

1. Introduction

Currently, fuel grade ethanol is used primarily as an additive in gasoline, but it is increasingly being used as a primary fuel source. Demand for fuel grade ethanol is driven by the automobile fuel market. Demand is also driven by the societal goal to use environmentally friendly fuels. Fuel grade ethanol offers many advantages as an environmentally friendly fuel. The combustion of fuel grade ethanol produces cleaner emissions than gasoline. The use of fuel grade ethanol reduces the use of fossil fuels. Also, ethanol can be generated from renewable resources, notably corn. However, to realize these benefits, the production of fuel grade ethanol must be efficient and profitable. Processes for the production of fuel grade ethanol are the study of this project.

2. Problem Statement

The team will design an environmentally friendly process for the production of fuel grade ethanol while reducing the strain on foodstuff production. The process must be capable of generating a steady supply of ethanol. These goals will be achieved by increasing the efficiency of ethanol processes based on foodstuffs or by using a source that does not strain the food supply.

3. Objectives

The proposed plant must meet these design objectives:

1. Design an economically feasible plant for the production of fuel grade ethanol.
2. Determine the best source of ethanol production.
3. Determine the amount of ethanol to be produced.
4. Design a plant that promotes safe working conditions.
5. Design a plant that promotes environmental stewardship
6. Design for efficient use of energy.
7. Produce fuel grade ethanol according to American Society of Testing Materials (ASTM) standards.

8. Simulate and optimize the plant process.

4. Importance of Fuel Grade Ethanol

The production of fuel grade ethanol steadily increased over the past two decades. Ethanol is most commonly used as a gasoline additive. Ethanol is blended with gasoline to increase the octane rating as well as to improve the emission quality of the gasoline engine. Fuel grade ethanol has a high octane rating of 116. Ethanol burns cleanly due to its oxygen content. In most regions of the United States, ethanol is blended up to 10% by volume with conventional gasoline, this blend is called E10 and can run in any engine designed to run on conventional gasoline.

The increase in demand of ethanol can be traced to the passing of the Clean Air Act in 1990, which set limits on the amount of pollutants found in the air anywhere in the United States. States with heavy air pollution must use oxygenated gasoline to reduce emissions from motor vehicles. The demand for ethanol did not begin to increase rapidly until 1999 (Figure 4.1). Until 1999, methyl tert-butyl ether (MTBE) was the fuel additive of choice. However, MTBE, a potential carcinogen, was found in the groundwater that supplies cities. The source of the MTBE was traced to leaking underground gasoline storage tanks. Since MTBE is highly soluble in water, it quickly contaminated the ground water. Due to ethanol's increased use as an additive, the production of ethanol increased tenfold from 1996 to 2004. The increased percent of ethanol in gasoline has one drawback: ethanol has a lower heat of combustion than conventional gasoline. This means the blended gasoline provides less energy than conventional gasoline. Thus, an engine will require more of the blended fuel to do the same amount of work as an engine running on conventional gasoline. However, when blended at low levels, around ten percent by volume, the effect on fuel economy is small.

Ethanol can also be used as a motor fuel in concentrations up to 85 percent by volume. This mixture, called E85, powers flexible-fuel vehicles. These vehicles can run on fuels that range in ethanol

concentration from 0% to 85%. A standard conventional gasoline engine can run on fuel with an ethanol concentration from 0-20% without modification.

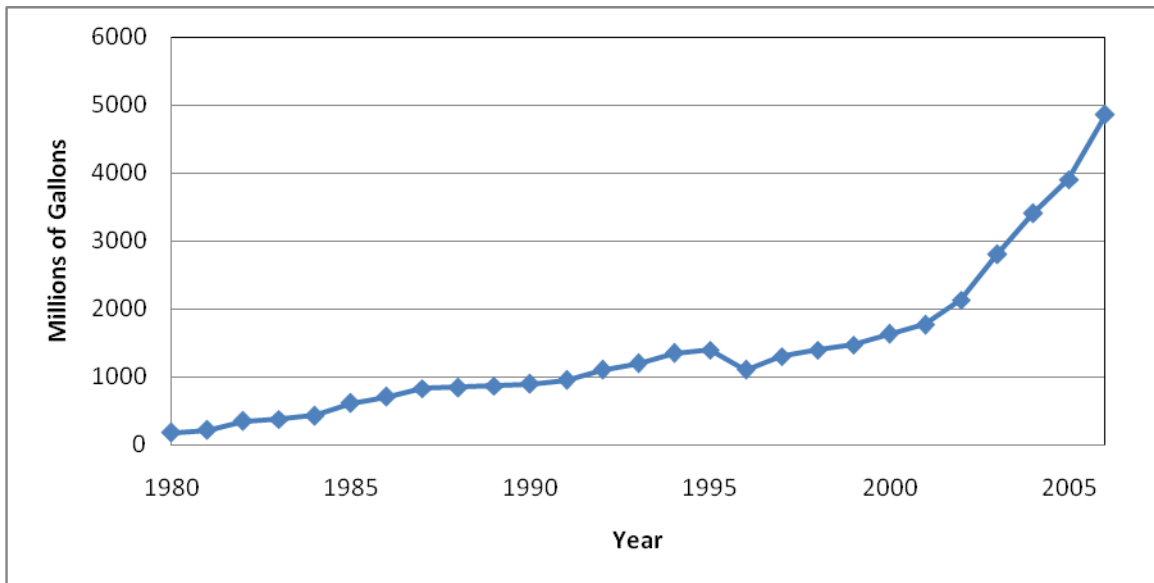


Figure 4.1: Annual Production of ethanol has grown more rapidly in the last decade in the U.S.

