid process. While this information is important, it does not yet consider the necessary economic analysis of the two processes.

Variable Costs and Fixed Capital Costs

The focus of this project was to explore the differences and feasibility of two pretreatment methods that are utilized during the production of lignocellulosic ethanol. One of the most important considerations for this project was to understand the costs associated with each of the proposed pretreatment methods. This required an understanding of both the variable and fixed costs of each pretreatment method, breaking down such important costs including equipment, raw materials, and energy usage for the process, among others. Each pretreatment method requires differing raw materials and amounts of such materials, as well as types and sizing of equipment.

The costs of the pretreatment method are broken down into two major categories. The first is the variable costs of the project, such as how much raw material and energy is required to produce the desired product of the pretreatment process. These costs mostly focus on the differences between what is required between the dilute acid process compared to the hot water process. For example, the dilute acid method requires the addition of sulfuric acid in the process, which is one additional raw material cost that the hot water process does not require. Therefore, this is an added cost that is considered when comparing the two processes. The steam usage for heating purposes were also different between the two processes, with the hot water process using almost twice as much steam as the dilute acid process. Table 5 contains a summary of the variable costs between the dilute acid and hot water pretreatment processes. The prices in this calculation can be seen in Table 11 in the appendix.

Category	Units	Dilute Acid	Hot Water
Biomass	\$/hr	24,000	24,000
Sulfuric Acid	\$/hr	190	
Water	\$/hr	240	420
Ammonia	\$/hr	480	370
Steam	\$/hr	1.430	2.250
Total Variable Costs	\$/hr	26,600	27.300

Table 5 – Variable Cost Comparison

The second category to consider is the fixed costs associated with both processes. With respect to this project, fixed costs refer only to the required equipment costs for the dilute acid pretreatment process and the hot water pretreatment process. Table 6 contains a summary of the fixed costs associated with each pretreatment method. As Table 6 shows, the fixed cost of the dilute acid pretreatment process is significantly higher than those of the hot water pretreatment process, specifically driven by the cost of the pretreatment reactor that is required for the process.

Category	Units	Dilute Acid	Hot Water
Pretreatment Reactor		26,000,000	403,000
Blowdown Tanks		163,000	261,000
Ammonia Conditioning		147,000	196,000
Total Fixed Cost		26,310,000	860,000

Table 6 – Fixed Cost Comparison

Further equipment specifications can be found in Table 12 in the appendix. The information gathered from reference materials was scaled using 2019 CEPCI to estimate the most accurate costs of the equipment used for both dilute acid and hot water pretreatment processes. The sizing of the equipment was also scaled as needed for the flow rate of the necessary raw materials into the reactor. An example of the scaling calculations for the equipment costs can be found below:

Cost New $=$ Cost Old x (CEPCI New / CEPCI Old) x (Size New / Size Old) s caling Factor

The fixed capital costs of the project are important to consider, and their costs relative to the whole process decrease over time. Therefore, the costs calculated for the pretreatment section alone are not a good representation of the costs for the entire process though. It's generally agreed that the overall costs for the entire ethanol production process are similar, regardless of pretreatment method, but that's difficult to see given the huge gap in fixed costs between the pretreatment processes. For this scenario, the fixed cost for hot water is less than \$1,000,000 but the cost for dilute acid is more than \$26,000,000. This difference comes almost solely from the cost of the more sophisticated dilute acid pretreatment reactor which requires acid-resistant metals, but is made up for with the cost of downstream equipment in the hydrolysis stages and further. The downstream equipment for the hot water processes is significantly more expensive for two critical reasons. The first is that the hot water pretreatment method doesn't do as effective of a job breaking up the biomass as the dilute acid process, thus requiring more extensive treatment during the hydrolysis stage. The second and most important cost factor comes simply from the fact that there's so much more material coming out of the hot water pretreatment process. Because the hot water process has lower solids, all of the downstream equipment needs to be significantly larger (and more expensive). This wasn't significant for the hot water pretreatment reactor because it's essentially just a large tank, but it becomes a big deal in the more complicated hydrolysis reactor, which is otherwise not considered in this report.

The total variable and fixed costs of each pretreatment method are estimates based on literature and academic studies found online and through their respective vendor estimates. No actual quotes were able to be obtained for this project, leading to the possibility for error in the provided cost information. Sensitivity to costs as well as other variables will be discussed in the following economic analysis.

