Process Design Considerations for the Production of Ethanol

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Abstract

This paper details the conversion of bio feedstock to fuel grade ethanol on an industrial scale through thermochemical ethanol production. This conversion process includes preparation of sugarcane bagasse, conversion of sugarcane bagasse to syngas through a gasifier, cleaning of the syngas, conversion of the syngas to ethanol via catalytic-based conversion, and extracting the ethanol using distillation columns. This continuous process produces 590lb/hr of 99.8% ethanol.

Objectives

The objective of this paper is to design an efficient continuous process to produce 99.8% ethanol at a rate of 590 lb/hr.

Introduction

Henry Ford once said, “The fuel of the future is going to come from fruit like that sumac out by the road, or from apples, weeds, sawdust – almost anything.” In 1925, reporting to a New York Times reporter, Ford claimed that ethyl alcohol was the fuel of the future. Ford built his first automobile that ran off of pure ethanol in the late 1800’s. From here, there was room for improvement and multiple doors opened for others to go through and continue this trend on using biofuels. In order to help ethanol production, technology was created with the main purpose to be more cost effective, environmentally beneficial, and to have a greater energy output to input ratio (Solomo).

Ethanol is a clear, odorless chemical made from the fermentation of plant sugars from biomasses and agricultural crops. It is an ecological fuel, as it is obtained from renewable energy sources. Ethanol also known as ethyl alcohol or grain alcohol can be abbreviated as EtOH. Its chemical formula is CH₃CH₂OH and it belongs to an organic class of compounds known as alcohols. Ethanol has many different functions (Ethyl Alcohol). It can be used by industries as a solvent in the synthesis of other organic chemicals and it can be added to gasoline to produce a fuel with higher-octane levels and fewer harmful emissions than unblended gasoline. Ethyl alcohol is also the intoxicating factor in many alcoholic beverages such as beer, wine, and distilled spirits (West).

In the 1850’s ethanol was used as a burning fluid. However twelve years later in order to fund the Civil War the U.S. Congress imposed a two-dollar tax on ethanol, making it too expensive for an average families everyday use. When President Theodore Roosevelt came into office he passed the Free Alcohol Bill making ethyl alcohol cheaper than gasoline once again. During World War I (1917-1918) the demand for fuel rose exponentially, thereby increasing the demand for ethyl alcohol. During this time sixty million gallons of ethanol was being used.
Prohibition brought the rise of ethanol use to a halt. The 18th Amendment only allowed for ethanol to be sold when mixed with five percent of petroleum. Gasoline became the most widely used motor fuel from the 1920’s to around the year 1934 when Congress passed tax incentives to promote ethanol production and reduce unemployment among farmers. Prohibition was repealed. When World War II came, it hiked up the demand for ethanol to be used for aviation fuel and synthetic rubbers. By the 1950’s citizens realized that foreign oil fuels were cheaper than the commercial ethanol being produced in the states. With the start of Nixon’s “Project Independence” in 1974, he was able to reach total independence from foreign energy sources by 1980. Jumping forward to the year 1990, there was a push to reduce the cost of ethanol production by using plants such as corn and sugarcane as feedstock. This increased the production of ethanol to around one billion gallons per year. The vehicle industry began producing more vehicles that could run on a blend of 85% ethanol and 15% gasoline (Cole). Also, farmers altered their land use decisions in response to the high demand for corn and soybeans to be used as ethanol feedstock (Wallander).

The reason for the increased production of ethanol in today’s world is because of the benefits it offers us compared to those of gasoline. Anhydrous ethanol has a purity of at least 99% and is the standard ethanol used as motor fuel because it is an excellent alternative clean burning fuel as opposed to gasoline. Ethanol has the potential to achieve very low emission levels in properly designed automotive systems, and the combustion products are considered to be environmentally safe from a greenhouse standpoint (Kumar). In an article titled “When is Pure Ethanol Attractive as a Fuel Option? Quantifying the Gasoline vs. Ethanol Dilemma Faced by Consumers in Brazil”, ethanol is also said to be more “cost-efficient and technologically mature.” Today, the United States and Brazil are the top two producers of fuel ethanol worldwide (Solomon). Brazil’s focus has been to reduce their dependence on oil imports and the United State’s focus has been to promote ethanol production to promote agriculture. In Brazil 20% of anhydrous ethanol is blended with gasoline, and in the United States ethanol is blended with gasoline to form an E10 blend. This is a blend of 10% ethanol and 90% gasoline. Because of ethanol’s high octane levels it makes it a great blending component with gasoline because it helps to keep vehicle fuel systems clean for optimal performance and it helps vehicles run more smoothly. One downfall of ethanol is that it has a higher heat of evaporation than that of gasoline so ethanol-filled engines may develop cold-start problems. However, ethanol has a lower flame temperature than gasoline; therefore it reduces the nitric oxide emission yield. Also unlike gasoline, ethanol contains 35% oxygen so that less air is needed for combustion. This helps to reduce carbon monoxide, volatile organic compounds and toxic emissions that can pose as a health hazard, particularly to children and seniors. In groundwater, surface water, and soil ethanol is quickly biodegradable. Because ethanol is a renewable fuel, it drastically helps to reduce emissions of several greenhouse gases that contribute to global warming. All together ethanol helps to reduce pollution levels (Kumar).
General Flow Chart
Final Flow Chart
Ethanol Production

Production Summary

The conversion of bio feedstock to fuel grade ethanol is a multistep process involving variable raw materials and unit operations. Industrial companies capitalize on older conversion processes discussed in current production trends; however, progressive developments have increased the efficiency of specific unit operations while reducing environmental impact due to byproduct disposal. Development of a superior conversion process involves careful consideration and integration of the most cutting edge technologies currently available.