5. Alternative Feedstock Solutions

An important decision in the process is determining the type of feedstock to be used. The feedstock is the material that will be converted into fuel grade ethanol. Research identified three potential options: corn stalks, switch grass, and carbon dioxide. These options are discussed in detail in the following sections.

5.1. Corn Stalks

The process for producing ethanol from corn takes place in eight steps (Appendix A). The process begins with the cleaning of the corn and removal of the unwanted sections such as stalk and cob. These rejected components are combined with the byproducts stream, which becomes animal feed. Most processes use only the starch-rich corn kernels for ethanol production. An alternative is to take these rejected components and convert them to ethanol, using a process similar to switchgrass conversion to ethanol (see section 5.2).

After being separated, the starch-rich kernels move to the steeper where the larger molecules are broken down to smaller molecules for the later fermentation process. The steeper is a humid environment with sulfur dioxide fed to increase acidity and to prevent unnecessary bacteria growth. This product moves to a cyclone separator, which removes the germ from the rest of the kernel. Then, oil is washed out of the germ. The germ becomes part of the animal feed, while the oil is sold as corn oil. The remaining kernel fibers, cornstarch, and gluten are combined with water to form a slurry. The remaining kernel fibers are removed and combined with the animal feed. The cornstarch and gluten are separated by their differing densities using a hydrocyclone. The gluten is sent to the animal feed. Once the cornstarch is separated from the gluten, it is converted to a syrup of dextrose, which is used as the feed for the fermentation process. The syrup is fermented by bacteria producing carbon dioxide and an ethanol solution. The ethanol is then separated from the solution and sold. The remaining solution is dried and combined with the animal feed.

5.2. Switchgrass

Switchgrass is comprised mainly of lignocellulosic materials, making switchgrass more difficult to ferment into ethanol than conventional starch and sugar crops. This challenge stems from the structure of the lignocellulose, which is comprised of three major components. The three primary components are crystalline cellulose, hemicellulose, and lignin comprising roughly of 50, 25, and 25 percent by mass of the cellulosic material, respectively. Extra processing steps are required for each component.

Ethanol is generated from switchgrass in a multi-step process (Appendix A). Upon entering the system, lignocellulose is pretreated to separate the crystalline cellulose from the xylose (hemicellulose) and the lignin. The crystalline cellulose, the most difficult to break down, continues to an acid or enzyme catalyzed hydrolysis which breaks the cellulose down to glucose. The glucose

and xylose undergo fermentation. The resulting product is sent to a distillation train and concentrated to fuel grade levels.

The lignin is a phenolic polymer which is catalytically broken down into one or two phenyl groups. These phenol groups are then reacted with oxygen to remove their side groups and are further reacted with methanol to form Methyl-aryl esters. These esters are a valuable additive to gasoline for their octane enhancing properties. These esters increase the profitability of this process.

5.3. Carbon Dioxide

Another alternative for an ethanol production process feedstock is carbon dioxide, through the use of genetically modified cyanobacteria. A Process Flow Diagram (PFD) for this process is shown in Appendix A. A strain of *Synechocystis* has been genetically modified by Professor Fu at the University of Hawaii to produce ethanol from carbon dioxide via a photosynthetic pathway. The aqueous cyanobacteria in solution use sunlight in a photobioreactor to convert the carbon dioxide to ethanol. Currently, the process can produce concentrations of 15 mM of ethanol in 5 days in a batch reactor. The concentration of ethanol is limited to 15 mM because higher concentrations of ethanol kill the bacteria. The liquid solution containing water, nutrients, and carbon dioxide is then separated using several techniques to yield a high purity ethanol product. As this is a new process, no large scale industrial processes exist to base the separation process on. Separation possibilities are discussed in section 10.3.

6. Process Determination – Decision Matrix

The processes described above were evaluated using the criteria in a decision matrix (Table 6.1). The process chosen was cyanobacteria. Cyanobacteria excelled in the areas of sustainability, renewability, stewardship, cost, environmental acceptance, and environmental impact. In the following section each of the criteria are discussed in detail to explain the evaluations.

Table 6.1: Decision Matrix Criteria

	Criteria	Weight	Process		
			Corn	Grass	Algae
1	Resource Availability	5	5	4	3
2	Convenience of energy utilization	10	4	4	6
3	Efficiency of conversion	10	5	2	4
4	Technological feasibility	10	8	7	5
5	Portability and ease of transportation	5	3	2	5
6	Sustainability	10	3	3	8
7	Renewability and Stewardship	10	7	8	10
8	Cost and affordability	15	8	5	11
9	Safety and health effects	10	8	8	8
10	Environmental acceptance and impact	15	10	9	14
	Total	100	61	52	74

6.1. Availability, Renewability and Stewardship, and Sustainability

Important considerations for alternative fuel sources are the availability, renewability and sustainability of the feedstock. The source for ethanol production needs to be readily available to produce ethanol year round. Corn and switchgrass are grown in enormous quantities and are easily replanted and regrown annually. The cellulose based sources are readily available in large quantities, especially in the Midwest. Professor Fu's modified cyanobacteria are easily sustained once initial growth has begun, but his cyanobacteria are not yet commercially available. Consequently, cellulose sources are rated higher in availability, while cyanobacteria are rated higher in renewability and sustainability. These factors could be tied in to one higher weighted factor, but it was decided that the differences between renewability, sustainability and availability were significant enough to be independent categories.