Economic Analysis

The true costs associated with each pretreatment method require a full techno-economic analysis of the entire ethanol production process. This report is limited to only the pretreatment methods, so the full impacts of each method are not accounted for. Since this report only focuses on a small part of the process, there is no "sellable product" to consider. Also, since there are many financial impacts not within the scope of the project, there is no reasonable way to account for the costs and savings of either method or to consider the time value of money. Instead, the project aims to look at the possible pros and cons of either process in respect to relative cost, safety, efficiency, and feasibility. Since the overall process costs (for the entire ethanol production process) are very similar for both pretreatment methods, it's beneficial to understand what factors could make one pretreatment method more attractive than another. The economic analysis section of this report will focus on what factors drive the costs for each process and the relative impact that each of these have. The goal is to find different scenarios that would clearly benefit one process versus another, which would simplify the otherwise grueling process of selecting a pretreatment method. The different scenarios considered are essentially just a sensitivity analysis to give benefit to one process or another. Variables looked at will include changes in the cost of raw materials, energy, and water, as well as changes in process conditions and biomass flows.

The best way to look at the relative costs of the two pretreatment processes is to compare them on the basis of the same sugar yields. Unfortunately, the pretreatment methods have a wide-reaching impact, and influence the sugar yields not just out of the pretreatment step, but after the hydrolysis step. It is estimated that a typical dilute acid process will have total sugar yields around 90%, and that a typical hot water process will be around 86.5% (Eggeman). This means that the dilute acid process only requires 96.2% of the biomass that the hot water process needs for the same sugar outputs, as shown in Table 7 below.

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Process		Yields after Pretreatment	Yields after Hydrolysis		Total Sugar Yields	
	Xvlose	Glucose	Xvlose	Glucose	after Hydrolysis	
Dilute Acid	90		95.6	85.1	89.9	
Hot Water	50.8	4.5	81.8	90.5	86.5	

Table 7 - Total Sugar Yields

To truly compare the two pretreatment methods and how they react to different variables, the inputs should be based off of the same sugar yields. In this case, scenarios will be based on 100,000 kg/hr of biomass into the dilute acid process and 103,734 kg/hr into the liquid hot water process. The variable and fixed costs for the new base case for each process can be seen below in Figure 6. From this figure, it can be seen that the hot water pretreatment method has higher variable costs but significantly lower fixed costs. The variable and fixed costs for the hot water method are \$28,327/hr and \$885,828 respectively. For the dilute acid method, costs are \$26,605/hr and \$26,230,000.

Dilute Acid			Hot Water				
Basic Process Costs					Basic Process Costs		
	Raw Material Costs				Raw Material Costs		
Biomass	24,267 \$/hr			Biomass	25,173 \$/hr		
Sulfuric Acid		190 \$/hr		Sulfuric Acid		0 \$/hr	
Ammonia		482 \$/hr		Ammonia		382 \$/hr	
	Utility Costs			Utility Costs			
Water		241 \$/hr		Water		438 \$/hr	
Steam	1,425 \$/hr			Steam	2,334 \$/hr		
	Equipment Costs				Equipment Costs		
Pretreatment Reactor		25,920,421		Pretreatment Reactor		414,790	
Blowdown Tanks		162,945		Blowdown Tanks		270,431	
Conditioning (Ammonia)		147,605		Conditioning (Ammonia)		200,607	
Variable	26,605 \$/hr			Variable	28,327 \$/hr		
Fixed	26,230,971 \$			Fixed	885,828 \$		

Figure 6 - Base Case Pretreatment Costs

Now that the base case has been established, certain variables can be manipulated to show what changes would make one process more favorable than another. Variables will include raw material costs, energy costs, and process conditions. Different biomass flows will also be compared to show the economy of scale for each process in regards to the fixed costs.

The most significant cost of pretreatment is the biomass, and that holds true for both processes. Because the hot water method has slightly lower yields than the dilute acid method, the hot water method becomes slightly more favorable as biomass costs decrease. These costs could change based on biomass availability and type of biomass, so a range of price points were explored to see their impact, which is shown in Figure 7.

Figure 7 - Variable Costs vs Biomass Cost

The variable costs for LHW are slightly higher to begin with, but from Figure 7, it can be seen that the difference is narrowed as biomass costs are lowered. The next variable explored was the cost of sulfuric acid, which is shown in Figure 8.