The ideal conversion process begins with the selection, washing, and preparation of feedstock. Wet or dry feedstock chips are then broken down by means of hydrolytic or thermochemical breakdown, resulting in the production of a liquid mixture of impurities and desired products. This fluid is cleaned up and undergoes fermentative or catalytic conversion to an unpolished form of ethanol. Finally, water is removed through distillation or dehydration and results in the production of fuel grade ethanol.

Current Production Trends

![Graph showing biofuel production methods](image)

**Figure 1**: Current biofuel production methods installed or under construction in the United States (Dwivedi)
In a critical review of current conversion technologies in Figure 1, Dwivedi et. al. compares the output of multiple operations currently set up in the United States including:

- Concentrated Acid Hydrolysis
- Dilute Acid Hydrolysis
- Organosolve
- Gasification, fermentation, and distillation
- Gasification catalytic conversion, and distillation
- Enzymatic hydrolysis
- Simultaneous saccharification and fermentation

Concentrated acid hydrolysis is one of the several processes. To achieve near-theoretical yields, cellulose undergoes concentrated acid decrystalization followed by dilute acid hydrolysis (Concentrated Acid Hydrolysis). Downfalls of this process are the excess amounts of concentrated acids, expensive cost, and disposal problems (Janga).

Dilute acid hydrolysis is one of the oldest methods for converting biomass to ethanol. In order to get the maximum yield the hydrolysis part must be completed in two stages. First, is a process under mild conditions to hydrolyze hemicellulose and the second stage is a little harsher because it is optimized to hydrolyze the more resistant cellulose fraction. From each of these steps liquid hydrolyzates are recovered. They are then neutralized, and fermented to ethanol. The pros of dilute acid hydrolysis is that this process reaction occurs in seconds or minutes, about less than one percent of acid is used, and neutralization is relatively easy. While the pros would persuade one to choose that process it does have several cons that outweigh the pros. Some of the cons of dilute acid hydrolysis are that it requires processing under pressure and it also is limited to smaller yield around fifty gallons per dry ton. Also another con is that the combination of acid, pressure, and high temperatures require that exotic metals be used (Dilute Acid Hydrolysis).

Future Biofuels for Australia states that, “The organosolve pretreatment process involves cooking the raw biomass in acidified (usually with hydrochloric or sulfuric acids) aqueous ethanol under various pH, temperature, pressure and time conditions.” Using a solvent-to-wood ration of 7:1 or 10:1 has been proven to yield a biomass product with less lignin. Not only does it give you a product with less lignin but it also yields a clean lignin product that adds value to the final product. A disadvantage of using the organosolve technique is that it uses solvents and acids but these can be recycled to some extent (Warden).

A very efficient way of producing ethanol is through the processes of gasification, fermentation, and distillation. Gasification uses a minimal oxygen level that is combined with steam and cooked under very intense pressures. Under these conditions it initiates a set of reactions that create a gaseous mixture of primarily carbon monoxide and hydrogen (Harris). This mixture is known as syngas or synthetic gas and can then be transported to the fermentation step of the process. Fermentation is an anaerobic metabolic breakdown of nutrient molecules
without net oxidation. Basically it is a sequence of reactions that release energy from organic molecules in the absence of oxygen. In the step, it breaks down the syngas into ethanol and water. Nutrients are then added to help with maximize cell growth and automatic regeneration of the biocatalyst. The resulting stream of ethanol is sent to the distillation stage. Here, adding heat to them separates the fermented ethanol and water that remains. Ethanol evaporates faster than water so the ethanol rises through a tube and condenses into another container and the water is left behind. The final product is pure ethanol (Martin).

Gasification catalytic conversion and distillation is a process that starts with gasification where the conversion of biomass in steam or oxygen is used to produce gas. After going through the gasifier, the product, or syngas (mixture), must then go through the catalytic conversion process, also known as Fischer- Tropsch, where different compounds can be produced. Next is distillation. This physical step is for separation to get the final product of ethanol. A positive to this entire process is that the gas is cleaned. The distillation process is in energy-intensive step. In other words, you start with a lot and end with a little (Badger).

According to a review titled “Enzymatic Hydrolysis of Cellulosic Biomass,” “biological conversions of cellulosic biomass to fuels and chemicals offers the high yields to products vital to economic success and the potential for very low costs.” The process, enzymatic hydrolysis, has its pros and cons. Due to the dealings of substrate and enzyme related effects, this process or step is complex. This has led to small success in high sugar yields at low costs. Enzymatic hydrolysis is manipulated by cellulose structure and the mode of the enzyme’s action. It is a multi-step where cellulose is broken down into its solid and liquid components endoglucanases and exoglucanases. This is followed by the “liquid-phase hydrolysis of soluble intermediates…which are catalytically cleaved to produce glucose by the action of β-glucosidase (Yang). In simplest terms, the process is pretreatment, where then a cellulose enzyme is added at the enzymatic hydrolysis step where lignin is produced. Next, is fermentation followed by distillation and finally, stillage (Badger).