6.2. Environmental Impact, Health and Safety Effects

Important factors in deciding on a process are environment effect and any health and safety issues for the operators. The source should have a minimal impact on the environment,

meaning that waste streams from the process are either non-toxic or will be treated before released into the environment. Also the production of the source needs to have a minimal impact on the environment as well. Corn stalks and switch grass have an environmental impact during the growth phase because of the land required to produce these crops. Also, pesticides and fertilizers can have a negative impact on the environment. The use of cyanobacteria has a minimal impact on the environment because it is grown in a reactor and all waste streams are controlled and treated. Cyanobacteria have a neutral effect on the environment because it uses CO₂ as a source for producing ethanol. When the ethanol is used, the same amount of CO₂ is released into the atmosphere as was supplied by the CO₂ feed stream used to create the ethanol.

All three fuel source options have minimal health and safety issues because a minimal amount of hazardous materials are present in the process. The main safety issues that arise are from plant design. A plant that promotes safe working conditions for operators and residents in the area of the plant is an important aspect of the design.

6.3. Cost and Affordability

The costs associated with a given fuel source are an important consideration for the design process. Maintaining low cost is a high priority in a competitive market. Each of the fuel source options have different costs associated with production. Corn stalks and switchgrass have relatively high costs in the growing process, and the techniques to convert these to ethanol are inefficient. Cyanobacteria are a lower cost option because the cyanobacteria reproduce while making ethanol. The major cost with using cyanobacteria is that the process requires a large volume of cyanobacteria in solution to produce a significant amount of ethanol. A large volume results in high equipment costs.

6.4. Convenience of Energy Utilization, Efficiency of Conversion

To provide a feasible fuel ethanol production process, the ease of obtaining the feed source and efficiency at which the source can be converted to fuel must be taken into account. Corn and switchgrass were not rated highly in the convenience of energy utilization because they must be transported to the production facility. This fuel cost for transportation detracts from the goal of providing fuel. The cyanobacteria can be grown and regenerated on site, right next to the acid gas stacks of a gas sweetening processes. Gas sweetening plants refine natural gas and can provide a vapor stream rich in carbon dioxide directly the cyanobacteria.

No sources agree on the efficiency of cellulose based conversions where the efficiency is defined as the amount of energy provided to the process versus the amount of energy produced. Corn based plants claim an efficiency of around 50%. The process of conversion is highly energy intensive which lowers the score in this category. Switch grass is claimed to be anywhere from 50% to 400 % from cellulose to energy conversion. The cyanobacteria has the lowest conversion, producing only 15mM ethanol solutions, but the conversion process involves no extra energy since it is a photosynthetic reaction. Since the actual efficiency is unknown, the cyanobacteria feed was scored the same as corn.

6.5. Technological Feasibility

Another consideration for the design of an ethanol producing process is the technological feasibility. Technological feasibility was a criterion for deciding on alternatives to research. The score is based upon the actual documentation of processes that would contribute to design. The availability of literature, research, and operating experience contribute to determining if the process could be taken from concept to reality.

For a corn based plant, determining feasibility is obvious, as several corn based ethanol plants are in operation throughout the Midwest. Feasibility was, however, ranked somewhat lower for corn based process because the project would focus on using the entire corn stalk, which is not the case with current corn fed ethanol processes. A switch grass based plant is also technologically feasible. The processes needed to convert the grass to ethanol are very similar to the corn plants already in use, although they have not already been commercialized specifically for grass. The process to convert carbon dioxide to ethanol has been proven feasible on a bench top scale by Fu's patent. The feasibility of a full scale separation process from a low concentration of ethanol is feasible, but unconventional. Further discussion of the separation feasibility is discussed in section 10.3. Since much is unknown about scale up of this process, it was given a lower ranking than cellulose bases.

7. Intellectual Properties Issues

Intellectual property is the basis for technological innovation. The ideas of others will be and have been used to complete this project, but these ideas must be respected. Some of the technology and information used in this ethanol production process is covered by patents, while other information is provided by research publications. These sources must be properly recognized, avoiding infringement and plagiarism. Also, to gain access to Professor Fu's patented research, this team signed non-disclosure agreements with him. Care must be exercised to respect this agreement, and confidential information may not be divulged.

7.1. Professor Fu's Patent

Professor Fu of the University of Hawaii genetically modified a strain of *Synechocystis* cyanobacteria to produce ethanol from carbon dioxide via a photosynthetic pathway. Professor Fu holds a patent on this technology. The patent governs the sequence of the gene used to modify

the cyanobacteria. An ethanol production process developed using this technology must work with the patent holder.

Professor Fu also provides this team with details of his own research. He has been contributing his experience and sources for further investigation for the development of the production process.

7.2. Keyes Patent

The Keyes patent established heterogeneous distillation of ethanol from an ethanol-water mixture. This technology provides a means to achieve ethanol concentrations above the ethanol-water azeotrope (see section 10.3.4).