Figure 8 - Variable Costs vs Sulfuric Acid Cost

From Figure 8, it can clearly be seen that the variable costs for the dilute acid process rise as the cost of sulfuric acid increases. Obviously, since sulfuric acid isn't used in the hot water process, the variable cost remains constant. The cost of sulfuric acid is low relative to other process costs, so even a significant change wouldn't have much of an impact on the overall variable costs for the dilute acid process. Similarly, ammonia is used in similar doses for each process, so dramatic price changes don't impact either process much more than the other.

Utility costs have a significant impact on overall cost, which is mainly driven by steam. Water, though heavily used, is relatively cheap and doesn't have a strong impact. If treatment and pumping costs were to increase, the dilute acid process would be favored slightly because it uses about half as much water. Steam costs, on the other hand, are very important, which can be seen in Figure 9.

Figure 9 - Variable Costs vs Steam Costs

From Figure 9, it can be seen that as energy costs rise, the hot water pretreatment is more negatively impacted than the dilute acid process. Because so much more water is used and higher temperatures are required, more steam is used in the hot water process, which makes it more sensitive to price fluctuations.

As discussed in the Variable Costs and Fixed Capital Costs section, the fixed costs of the two pretreatment processes are not a fair indicator of the total fixed costs for the entire ethanol production process. Because of this reason, the relative fixed costs will be used to compare different variables instead of the actual fixed costs. The relative costs are based on a percentage of the given base case scenario, which was \$886,000 for hot water and \$26,231,000 for dilute acid. Variables impacting equipment sizing include dwell time and general flow rates (determined by biomass addition rates). Both variables had a significant impact on the pretreatment fixed costs, and should be fairly representative of cost scaling for the entire process. Dwell times were compared as a fraction of the base case, and results showed that the hot water pretreatment process benefited slightly more than dilute acid from decreased dwell times, which is shown in Figure 12 in the appendix. Changing the production rate is the best representation of how processes are impacted by equipment scaling, and is depicted in Figure 10 below.

Figure 10 - Relative Fixed Costs vs Production Rate

From Figure 10, it can be clearly seen that hot water pretreatment method responds well to downscaling. Due to the economy of scale, the more that's produced, the less the relative cost of equipment, but the processes are impacted by that differently. At 10% production, so if the plant were to be produced on a smaller scale, the relative cost for the hot water process is 16%, compared to the cost of dilute acid at 25% of at 100,000 kg/hr. On the flip side though, if production were increased, the dilute acid pretreatment becomes more attractive. The actual fixed cost for the dilute acid pretreatment is always going to be significantly higher, but Figure 10 shows that the dilute acid option becomes more and more attractive relative to hot water as the production rate is increased. For a large process, it appears that the dilute acid pretreatment method is more favorable, but for a smaller operation or pilot process, it is clear that the hot water pretreatment method is more advantageous.

Feasibility

Safety is considered one of the most significant factors to consider when analyzing the feasibility of this project. In the dilute acid pretreatment process, there is the use of the sulfuric acid in the pretreatment reactor which can be considered a hazardous material. However, the concentrations at which this acid will be utilized are very small and are expected to remain such. Proper handling according to the MSDS should be demonstrated at all times, including the use of mandatory personal protective equipment (PPE). The most significant danger that H2SO⁴ would present is when it's in pure form before being diluted with water. In the LHW pretreatment process, the high pressure required to maintain the hot water in liquid form is an important safety consideration of the process, as well. High pressure systems have the potential for bursts and must be carefully operated and monitored. However, the pressure required to maintain the hot water at the desired temperature is feasible, according to literature reviewed for this project. As for handling of all raw materials during both processes, the safety precautions are very similar, as both require the use of water, ammonia, and the same biomass, and do not pose serious hazards, thus making both processes feasible. Operating safety constraints between the two processes are similar. One common safety consideration between the two processes is the use of ammonia, which is a highly caustic material. While the concentration of ammonia used in the ammonia conditioning step is small, the concentration of the material before entering the process is high and one must use caution when handling this material. The MSDS for this material should be present and followed, utilizing all the necessary PPE. The availability of the raw materials required for both the dilute acid and hot water processes is not considered a risk, as they are common materials that are used in many different applications.

Impacts on the environment were also an important consideration when determining the feasibility of both pretreatment processes explored during this project. The first consideration was the use of biomass and the amount that is utilized in the process, and how harvesting these materials may impact the environment. However, it was determined that the biomass utilized for this process can be a by-product of another industry, such as corn stover or saw dust, which is beneficial to the environment by repurposing what would have been wasted. The water used in the process is sent to a wastewater treatment plant and can be recycled back into the system (Kumar).