In a review “Plants to Power: to Bioenergy to Fuel the Future,” saccharification is “the release of products such as cellulobiose and glucose from cellulose via chemical hydrolysis or enzymatic reactions.” Fermentation is the “conversion of sugars into ethanol by microorganism under anaerobic conditions.” Simultaneous saccharification and fermentation, SSF, produces ethanol by improving the yields of those produced by hydrolysis and fermentation separately. It is a method that converts the sugar to products in a single reactor versus several different ones, like described in the previous technologies above (Rohowsky). In the same review stated above, an advantage of SSF is reducing the cost of lignocellulosic ethanol production. In performing this separately, the steps occur at optimum conditions (Hahnhagerdal). Each of these technologies create a final product of ethanol; however, due to their negatives, our chosen methods outweigh the technologies cons, which will be further discussed in a later section.
Raw Materials

Feedstock Selection

Feedstock selection begins with careful consideration of the cost to extract and convert organic material to biofuel. The most prevalent and reliably convertible source of organic material exists in the form of carbohydrates including cellulose, hemi-cellulose, sucrose, and starch (Department of Energy). Feedstock option possesses a specific percent mass of each carbohydrate resulting in differential percent yields of ethanol. The percent mass of each carbohydrate type varies in different plants and offers a basis of comparison while selecting among feedstock options. Each type of carbohydrate has an associated conversion capacity, so it would seem the ideal feedstock contains the largest percent mass of the carbohydrate possessing the greatest conversion capacity and smallest production cost; however, governmental regulations have been created which limit the overall yearly biofuel production from any one major carbohydrate source. For example, the major carbohydrate source available in corn is starch based, and the use of corn as a feedstock has been regulated by the government for a good reason. As the production of biofuels from corn becomes more efficient, the utilization of corn as a feedstock becomes more prevalent and increases the demand for livestock feed, thereby, driving the price of other consumer goods. These types of governmental regulations create opportunities for the production of biofuels from a variety of feedstock containing a high percent mass of carbohydrates other than starch. As a result, various feedstock options are under investigation and could possibly result in agricultural stimulation in each region of the United States where optimal growing conditions are present for specific feedstock options.

Our final feedstock selection will be catered toward stimulating local economic growth and generation of jobs in Louisiana. The simplest solution involves integration of Louisiana’s previously established agricultural infrastructure. As a result, we consider Louisiana’s top produced crops in order to minimize feedstock costs. The Department of Administration has concluded “Louisiana is among the top ten states in the production of sugar cane (2nd), sweet potatoes (2nd), rice (3rd), cotton (5th) and pecans (5th)” (Louisiana Industry). Of these crops, sugar cane shows promise as a future competitor for the top feedstock in ethanol production. Corn is the most utilized feedstock source in America; however, the Renewable Fuels Standard limits the production of starch based ethanol to 15 billion gallons (Department of Energy). By 2022, this standard demands fuel producers to create 37 billion gallons of biofuels per year (Mark). Limitations set by this standard create a marginal gap in the required biofuel production and opens an opportunity for sugar cane to sneak its way to the top as a regional feedstock source; however, in its current production state, sugar cane cannot fulfill this position. In a critical review of cellulosic ethanol production in Louisiana, Tyler Mark refers to energy cane, a selectively bred variation of sugar cane containing a larger fiber and smaller sucrose content relative to traditional sugar cane breeds (Mark). He explains the larger fiber content translates to a greater biofuel yield and even refers to a specific energy cane variety with the potential to
produce 65 more tons of biomass per acre than traditional sugar cane (Mark). Innovation like this is required before sugar cane can compete with corn. Finally, we consider lolly pine as a potential feedstock due to its prevalence in the southern region of the United States. The chemical constituents of lolly pine are examined in Table 1 (Dwivedi).

![Table 1: Chemical constituents of lolly pine (%) (Dwivedi)]

Depending on the conversion process, anywhere from 63.2 to 90% of lolly pine can be converted to biofuel (Dwivedi). Because lolly pine is not utilized as a food source, it offers a great potential as a cheap alternative feedstock and will be considered in our final decision. In conclusion, the ideal feedstock is converted to the largest volume of biofuel for the smallest possible cost. Current standards limit the use of specific crops as feedstock in order to minimize the inflation of food costs for the everyday consumer. The ideal feedstock will not come from a single source, but rather a variety of crops grown specifically to maximize the biofuel production. Furthermore, it appears the Renewable Fuel Standard demands a production rate no single region can handle. If this is true, multiple regions harvesting a variety of crops will be required to meet the standard.

**Feedstock Preparation**

Preparation of feedstock begins with washing and reduction in size. Washing is the first step in removing unwanted impurities that may retard downstream operations, and can potentially lead to the destruction of expensive equipment. Feedstock is then reduced in the size using a grinder, chipper, wet mill, or an equivalent method. It appears each specific conversion technology has its own optimal chip size, but none of them are greater than 0.1 mm (Mondal). Reduction in size increases surface area exposed during the conversion step. Without this step, conversion of the feedstock would not be timely and the overall process would not be profitable. At this point, the material will be broken down by thermochemical or hydrolytic means.
Conversion

The “conversion step” depends on the process of choice. These steps convert the solid feedstock into a fluid that is prepared for fermentation.