7.3. Research Sources

Research literature is excellent resource for nearly all aspects of this project. Information from research literature is referenced (see section 14).

8. Task Specifications

Once a feedstock was chosen and the necessary research preformed, different tasks were completed to determine project feasibility. To establish feasibility three things must be determined: the purity and composition of fuel grade ethanol, an energy balance to find locations with sufficient sunlight, and a feasible level of production.

8.1. Ethanol Quality

The ethanol produced must comply with the ASTM specifications for Fuel Ethanol standard D4806-98. An abridged version of the specifications is shown in table 8.1.1:

Table 8.1.1: ASTM fuel specifications (abridged)

	Properties	Specifications
1	Ethanol, % v/v:	92.1 min.
2	Methanol, % v/v:	0.5 max. (5,000 ppm)
3	Water, % v/v:	1.0 max. (10,000 ppm)
4	Denaturant:	A min of 1.96% v/v, and a max of 4.76% v/v of natural gasoline, gasoline components or unleaded gasoline.

The full table of specifications required can be found in appendix B.

8.2. Energy Balance

One major specification for this design is providing the amount of sunlight needed by the cyanobacteria to produce ethanol. If no location provide the amount of light energy required for conversion, the process is not feasible. The energy balance must show that the cyanobacteria are able to harness at least 240 W/m^2 of sunlight, the amount of energy used in the successful experiments by Professor Fu. More information on the energy balance is provided in section 10.1.

8.3. Production Level

Many options were considered for a base case. The base case defines the approximate scale of the production process. A full scale ethanol production plant based on the production levels of current fuel grade ethanol production facilities was considered. However, to produce ethanol on that large scale and still remain competitive would take an excessively large reactor. Many small scale options were then considered. One possible option would be to use the CO_2 from an amine gas sweetening plant (see sections 6.4 and 10.2). Another option would use the CO_2 stack from a power plant. For both of these cases the idea would be to reduce CO_2 emissions and produce a sellable product. The amine gas sweetening plant was chosen as a basis because many of these plants are

located in Western Texas where there is ample sunlight to drive the photosynthetic reaction. More information on the basis is given in section 10.2.

9. Design Norms

Christian engineers are uniquely called to live out their faith and redeem the creation while maintaining profitability. When designing a project, one of the best ways to incorporate both of these views is to create a set of design norms on which to base decisions. Applying design norms can be as simple as designing an item that can be made cost-effectively but still be of high quality so as not to break after the millionth use by the consumer. The most relevant design norms are discussed further.

9.1. Stewardship of Resources

Engineers have a responsibility in designing projects to the environment and community. To maximize benefits of the plant design, and minimize the environmental impact, the design must be energy and resource efficient. By harnessing solar energy to power the bioreactor and by recycling water, this design is intended to use resources as efficiently as possible. At the same time, the plant is converting emissions, which normally are given off to the atmosphere in an amine gas sweetening processes, to a usable form of energy. This use not only provides a carbon dioxide source for our plant, but helps to preserve the environment.

9.2. Justice

Energy should be available and affordable for all people. Inexpensive energy should not have to compete with basic human needs for food. Current ethanol production processes deplete food resources by converting these resources into fuel. This plant design produces fuel ethanol from waste gas emissions and eliminates the need to convert food to fuel allowing agricultural lands to revert to food production. The plant also creates a fuel resource that the general public can afford as energy prices continue to rise.

9.3. Transparency

This plant is being designed so that it can easily be replicated for any natural gas pumping stations in West Texas. In this way a significant amount of fuel ethanol can be produced.

Requirements and parameters will be clear so that the plans can be transferred to other plants with only minor modifications to suit the unique configurations of each plant. The plant must be easy to operate and maintain.

9.4. Trust

When designing, the engineer's responsibility is to the public to make sure the plant is safe for the surrounding community. Worst case scenarios as well as conditions for steady state and unsteady state operations must be considered to ensure that the plant will not fail, or cause safety hazards in the event of plant failure.

10. Preliminary Design

When solving a problem a good starting point is a material and energy balance; this allows an initial determination of the feasibility of the process. Preliminary calculations were performed to address critical design issues. Initially an energy balance was performed to determine whether there were suitable conditions for ethanol production and at what regional locations. Next a material balance was performed to determine the basis, the amount of ethanol to be produced and the size of the reactor. Finally a series of alternative separation systems were chosen and their specifications were roughly calculated using HYSYS design software.

10.1 Energy Balance

The purpose of the energy balance is to determine if the proper amount of sunlight can reach the cyanobacteria. According to Professor Fu, the necessary light flux needed to convert CO₂ to ethanol is 100 $\mu\text{einsteins}/\text{m}^2\text{s}$. This can be converted into an energy flux of 240 W/m^2 . A

full calculation can be found in appendix C. To find the energy flux from the sun in different areas of the United States, the Average Daily Solar Radiation map was used (appendix C). This provided the basis for determining the possible location of the ethanol plant. The calculations were conducted using a value of 6.5 kWh/m²day because the majority of the US was in the region of 6-7 kWh/m²day. This provided an energy flux of 270 W/m², making the process feasible in sunny regions of the US. Since the calculated flux was close to the minimum amount necessary, it was determined to locate the ethanol production facilities in places that receive solar radiation greater than 7 kWh/m²day. A safety factor in this respect was necessary because calculations were based off of average values of solar radiation not minimums. This limits the plant location to regions of Arizona, New Mexico and Texas.