When looking at the overall feasibility of the project, the major challenge comes from the overall cost of the pretreatment methods. The processes are possible, and the equipment and technology exist to implement these processes on a larger scale. However, the costs associated with both the dilute acid and hot water processes are too expensive. While the scope of the project did not take into consideration the hydrolysis and fermentation steps to produce the final product, the costs associated with the pretreatment processes alone are significant. Based on the results of this project and factoring in the costs for the hydrolysis and fermentation stages found in literature, it can be inferred that the selling point of the final product will not be low enough for the consumer while still making a profit.

Conclusions:

The objective of this report was not to prepare a proposal for a bio-ethanol plant with all of the associated costs and financial calculations, but rather to provide a direct comparison of pretreatment methods to highlight which factors could make one method more advantageous than another. Numerous studies have been completed on the subject, all of which are significantly more in depth than this report, but few compare the two different pretreatment methods on the same level. This report looks at the relative costs associated with the dilute acid pretreatment method and the hot water pretreatment method, as well as considerations such as safety, efficiency, and overall feasibility. With such information, the goal of this project is to show which pretreatment method is more advantageous given certain scenarios when they otherwise appear to be about equal.

To gain an understanding of the costs for each process, material and energy balances were modeled around process flow diagrams, then costs for the materials and required equipment were calculated. Both processes follow similar steps and go through similar process units. Biomass, water, steam, and, in the case of dilute acid, chemicals are added together in the pretreatment reactor, where they are mixed and stay for a predetermined dwell time. Chemical reactions occur and some of the biomass is broken down and converted into sugars. The slurry then proceeds through a series of tanks where the pressure is decreased, some vapor is removed, and some residual reactions occur. The slurry then goes to ammonia conditioning, where the pH is raised before sending the mixture to the hydrolysis stage. To provide a basis for comparison, the same costs were assumed for each process (ie. same \$/ton for corn stover and steam), as well as the same biomass flow and composition. In this case, 100,000 kg/hr of corn stover was used as an input for both pretreatment methods.

In the dilute acid pretreatment method, sulfuric acid, steam, and water are added to the pretreatment reactor where they mix with the biomass. A total of about 375,000 kg/hr of material comes out of the reactor after a residence time of 3 minutes and a temperature of 180 C. Based on costs from reference material (Humbird, 108), adjusted with scaling factors for time and size, the pretreatment reactor was estimated to cost about \$26,000,000. The slurry, at 13% solids and 16% soluble solids, goes through a series of blowdown tanks where the pressure and temperature are reduced. With an estimated dwell time of 20 minutes through the tanks, the slurry is then pumped to ammonia conditioning tanks, where ammonia is added at a rate of 0.0047 kg NH3 per kg slurry to raise the pH of the solution. After a 20-minute dwell time in the ammonia tank, the slurry is then sent onwards towards the hydrolysis step. At this point, the stream contains about 60,000 kg/hr of target sugars for fermentation (including cellulose and xylose). The total variable cost is \$26,600/hr, and the total fixed cost for this portion of the process is estimated at \$26,231,000.

In the hot water pretreatment method, 4 kg of water is added into the pretreatment reactor for every kg of biomass, creating a much more dilute suspension. The mixture is then heated up to 190 C and held for 15 minutes in the reactor, which is estimated to cost \$415,000. The slurry, with 9% solids and 8% soluble solids and totaling 645,000 kg/hr, then goes through blowdown tanks, similar to those in the dilute acid process. Ammonia is then added, though at a lower addition rate due to the higher pH of the slurry and the fact that it's significantly more dilute. The product stream contains about 64,000 kg/hr of target sugars as it heads to the hydrolysis step. The total variable cost for the hot water pretreatment is \$28,327/hr and the total fixed cost is estimated to be \$886,000.

The Liquid Hot Water (LHW) method saw slightly higher variable costs, but massively lower fixed costs. It is very important to note that the fixed costs for the pretreatment section alone are not a strong representation of costs for the overall process. The massive cost difference almost solely comes from the cost of the more sophisticated dilute acid pretreatment reactor, but the fixed costs are made up for by the LHW process downstream. The LHW process does not break up the biomass as well, and because its streams are so dilute, downstream equipment is required to be significantly larger. This impact isn't seen in the LHW pretreatment reactor, which is essentially a large tank, but is significant in the hydrolysis reactor, which is much more expensive and otherwise not considered in this report. Though the huge fixed cost gap is justified, the equipment costs still provide insight into the fixed cost behavior for both processes and how they respond to different scales. An important part of this project is seeing which conditions would lead to one project being more favorable than the other. With both the processes based off of the same final sugar yield, numerous variables were manipulated to show what would give favor to one of the processes. One important consideration for any process is production rate. As seen in Figure 10, as the production rate is changed, so do the relative fixed capital costs (relative to themselves at 100,000 kg/hr of biomass input). At lower production rates, the LHW process is seen to be more advantageous because it scales down better. Inversely, if production rates were to increase, the dilute acid process is able to scale up with lower relative costs.