![Diagram of hydrolysis-based cellulosic ethanol production technologies](image)

**Figure 2:** Diagram of hydrolysis-based cellulosic ethanol production technologies (Dwivedi)

Hydrolysis based conversion technology

As stated above, two major methods of feedstock conversion include hydrolysis and thermochemical technologies. Figure 2 shows a generalized flow chart diagram of hydrolysis-based cellulosic ethanol production technology. In general, hydrolysis based ethanol conversion is a two-step process. The feedstock must undergo pretreatment before it can be converted to ethanol. Pretreatment is broken up into two steps. In both steps, the feedstock is exposed to various factors and conditions. Any introduced factors should be removed as early as possible to prevent high production costs. The first pretreatment step hydrolyses hemi-cellulose and some cellulose into monosaccharides in one of the following methods: thermal pretreatment, acid pretreatment, alkaline pretreatment, oxidative pretreatment, organosolve pretreatment, or biological pretreatment (Dwivedi). The first pretreatment step also breaks lignin bonds holding the plant material together and converts the feedstock to slurry that is able to continue through the process. Of these pretreatment methods, Dwivedi explains the most favorable includes acid pretreatment as it can simply be neutralized before the fermentation step. The fluid flows into a separator where solids and liquids are separated. Liquids flow through a filter where contaminants and impurities are removed. The filtered slurry is ready for fermentation. Any remaining solids move on to second stage hydrolysis. The remaining solids are composed mostly of lignin and remaining cellulose. Second stage hydrolysis may be achieved through acid
hydrolysis or enzymatic hydrolysis. At this point, the remaining solids are broken down and separated. The liquid slurry continues on to be fermented. Hydrolytic conversion is currently utilized in most industrial scale operations. Some of these industries were founded on primitive technologies, and are due for an upgrade. It might even be possible for some of these companies to integrate new technologies into their existing process to increase efficiency or even reduce environmental impact.

**Figure 3:** Diagram of cellulosic ethanol production through gasification technology (Dwivedi)

**Thermochemical Conversion Technologies**

Thermochemical breakdown takes place in a gasifier. During the gasification process, large carbohydrates are broken down to syngas consisting of simple monomers of carbon monoxide, hydrogen gas, and carbon dioxide. These simple molecules will be converted to ethanol further down the line. Some common gasifiers include fixed bed gasifiers, fluidized bed gasifiers, and entrained bed gasifiers. Each of these operate at specific temperatures and pressures. Due to biomass containing a large percentage of volatile matter, the temperature at which thermochemical breakdown takes place ranges from 800-900°C (Mondal). A flowchart diagram describing the generalized gasification process is shown in Figure 3 and a generic gasifier is shown in Figure 4.
Gasification begins with feedstock entering from the top of the gasifier. Pressurized gasifiers require feedstock chips to be converted to a fluid before entering the chamber. As the feedstock falls, it is dried and pyrolysed by reacting with steam or carbon dioxide (Mondal). Gasification may act to reduce the emission of greenhouse gases due to the use of carbon dioxide. Heated gas present in the reduction zone acts to gasify the feedstock and char falls out. Various gasses have been tested and optimized for use in different gasifiers (Mondal). Some of these gasses include steam, oxygen, air, or a mixture. Remaining char falls into the oxidation zone where it is combusted by the hottest temperatures. Combustion of char produces ash, which may exit the gasifier or float around in the newly formed gas, exits the gasifier. The exiting gas is called syngas and contains a combination of organic gasses at a high temperature. To reduce the heating costs associated with gasification, some gasifiers utilize the energy from the heated gas to preheat incoming feedstock (Mondal). The exiting gas is cleaned by removal of remaining char and ash. The cleaned syngas is sent to a conversion chamber where various methods will turn it into ethanol.

In general, gasification is a relatively simple process and results in the complete reduction of incoming fuel. This idea leads to its superiority over hydrolysis technologies as a conversion technology. Ultimately, the final product of both processes is now ready to be converted to ethanol.

**Purification**

Ethanol synthesis is the heart of the ethanol production process. After syngas is produced from the gasifier, it is cleaned and cooled in preparation to enter the ethanol conversion chamber.
While in the chamber, the syngas is converted to ethanol via either fermentation or catalyst-based processes.

The conversion of syngas into ethanol through fermentation has several advantages over catalytic conversion, including (a) higher specificity of the biocatalyst resulting in less side products; (b) elimination of costly enzymes and lower energy costs; (c) greater resistance to catalyst poisoning; (d) independence of H₂:CO ratio for bioconversion (Henstra) (Munasinghe).

Catalytic based ethanol synthesis

Before the syngas enters the chamber, it is treated to meet the requirements of the particular catalyst that is being used. This includes the removal of particulates, tars, and concentrations of acid compounds as well as the adjustment of the H₂:CO ratio. Lastly, the clean syngas stream is compressed to the reactor pressure depending on the catalyst (Van Der Heijden). When prepared, the gas enters the reactor where it goes through a network of chemical catalytic reactions. The production of ethanol via direct synthesis (involving hydrogenation of CO) or methanol synthesis followed by methanol homologation is accompanied by multiple side reactions. The side reactions lead to various by-products including acetic acid, methane, C₂-5 alkanes and olefins, aldehydes, ketones, and esters (Van Der Heijden).

The most commonly used catalysts are Rhodium-based and MoS₂-based Dow chemical catalysts (Van Der Heijden). Their properties are specified in Table 2 (Van Der Heijden). The MoS₂ catalyst operates at a higher reactor pressure of 104.5 bar but at a lower H₂:CO molar ratio of 0.980. Both catalysts require a similar temperature of about 303°C. Rh-based catalysts produce mainly water and methane as byproducts, whereas MoS₂ based catalysts produce methanol and carbon dioxide.