10.2 Material Balance

Initially a production volume of 1,000,000 liters of ethanol per year was chosen as the basis for calculations. From data acquired from Professor Fu, the final concentration of ethanol in the reactor solution was 15 mM of ethanol after a five day operational cycle. Accounting for maintenance and other down time, an operational time of 300 days per year was chosen. On the basis, the necessary reaction mixture volume for a five day run, or five day residence time, would be very large. Subsequently, a tubular or plug flow reactor (PFR) providing adequate surface area for sunlight would be several hundred kilometers long (Table 10.2.1). A continuous stirred tank reactor (CSTR) would also be large – large enough for the reaction mixture volume.

Upon completion of the preliminary basis the equipment sizes were found to be excessively large. It was then decided to design a plant to complement current CO₂ producing facilities instead of designing an autonomous, full scale production facility. Gas sweetening plants in western Texas seem suitable due to their steady production of CO₂ and the large amount of annual sunlight. The information of a gas sweetening plant was obtained from Steve Brusso, an engineer with NATCO Group Inc. (Appendix D). With the information provided on process

outputs, a decision was made to use the overhead product gas from the contactor, which contains primarily CO₂ and water, as the carbon feed stream for the process. The cyanobacteria are assumed to produce one mole of ethanol per two moles of CO₂ injected into the system to maintain a carbon balance. With these numbers (Table 10.2.1) the ethanol produced annually is reduced to around a quarter of that which would be produced from the original basis. This reduction applies proportionally to the required volume of reactor solution and the reactor size (Table 10.2.1).

Table 10.2.1: Calculated Values for Basis

Basis	Production Amount		Reactor type	Solution Amount (L)	Reactor Specs	
	(L/yr)	(L/5day)			Volume (L)	Length (km)
1	1000000	16667	CSTR	19033145	19100000	N/A
1	1000000	16667	PFR	19033145	N/A	367.2
2	132962	585	CSTR	5060458	5100000	N/A
2	132962	585	PFR	5060458	N/A	367.2

The tubular reactor (PFR) size is still prohibitively large for the given volume and five day residence time. An alternative design was proposed and is being investigated as the project progresses.

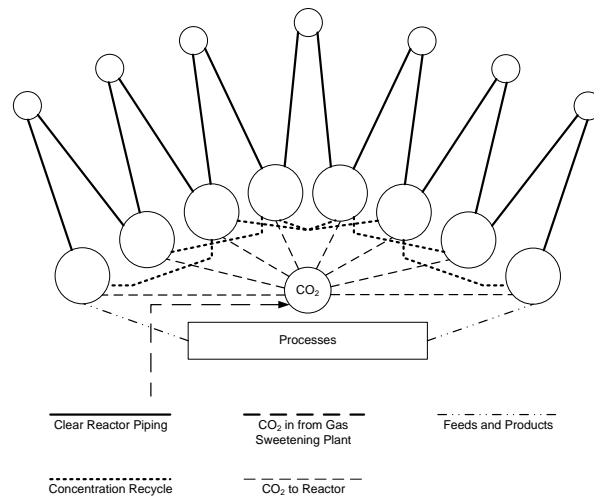


Figure 10.2.1: Preliminary Reactor Design

In the preliminary design (Figure 10.2.1), the large circles that make up the array are Continuous Stirred Tank Reactors (CSTRs) where the CO_2 is injected into the system. Also, a small recycle stream connects different CSTRs to maintain a constant concentration of ethanol over the whole reactor to generalize it as a large CSTR. The lines leading to and from points on the “crown” are banks of clear tubes used to maximize the cyanobacteria’s solar exposure. The circles at the ends could possibly be more mixing points or just representative of return points. This array would be arced around the sweetening plant facing the southern hemisphere to create more surface area for the solar contact. This design also centralizes all points where the CO_2 is injected reducing the piping requirement for transporting the CO_2 . As a final note, the amount of CSTRs and pipe banks is representative of reactor layout and not design specification.

The design of the CSTR reactor was changed from the outward arcing array seen above in Figure 10.2.1 to the rectangular design in Figure 10.2.2. The decision to make the change was based on the amount of land required for each reactor. The rectangular design uses less land area for the same reactor volume.

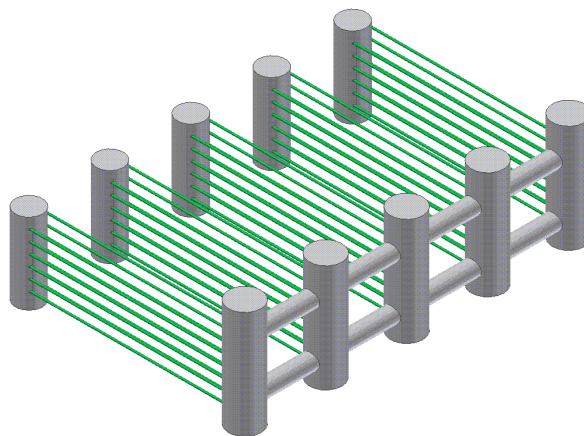


Figure 10.2.2: Second Preliminary Reactor Design

From calculations based on the desired ethanol production level and the residence time required in the reactor, it was determined that 38 pairs of mixing vessels are required. The large mixing vessels will incorporate a heat exchanger designed to cool the reactor fluid preventing the temperature from increasing to the point where the bacteria die. Each tube bank is comprised of 4 rows 32 tubes high with an equal number of tubes having flow in each direction. These tubes are $2\frac{3}{8}$ inches in diameter with a span of 48 m. This allows for optimal sunlight for conversion as well as aiding to maintain a stable concentration throughout the overall reactor.