Variable process costs are also important to consider, and are driven by raw material and energy costs. The variable costs for the two processes are similar, and in the case of equal sugar yields, the dilute acid pretreatment costs \$26,600/hr and the LHW pretreatment costs \$28,300/hr. The driving cost for both processes is the biomass, which represents almost 90% of the variable costs. Because the LHW process only yields 96% as much sugars as the dilute acid process, it is more sensitive to high biomass costs. The next most significant variable cost is steam. Since the LHW process has more liquid and is run at higher temperatures, it is more sensitive to energy costs. If energy costs were particularly high, conditions may favor the dilute acid pretreatment process. Other raw materials have only a small impact on the overall process, and even significant changes in their price wouldn't result in considerable changes in variable costs. One consideration, though not important in terms of cost, is water usage. The dilute acid method is better in areas if water use is restricted or significantly more costly due to its lower consistencies.

Safety should be a priority when selecting a pretreatment method, and each process has their pros and cons. The dilute acid process requires the use of sulfuric acid in its concentrated form and involves more acidic conditions, but such risks can be managed with the use of proper PPE usage and system design. On the other hand, though less acidic, the LHW process requires higher temperatures and higher pressures in the pretreatment reactor. The pressure and temperature requirements are within reason though, and are able to be managed safely. In terms of safety, neither process shows a clear advantage. Both processes share the same raw materials, with the exception of sulfuric acid, which isn't known to be a risk to the environment. All of the raw materials are commonplace and not a risk to the operational security of either process. In terms of overall feasibility, neither dilute acid nor LHW show any issues - instead, the concern arises in the feasibility of the entire lignocellulosic ethanol production process. The technology exists, but is just not competitive enough with traditional ethanol production methods on an economic level.

Recommendations:

Lignocellulosic ethanol production on a commercial scale isn't feasible at this point because of its overall costs relative to other ethanol production methods, no matter the selected pretreatment method. Regardless, the goal of this report was to determine which pretreatment method in lignocellulosic ethanol production, either dilute acid or hot water, would be advantageous given certain conditions. The overall costs of ethanol production using both hot water and dilute acid pretreatments are very similar, but factors like raw material pricing, energy costs, and production rate give favor to one process over another.

The most significant factor to consider between the two processes is production rate. Lower production rates favor the fixed costs related to the hot water pretreatment method, while more sizable operations favor dilute acid. For example, the fixed cost at 10,000 kg/hr of production is 16% of production at 100,000 kg/hr for hot water, but 25% for dilute acid. Similarly, at 300,000 kg/hr production, the fixed costs are 250% of those at 100,000 kg/hr for hot water and only 200% for dilute acid. The next most important factor to consider is energy/utility costs, which have a significant impact on the variable costs for each process. Since the hot water process uses more water at higher temperatures, it is more disadvantaged by higher utility costs. Other factors include chemical pricing and raw material pricing, but such factors impact both processes equally and wouldn't give the advantage to either one.

Though the demand for bioethanol exists, the processes are currently not competitive with traditional ethanol production methods. If a bioethanol production facility were to be produced through, the most significant factor in selecting a pretreatment method should be the size of the facility. If the facility is to be a pilot plant with biomass use at less than 50,000 kg/hr, hot water is the best choice. If the facility is to be large in scale with production over 200,000 kg/hr, dilute acid is the most attractive pretreatment method.