### Table 2: Selected catalysts for the direct conversion of syngas to ethanol (Van Der Heijden)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rhodium-based (Ru)</th>
<th>Molybdenum-disulfide based (MoS₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar</td>
<td>bar</td>
</tr>
<tr>
<td>H₂/CO molar ratio</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO conversion</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Carbon selectivity</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Methane</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Ethane</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Methanol</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Propanol</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Butanol</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>CO₂</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Oxygenates C₄</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>H₂O</td>
<td>wt%</td>
<td>wt%</td>
</tr>
</tbody>
</table>

*a Carbon selectivity is defined as the moles of carbon present in a product fraction divided by the total moles of carbon in all products excluding unconverted feed.
*b Water is calculated as weight percent of the liquid phase.
Researchers in the Chemical Engineering Department at Eindhoven University of technology performed an exergy analysis comparing the exergetic efficiencies of the catalysts discussed above, Rhodium and MoS2. Figure 5 shows the ethanol only based efficiency ($\Psi_1$), ethanol plus steam and electricity generation based efficiency ($\Psi_2$), and ethanol plus steam and electricity generation plus by-products based efficiency ($\Psi_3$) (Van Der Heijden). The MoS2 based catalyst had higher exergetic efficiency $\Psi_3$ due to its extra by-product.

![Exergetic efficiencies for different catalysis](image)

**Figure 5:** Exergetic efficiencies for different catalysis (Van Der Heijden)

The chemical reactions in the synthesis reactor are exothermic and produce heat. Therefore, the effluent (product stream) leaving the reactor is cooled down to 40°C before it is sent to distillation for ethanol recovery.

**Fermentation based ethanol synthesis**

After the syngas leaves the gasifier, it must be cleaned and conditioned to remove unwanted pollutants like solid particles and tar. The purified syngas then enters the bioreactor to be fermented by mesophilic microorganisms. This species of biological catalysts convert CO and H$_2$ (the key components of syngas) to acetic acid, ethanol, and other byproducts using the acetyl-CoA pathway (Munasinghe). This is a pathway of carbon dioxide fixation used by obligate anaerobes.

One of the more commonly used microorganisms in production of ethanol is *C. ljungdahlii*. The reported ability of an ethanol to acetate production ratio of about 1:20 in the ‘wild’ state of the microorganism has interested various researchers (Mohammadi). A research team at the Tarbiat Modares University monitored the effect of gas composition and culture pH on the cell density and the conversion efficiency in the continuously stirred tank reactor (CSTR). They compared their results to the findings of others to produce Table 3 (Mohammadi). The maximum acetate and ethanol production were with a syngas composition of 55% CO, 20% H$_2$, 10% CO2.
It is believed that pH was able to produce ethanol from H. The growth stage and production of ethanol and NAD(P) during the conversion of acetic acid and adenosine triphosphate (ATP) during the final to ethanol via alcohol dehydrogenase (ADH).

After fermentation is complete, the liquid is sent to distillation in order to separate the organisms and growth. They controlled the net carbon recovery in the products and cells was recovered by coupling the process with a heat recovery system.

**Table 3:** Table displaying composition of ethanol and acetate production (Mohammadi)

There are multiple types of bioreactor designs used today. The most common reactor employed in syngas fermentation is the continuous stirred-tank reactor. Due to its high level of mixing and rotational speed of the impellers, the gaseous substrate becomes highly accessible to the microbes. Also, long gas retention in the aqueous medium due to the slow rising velocity of fine bubbles makes for high mass transfer rates (Mohammadi).

Optimal growth conditions in the reactor vary for biological catalysts as shown in Table 4 (Munasinghe). For the microbes producing ethanol, the favorable operational temperature is about 38 °C and pH range is 5.7-7.2 depending on the microorganism.

After fermentation is complete, the liquid is sent to distillation in order to separate the ethanol from the other products.

<table>
<thead>
<tr>
<th>Bioreactor configuration</th>
<th>Gas composition (v/v %)</th>
<th>Culture pH</th>
<th>Cell density (g L⁻¹)</th>
<th>Conversion efficiency</th>
<th>Product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTR (30 days)</td>
<td>CO/H₂/CO₂/Ar (55:20:19:15)</td>
<td>4</td>
<td>2.34</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 98%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 100%</td>
<td>6.50 g EthOH L⁻¹</td>
</tr>
<tr>
<td>CSTR (105 days)</td>
<td>CO/H₂/Ar (70:15:15:15)</td>
<td>4</td>
<td>2.10</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 96%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 100%</td>
<td>5.43 g Ac L⁻¹</td>
</tr>
<tr>
<td>CSTR (105 days)</td>
<td>Pure CO</td>
<td>4</td>
<td>1.92</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 83%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 100%</td>
<td>4.46 g EthOH L⁻¹</td>
</tr>
<tr>
<td>Cell-recycled CSTR (560 h)</td>
<td>CO/H₂/CO₂/Ar (55:20:19:15)</td>
<td>4.5</td>
<td>4</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 90%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 70%</td>
<td>3.43 g Ac L⁻¹</td>
</tr>
<tr>
<td>ICR*</td>
<td>CO/H₂/CO₂/N₂ (13:14:68)</td>
<td>4.9</td>
<td>0.18</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 100%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 78.6%</td>
<td>2.82 mol EthOH mol⁻¹ Ac</td>
</tr>
<tr>
<td>CSTR</td>
<td>CO/H₂/CH₄ (45:50:5)</td>
<td>5.05</td>
<td>Na</td>
<td>X&lt;sub&gt;CO₂&lt;/sub&gt;: 85%</td>
<td>X&lt;sub&gt;H₂&lt;/sub&gt;: 50%</td>
<td>5.60 g Ac L⁻¹</td>
</tr>
<tr>
<td>Liquid batch, continuous gas (4 h)</td>
<td>CO/H₂/CO₂/N₂ (20:10:20:50)</td>
<td>6.8</td>
<td>0.562</td>
<td>Na</td>
<td>4 mol EthOH mol⁻¹ Ac (2°C)</td>
<td>0.29 mmol EthOH g⁻¹ h⁻¹</td>
</tr>
</tbody>
</table>

* ICR: Immobilized cell reactor.