10.3 Separation

Once ethanol is produced in the reactor, the ethanol must be separated from the reaction mixture and purified to ASTM standards for fuel-grade ethanol (Table 8.1.1). The challenges to the design of the separation process include recovering ethanol from the dilute reaction mixture, purifying the resulting ethanol-water mixture, and moving the ethanol-water mixture past its azeotrope up to fuel-grade specifications. An azeotrope occurs when the composition of a mixture is the same in the liquid and vapor phases. At an azeotrope, separation technologies that function based on difference in liquid and vapor composition fail to separate the components of a mixture. Many separation technologies are investigated with regard to these challenges. Possibly, one

technology could fulfill this separation process. However, the separation process will likely make use of many of the separation technologies. The technologies investigated include membranes, pressure swing distillation, extractive distillation, heterogeneous distillation, adsorption, pervaporation, and distillation.

10.3.1 Membrane

The selectively permeable membranes represent an attractive and efficient method of separation. Ideally, one component in a liquid mixture can diffuse through the membrane at a much higher rate than the other components. The membrane's composition and structure control diffusion based on molecular size and dielectric constant. This difference in diffusion rates gives the membrane selectivity. The structure of a membrane is porous to encourage mass transfer. Most membranes are plastics such as polyvinyl alcohol, polyamide, nitrile, styrene butadiene, polydimethylsiloxane, cellulose acetate, polyvinylidene fluoride, and polysulfone. However, inorganic zeolite membranes are also used.

Because of their selectivity, membranes are suited for removing a minor component in a liquid mixture – instead of forcing the bulk of a feed liquid through a solid membrane, only a minor component passes through the membrane. The retentate is the liquid that does not pass through the membrane, while the permeate does pass through the membrane. Thus, the retentate is diluted and the permeate is concentrated with respect to the minor component. This separation is driven by a difference in chemical potential across the membrane. When the permeate is under vacuum, the process is called pervaporation, because the permeate is often a vapor at low pressures. This pressure gradient also drives mass transfer across the membrane.

Pervaporation is often a cost effective alternative to conventional separation techniques like distillation because no energy is required for the membrane to function, though vacuum pump often aid the process. However, membranes may have large equipment costs, short lifetimes, and high maintenance. Pervaporation should be very useful in two segments of the ethanol separation and purification process: concentrating the reactor solution and breaking the ethanol-water azeotrope.

The reactor solution will contain only dilute amounts of ethanol. The cyanobacteria convert carbon dioxide to ethanol at a concentration of approximately 15 mMol, or 0.07 percent ethanol by weight. Due to this low concentration, the only economic way to increase the concentration of ethanol is by using pervaporation. Many different hydrophobic membranes are being explored with several promising leads. Research publications indicate effective membrane separation with solutions of 0.1 percent ethanol by weight. The membrane will be chosen based on efficiency, cost, and availability. The membrane must also be able to increase the concentration of ethanol up to at least 10 percent by weight. Once the ethanol is at this concentration, many different options are available to further increase concentration. Thus, pervaporation will be the first segment in the separation process.

Pervaporation may also be employed in breaking the ethanol-water azeotrope and dehydrating this ethanol-water mixture to fuel-grade anhydrous ethanol. At the ethanol-water azeotrope, distillation cannot continue because the liquid and vapor phases of the ethanol-water mixture have the same composition. However, a hydrophilic membrane can selectively remove water. Selectively removing water produces a retentate with a high concentration of ethanol and a permeate of mostly water. Pervaporation moves the ethanol-water solution past the azeotropic composition while removing water from the final product. This process is further discussed in section 10.3.6.

10.3.2 Pressure Swing Distillation

The separation process of ethanol from water is difficult due to the azeotrope formed by the two compounds. The minimum boiling azeotrope is at 89.43 mol percent ethanol at 760 torr and increases to 98.35 mol percent at 90 torr and disappears at a pressure of less than 70 torr (Figures 10.3.2.1 and 10.3.2.2). Pressure swing distillation can be incorporated to achieve high purity ethanol. The process (Appendix E) usually involves two distillation columns operating at different pressures. The first column operates at a higher pressure and brings the solution up to the azeotropic composition. The azeotropic mixture is sent to the second column operating at a lower pressure where the mixture is further distilled resulting in high purity ethanol.

Pressure swing distillation to separate ethanol from water is uncommon because of the capital and energy costs. Column 2 must operate under a vacuum resulting in a large column with refrigerant, which could become more of a problem as it could be located in a warm climate. Also the recycle rates are very high because the distillate from the second column is at the azeotropic composition which contributes to larger columns and more expensive distillation.