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Appendix:

Sample Calculations

Material and Energy Balance Calculations:

 Ammonia Addition Rate = Addition Ratio x Solution Flow $= 0.0047$ kg NH₃ / kg Solution x 340,421 kg/hr $= 1,600$ kg/hr NH₃

Equipment Cost Scaling:

Pretreatment Reactor

Size = Total Flow x Volumetric Conversion x Dwell Time

- $= 374,089$ kg/hr x (1hr / 60min) x (1m₃ / 1000 kg H₂O) x 3 min = 18.7 m₃
- $Cost = Cost$ from Reference x (CEPCI New / CEPCI Old) x (Size New / Size Ref) scaling factor $=$ \$20,000,000 x (609.5/525.4) x (18.7 m₃ / 14.1 m₃)_{0.6} $=$ \$25,920,000

Blowdown Tanks

Size = Total Flow x Volumetric Conversion x Dwell Time

- $= 374,089$ kg/hr x (1hr / 60min) x (1m₃ / 1000 kg H₂O) x 20 min = 124.7 m₃
- $Cost = Cost$ from Reference x (CEPCI New / CEPCI Old) x (Size New / Size Ref) scaling factor $= $108,000 \text{ x } (609.5/525.4) \text{ x } (124.7 \text{ m}^3/94 \text{ m}^3)_{0.93} = $162,945$

Conditioning Tank

Size = Total Flow x Volumetric Conversion x Dwell Time

 $= 340,421$ kg/hr x (1hr / 60min) x (1m₃ / 1000 kg H₂O) x 20 min = 114.0 m₃

 $Cost = Cost$ from Reference x (CEPCI New / CEPCI Old) x (Size New / Size Ref) scaling factor $= $236,000 \text{ x } (609.5/521.9) \text{ x } (114 \text{ m}^3 / 278 \text{ m}^3)$ 0.7 $= $147,605$

Figure 1 - Market Share of Ethanol

Figure 2 - Gasoline and Biofuel Consumption Trends

Figure 3 - Wholesale Prices of Gasoline and Ethanol

Figure 4 - **Dilute Acid Pretreatment PFD**

Figure 5 - Hot Water Pretreatment PFD

Figure 7 - Variable Costs vs Biomass Cost

Figure 8 - Variable Costs vs Sulfuric Acid Cost

Figure 9 - Variable Costs vs Steam Costs

Figure 10 - Relative Fixed Costs vs Production Rate

Figure 11 - General Bioethanol Production Steps

Figure 12 - Fixed Cost vs Dwell Time

Figure 13 - Dilute Acid Spreadsheet

Figure 14 - Hot Water Spreadsheet

Tables

Table 1 – Dilute Acid: Composition of Stream Exiting Reactor

Table 2 – LHW: Composition of Stream Exiting Reactor

Table 3 – Comparison of Input Variables

Table 4 – Comparison of Output Variables

Category	Units	Dilute Acid	Hot Water
Biomass	\$/hr	24,000	24,000
Sulfuric Acid	\$/hr	190	
Water	\$/hr	240	420
Ammonia	\$/hr	480	370
Steam	\$/hr	1,430	2,250
Total Variable Costs	\$/hr	26,600	27.300

Table 5 – Variable Cost Comparison

Table 6 – Fixed Cost Comparison

Category	Units	Dilute Acid	Hot Water
Pretreatment Reactor		26,000,000	403,000
Blowdown Tanks		163,000	261,000
Ammonia Conditioning		147,000	196,000
Total Fixed Cost		26,310,000	860,000

Table 7 - Total Sugar Yields

Biomass Component Mass Fractions		
Cellulose	0.334	
Xylan	0.222	
Other Hemi Sugars	0.060	
Lignin	0.107	
Ash	0.059	
Acetate	0.054	
Other Components	0.163	
Moisture Content	0.250	

Table 8 - Biomass Mass Fractions

Dilute Acid Pretreatment Reactor Conversions				
Cellulose + H20 --> Glucose	0.099			
Cellulose -- > Glucose Oligomers	0.030			
Cellulose -- > HMF + H20	0.030			
Xylan -- > Xylose Oligomers	0.210			
Xylan + H20 --> Xylose	0.600			
Xylan -- > Furfural + 2H20	0.110			
Acetate -- > Acetic Acid	1.000			
Lignin -- > Soluable Lignin	0.100			

Table 9 - Dilute Acid Pretreatment Reactor Conversions

Table II- Naw Material and Uthily Costs					
Dilute Acid - Material and Utility Costs					
Biomass (Corn Stover)		182 \$/1000kg			
Sulfuric Acid		43 \$/1000kg			
Ammonia		301 \$/1000kg			
Water		0.90411 \$/1000kg			
0.13 $\frac{\text{S}}{\text{K}}$ Wh Eletrical					
Steam		22.64 \$/1000kg			

Table 11- Raw Material and Utility Costs

Table 12 - Equipment Specification Lists