**Table 4:** Table displaying examples of microorganisms and growth conditions (Munasinghe)
Polishing

The polishing of ethanol involves a separating step to achieve fuel grade ethanol, which is greater than 99.2% (Sato). After the product goes through the ethanol conversion chamber, the liquid must enter distillation to separate ethanol from the other products, such as other alcohols, unconverted gases, and water (Van Der Heijden). This can be seen in the General Flowchart on page 6. An example of a distillation column is shown in Figure 6. A mixture of two liquids is submitted into the distillation chamber, each having a specific volatility. The liquid with a higher volatility, or lower boiling point, will reach a vapor stage first and appear in the overhead product. This is one of the most important steps in the separation process because it allows the separation of the mixture in large-scale amounts (Ravagnan). While it is the most efficient separation process, careful consideration must be given to temperature. It has to be in between the boiling points, so that one liquid will evaporate with the other liquid remains in the bottom tray. However, it does not separate perfectly and will contain small percentages of the other liquid. Dehydration then occurs to produce fuel grade ethanol by removing the remaining water to the preferred quality of ethanol (Dwivedi). Because there are many distillation and dehydration processes, the methods in consideration are the most feasible for the production of ethanol.

![Figure 6: A diagram of a typical distillation column (Distillation Column)](image-url)
**Extractive Distillation**

*Extractive Distillation with Liquid Solvent*

Extractive distillation with a liquid solvent is used to separate ethanol from a mixture of ethanol, water, and other liquids. The addition of a liquid solvent is needed with two or more components in the mixture have volatilities that are around the same temperature. The liquid solvents can be ethylene glycol, diethyl ether, toluene, and furfural. The ethylene glycol produces a high quality of product and is more suitable for large-scale production. However, the disadvantage is the high feed ratio of 5:1. The process includes placing the liquid solvent above the ethanol feed tray. The liquid solvent enhances the volatility of one of the feed components more than the other, depending on the composition of solvent. The best solvent would be one that enhances the volatility of the ethanol, so that the ethanol appears in the overhead product. The solvent must then be separated from the bottom product for recycling (Kumar). A diagram of this process with ethylene glycol is shown in Figure 7.

![Diagram of extractive distillation with ethylene glycol](image)

**Figure 7**: A diagram of the extractive distillation with ethylene glycol (Kumar)

*Extractive Distillation with Soluble Salt*

Extractive distillation with a soluble salt is used in the same process as a liquid solvent. The difference is the effect of the salt on the liquids, making it less volatile or increasing the boiling point (Kumar). The higher volatile liquid will appear in the overhead product, while the remaining liquid and salt remain in the bottom product (Rong). An advantage is that the salt is completely removed in the bottom product and requires less energy to remove. It also has a lower toxicity level to the liquid solvents. Some examples of the salts used are calcium chloride, cobalt chloride, strontium bromide, nickel chloride, cupric chloride, sodium acetate, potassium
acetate, calcium nitrate, sodium and potassium iodides, glucose, mercuric chloride, and cupric chloride. Extractive distillation can be expensive and has high-energy consumption (Kumar).

Azeotropic Distillation

Azeotropic distillation involves adding another that has the same volatility of the other liquid in the mixture. The difference in polarity forces the additional substance to form an azeotrope with one of the components of the ethanol mixture. This additional liquid is called an entrainer. The most commonly used entrainer is benzene. The mixture is distilled, where highly concentrated ethanol is fed out of the bottom tray. The overhead product reaches the decanter, and the entrainer is recycled back into the azeotropic distillation column. The rest of the mixture in the container is introduced into the stripping column where ethanol and entrainer are recovered. The reboiler is one of the most critical parts because trace amounts of water and isoctane can be found in the mixture. Disadvantages with this include high capital cost, high energy consumption, toxicity of chemicals, and sensitivity to feedstock. The high energy consumption is for maintaining and recirculating the large quantities of entrainer. Additional consideration must be given to the storage of the ethanol. Pure ethanol can absorb water from the atmosphere and dilute the product (Kumar). A diagram of azeotropic distillation is shown in Figure 8.

Figure 8: Diagram of Azeotropic Distillation (Kumar)

Solar Distillation

Solar distillation uses fatty acids from vegetable oils as a liquid solvent. This process can be used to concentrate until 80%. This is a specific case where further polishing is required in order to obtain a high quality ethanol. Because it does not give us the desired quantity, higher costs for further distillation would make this not a desirable choice. Solar distillation is a natural process that has recently been proposed (Ravagnani).
**Chemical Dehydration**

Chemical dehydration uses substances like quicklime, calcium chloride, or potassium carbonate to form hydrates with water; therefore, this leads to the separation of ethanol. The most common method is dehydration using quicklime. The ethanol and water mixture is mixed with quicklime. The reaction of the additive and water forms calcium hydroxide after 12-24 hours of settling, while stirring occasionally. This new hydrate is insoluble in the ethanol and denser than ethanol. The settling allows the hydrate to stay at the bottom of the container, while the ethanol remains at the top. Distillation is then needed to separate the ethanol from the rest of the products with a temperature at the boiling point of ethanol (78.38°C). A less desirable alternative is be decanting and filtering the ethanol manually. The calcium hydroxide can be recycled. This batch process is expensive and required high energy, but has a recovery of 97-98% (Kumar).