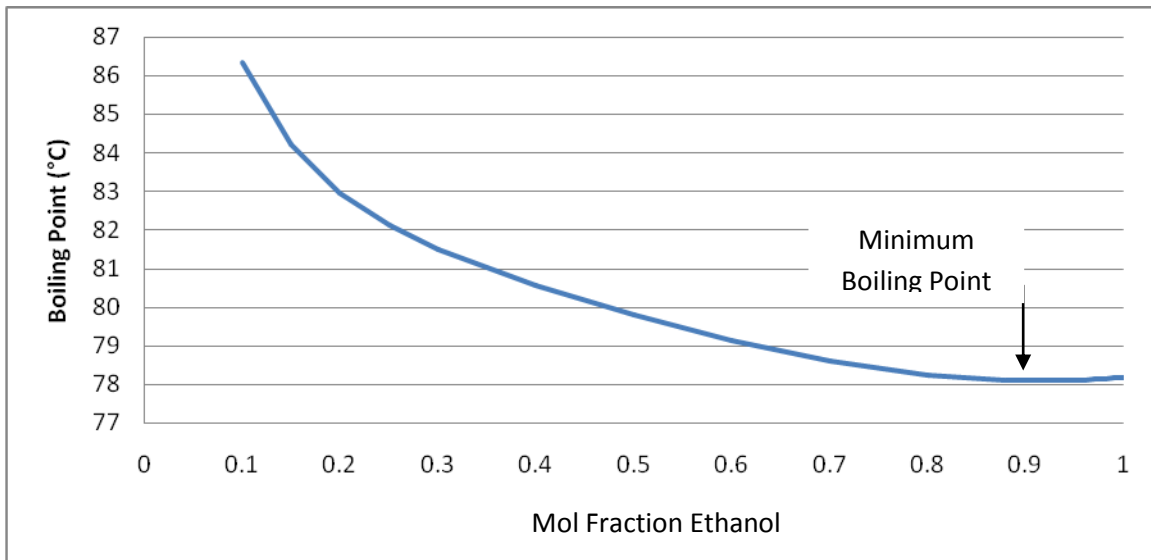


Figure 10.3.2.1: Azeotrope of EtOH in H₂O generated with HYSYS using NRTL fluid package at 760 torr. Azeotrope occurs around .89 mol fraction ethanol

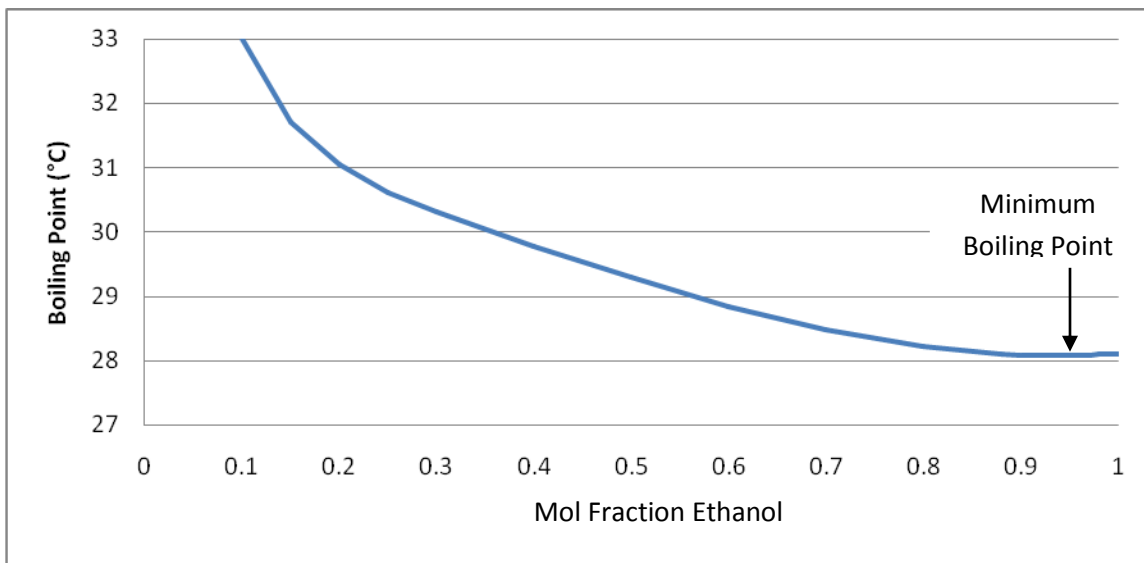


Figure 10.3.2.2: Azeotrope of EtOH in H₂O generated with HYSYS using NRTL fluid package at 70 torr. Azeotrope occurs around .98 mol fraction ethanol

10.3.3 Extractive Distillation

Extractive distillation works by adding a solvent that is less volatile than the components in the feed, and does not form an azeotrope with either component. The

solvent is added above the feed tray, and generally a few trays below the top of the column. Thus, the solvent is present in the down flowing liquid phase to the bottom of the column. In the presence of this solvent, the components of the feed no longer form an azeotrope and effective distillation can continue. Generally a solvent-to-feed molar flow of 1-to-1 is required to break the azeotrope.

This process uses three distillation columns (Appendix E). The first column brings the water-ethanol mixture up to near the azeotropic composition. The second column adds the solvent and distills the first column's distillate, resulting in near pure ethanol in the distillate and a water-solvent mixture in the bottoms. The bottoms stream is sent to a third distillation column where the solvent is recovered and recycled back to the second column. The two solvents being considered are glycerine and ethylene glycol (Table 10.3.3.1).