**Chosen Methods**

**Raw Materials**

**Feedstock Selection and Facility Location**

As residents of Louisiana, our desired product will stimulate economic growth and drive the synthesis of new job opportunities. Due to its large agricultural influence in Louisiana, post processed sugar cane bagasse will be utilized to create biofuels. Louisiana has a short growing season for sugarcane, so the demand for feedstock may not be met by bagasse alone. Energy cane is also considered as a potential feedstock, as its growing period is longer than that of sugarcane. A combination of the two feedstocks should meet the feedstock demand; however if it does not, the location of the facility should promote the use of alternative feedstock options.

A vast majority of the cost create biofuels comes from the price to ship feedstock. The biofuel factory will be located somewhere in Louisiana’s Sugarcane Belt in order to minimize this cost. This will allow the facility to receive the maximum amount of sugarcane bagasse and energy cane while ensuring its proximity to alternative feedstock production sites. In an economic analysis of feedstock, pricing strategies, and location strategies, Mark Taylor explains the ideal location for a factory is located in St. Landry Parish (Mark, Taylor). In his analysis, he assumes the mode of transportation to be by dump truck. This assumption takes into account the transportation cost between parishes which can become expensive as the feedstock is supplied from parishes farther from the facility. In order to lower this cost, our facility will be located close to the railroad running through Opelousas, Louisiana. Due to the scale of the operation, the 36 acres located at Opelousas, LA 70570 will be purchased. Any extra land will be sold or maintained for future renovation and expansion.

Once the land that is purchased, a large metal building will be constructed near the road. The size of the building will match that of a pilot ethanol production facility ran by Southern Illinois University (*The NCERC at SIUE: Advancing Biofuels Research*) and will be about 24,000 sq. ft. 10% of the cost of the metal building will be incorporated for the cost of utility setup and preparation of the area surrounding the building.
Prior to biofuel production from sugarcane, bagasse was considered waste and was typically burned to produce energy in an inefficient manner. Some sugarcane plants even pay to dispose of excess bagasse; however, due to recent biofuel production the cost has risen.

**Feedstock Preparation**

Incoming feedstock must be reduced to small particles before the conversion step. Dump trucks will deliver the feedstock and drop it off in a pile where it will then be loaded into a vibrating hopper. The feedstock will then enter a New Meadows Model 5 Hammer Mill. This model has a max capacity of 1,200 lb feedstock/hr. Upon exiting the mill, the particles will be less than 0.1mm in diameter. These particulates ride a conveyer belt to a high capacity single pass rotary dryer where the moisture content will be reduced from approximately 50% to about 5%. The capacity of this dryer is far greater than that of the hammer mill and will not impede the flow of material.

**Conversion**

**Gasification**

Of the two “conversion” technologies discussed, our facility will breakdown feedstock via a thermochemical pathway. This method is preferred due to the fact that feedstock is reduced to simple organic monomers that can then be recombined into ethanol. With this ability, thermochemical conversion can breakdown most organic feedstock options in the same process. In the case of a shortage of sugarcane bagasse or energy cane supplies, other feedstock options may be considered.

The chosen gasifier will break down biomass by direct gasification in a downdraft gasifier. Of the two types of direct gasification technologies, the downdraft gasifier is preferred over an updraft gasifier because it minimizes the production of tars and oils to less than 1% (United States of America). Any tar remaining in the product hinders downstream processes and would have to be removed. Thermal energy required for this step is provided by partial combustion of biomass in the presence of oxygen or air. The temperature of the gasifier is maintained at 850 °F by feeding oxygen into the chamber at a rate of .32 lb O₂/lb biomass. Upon combustion, the media becomes fluidized by mixing with steam fed into the chamber at a rate of 0.2 lb steam/ lb dried biomass. Any remaining particles are ash and will be removed from the syngas by passing it through a cyclone filter as the gas exits. In contrast with other thermochemical technologies, direct gasification is relatively inexpensive due to its self-sufficient heating nature.

Syngas exiting the gasifier is composed of mainly carbon monoxide and hydrogen gas. The percent mass of each is a function of the biomass gasified. The chemical constituents of both sugarcane and energy cane are shown in Table 5. The process incorporates an updraft gasifier described by Jorapur which can process feedstock at a rate of 158.73 lb/hr and has a syngas outflow rate of 170 m³/hr.
Purification

Syngas conditioning is the next step of the process. The raw gas produced from the gasifier needs to be treated in order to meet the requirements of the catalyst used in ethanol synthesis. First, particulates, like ash and char, are removed in cyclones. The product gas then leaves the cyclones and enters into the reformer. There the hydrocarbons and tars are converted to CO and H₂ while the NH₃ is converted to N₂ as well as H₂. Operation temperature in the reformer is 850°C (Van Der Heijden). Next, the syngas stream is compressed to a pressure of 30 bar and cooled to 40°C. This prepares the stream to enter the amine system where acid gas concentrations are removed. Lastly, the syngas stream leaves the amine system to be compressed to 54/70 bar for the Rh-based catalyst (Van Der Heijden).

The ethanol conversion chamber is the heart of the conversion process. In this step, the cleaned syngas is converted to ethanol via chemical catalytic reactions. Catalytic based ethanol synthesis using an Rh-based catalyst was specifically chosen due to its high ethanol selectivity. The operating parameters for the ethanol chamber are described below in Table 6. Rh-based catalysts require a reactor pressure of 54 bar and a stoichiometric ratio of H₂:CO equals. After the chemical reactions have taken place, the product stream leaves the reactor while being cooled down to 40°C (Van Der Heijden). Based on a mass balance equation, the syngas is converted into ethanol at a rate of 328 lbs/hr (TSS Consultants).

<table>
<thead>
<tr>
<th>Ethanol Reactor Operating Parameters</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Catalyst</td>
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</tr>
<tr>
<td>H₂/CO ratio in syngas feed</td>
<td>H₂/CO ratio in syngas feed</td>
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<td>2</td>
</tr>
<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>°C</td>
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</tr>
<tr>
<td>Pressure</td>
<td>Pressure</td>
<td>bar</td>
<td>54</td>
</tr>
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</table>

Table 6: Ethanol Reactor Operating Parameters.

Table 5: Various chemical constituents in sugarcane and energy cane (Rainey)
Polishing

The chosen purification uses both extractive distillation and standard distillation, which uses ethylene glycol as the liquid solvent. The reason why this process was chosen is because it is the best choice for a large-scale production of ethanol, whose consumption is increasing rapidly every year. While the main method is extractive distillation, the actual separation process is more complex and utilizes condensation and distillation. The proposed method is similar to the method found in Exergy Analysis of Thermochemical Ethanol Production Via Biomass Gasification And Catalytic Synthesis and can be found below in Figure 9. This can also be found with the Final Flowchart on page 7, along with the actual mass flow rates in each step.

**Figure 9**: Separation of ethanol from other products; Red arrows indicate heat.

The product from ethanol synthesis contains different gases, alcohols, water, and ethanol. The gases include methane and ethane. This product enters the first condenser which operates at ethanol reactor pressure. It proceeds to the second condenser operating at atmospheric pressure. This step separates the mixture from methane and ethane.

Now that the ethanol, water, and alcohols are separated from the gases, the mixture will continue into the first distillation column. This column uses standard distillation with heat applied to extract 6.3wt% propanol, 0.7wt% ethanol, and 93.0wt% water in the top product. The remaining liquids in the bottom tray are sent to the second distillation column, which uses extractive distillation. This method uses ethylene glycol as the solvent to increase the volatility (lower the boiling point) of ethanol, so that 99.6% of ethanol will be recovered in the top tray. The solvent to feed ratio is 5:1, where the feed is the solute that it will extract. This product of
ethanol does, however, include methanol. This mixture continues to the third distillation column from the top stream, while the water and used solvent in the bottom stream will continue to the turbine and fourth distillation column.

The purpose of the fourth distillation column is to separate the ethylene glycol from the water, so that the solvent can be recycled into the second distillation column. This recovers about 99.9% of the ethylene glycol using standard distillation, leaving the water remaining in the top tray. The water can be reused or saved for another source of consumption. Consideration must be taken when reusing the water, because it contains very minimal amounts of ethylene glycol.

The top stream of the second distillation column is then fed into the third distillation column for the ultimate fuel grade ethanol recovery of 99.5wt%. The ethanol is removed from the top tray, while the bottom tray contains a mixture of methanol and ethanol. Some of the ethanol is removed in the top tray, but this is to ensure the highest quality of ethanol in the bottoms stream. The mass balance of the entire process can be found below in Figure 10.

**Mass Balance**

The ethanol conversion process can be modeled in a mass balance equation utilizing a mass rate basis of flowing materials. Reactions include ethanol synthesis. Overall, the process should be in steady state so there is no accumulation of ethanol in the process; therefore, \( \frac{dE}{dt} = 0 \). The mass of ethanol can be calculated by isolating the out rate and substituting reactions shown in the Figure 10.

![Figure 10: Overall material flow for ethanol conversion process](image-url)
In rate-Out rate±Reaction=dE/dt
In rate-Out rate±Reaction=0
In rate±Reaction= Out rate
1687 [(lb syngas)/hr] * .4299 [(lb ethanol)/(lb syngas)]-134.43 lb/hr*1=x (lb fuel grade ethanol/hr)
X=590.81 [(lb fuel grade ethanol)/hr]

Where E=ethanol (lb)
E%=percent ethanol
Out rate= x+29.2 lb/hr

Cost Analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
<th>Quantity</th>
<th>Total Cost</th>
<th>Source</th>
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</tr>
</tbody>
</table>

Table 7: Cost analysis for the production of ethanol

Conclusion

Ethanol has been increasing its use over the past century, and has become a comparative alternative to gasoline. This paper demonstrates the use of thermochemical ethanol production to convert sugarcane bagasse into fuel grade ethanol. This continuous process starts with 1,200 lb/hr of sugarcane bagasse that goes through a milling and drying process. Next, it enters the gasification chamber where it is converted into syngas at a flow rate of 1,687 lb/hr. The syngas then gets cleaned through reformation in order to meet the required standards of the Rh-based catalyst used in the next step, being the ethanol conversion chamber. In the chamber, the syngas goes through a series of chemical catalytic conversions that convert the syngas into ethanol and other byproducts. The effluent from the ethanol conversion chamber goes through three distillation processes in order to separate ethanol from the other byproducts. The flow rate of
ethanol at the end of the process, out of the third distillation chamber, is 590.6lb/hr of 99.8% ethanol.
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TSS Consultants. *Gridley Ethanol Demonstration Project Utilizing Biomass Gasification*