Table 10.3.3.1: Summary of properties of solvent for Glycerine and Ethylene Glycol

	Boiling Point at 101 kPa in °C	Azeotrope with Water	Cost	Environmental Factors	Health Factors
Glycerine	290	No	\$0.29/lb	No	No
Ethylene Glycol	197.3	No	\$0.65/lb	No	Toxic

10.3.4 Heterogeneous Distillation

Heterogeneous distillation of ethanol-water mixtures was first discovered by Keyes in 1929. Heterogeneous distillation can be accomplished using three distillation columns (Appendix E). As in extractive distillation, a solvent or entrainer is used to break the azeotrope. However, unique to heterogenous distillation, the solvent and the feed form a three component, or ternary, azeotrope. The first column is used to increase the concentration of ethanol up to near the azeotrope. The second column combines the

entrainer with the azeotropic mixture of ethanol and water which forms a ternary azeotrope. The ternary azeotrope is unstable, and allows ethanol to be separated in high purity in the bottoms stream of the second column. The third column is for entrainer recovery and recycle back to the second column. The entrainers considered for the system of ethanol and water are benzene and diethyl ether.

10.3.5 Adsorption

Because the distillation of ethanol-water systems is energy intensive, adsorption is investigated as an energy-efficient process to concentrate ethanol before distillation. Concentrating ethanol before distillation reduces the energy required in the distillation column because less water is boiled which reduces both equipment sizes and operating cost.

A cyclic adsorption process works by passing the reactor solution through an adsorption column. In the column, the ethanol in the reactor solution is selectively adsorbed by a hydrophobic adsorbent. The ethanol-rich adsorbent is then separated from the reactor solution and passed to a second column where the ethanol is desorbed from the adsorbent. The regenerated adsorbent is removed from the desorption column and reenters the adsorption column. Effective adsorbents have a low cost, adsorb and release ethanol quickly, and absorb a large quantity of ethanol. Several promising adsorbents have been found and a few commercially available adsorbents, such as activated carbon pellets and powders, show promise in an ethanol-water adsorption system.

10.3.6 Pervaporation and Distillation

The PFD for a pervaporation and distillation system is shown in Appendix E. Pervaporation uses a distillation column operating near ambient conditions to increase the concentration of ethanol up to the azeotrope which is nearly 94 wt% ethanol at atmospheric conditions. The distillate, an azeotropic mixture of ethanol and water, is then sent past a

hydrophilic membrane such as polyvinyl alcohol, polyamide or zeolite. The solution is pulled through the membrane by creating a vacuum on the downstream side of the membrane. The pressure is usually around 15 torr which causes the permeate stream to be a vapor. The purity of the ethanol product and concentration of ethanol in the permeate stream depend on the membrane used, but in general the ethanol product can be obtained at 99.5 wt% pure with a permeate stream that is 25 wt% ethanol. Some membrane manufacturers offer pre-designed, deployable modules for this process.

11. Method of Approach

Preliminary research is complete. Over the next few months, the plant will be designed in detail from the preliminary PFD (Appendix A). From the design, an in-depth economic analysis will be completed with a final report and presentation. From the PFD, each process will be designed in full, the most difficult of which will be the separation section. The separation process will be chosen using a decision matrix (Table 11.1).

Table 11.1: Decision matrix for separation of EtOH and water

	Factors	Weighting	Extractive Distillation	Pressure Swing Distillation
1	Technological maturity	15	12	3
2	Energy Usage	12	7	4
3	Operating Cost	10	8	8
4	Equipment Cost	10	7	3
5	Technological feasibility	15	12	3
6	Equipment Life	10	8	8
7	Applicable To Scale of Operation	15	10	10
8	Safety and health effects	10	9	9
9	Environmental acceptance and impact	8	6	6
10	Recovery of Ethanol	10	9	7
	Total	115	88	61

Table 11.2: Decision matrix for separation of EtOH and water

	Factors	Pervaporation Distillation	Heterogeneous Distillation	Absorption
1	Technological maturity	10	15	4
2	Energy Usage	10	7	7
3	Operating Cost	7	8	6
4	Equipment Cost	5	7	5
5	Technological feasibility	10	15	4
6	Equipment Life	5	8	7
7	Applicable To Scale of Operation	12	10	9
8	Safety and health effects	9	7	8
9	Environmental acceptance and impact	6	6	6
10	Recovery of Ethanol	10	10	8
	Total	84	93	64

The design matrix indicates extractive, pervaporative, and heterogeneous distillation are attractive options for the separation process. These three options will be investigated in greater detail. A time schedule for this semester and a potential time schedule for the upcoming interim and final semester has been generated (Appendix G). This outlines what has been accomplished up to this point and what is planned for the coming months.

12. Economic Analysis

To determine the economic feasibility of an cyanobacteria-based, fuel grade ethanol production process, a preliminary economic analysis was completed. Using the reactor dimensions calculations, a reasonable estimate of costs was found. The economic analysis of the separation system was based upon heterogeneous distillation. The life of the plant was set as 15 years with a return on investment (ROI) of 8%. The analysis determined the annual cost to operate the plant and a break-even price (BEP). The BEP determines the price at which the fuel grade ethanol must be sold to begin making a profit. A BEP of \$23.47 per gallon of ethanol would be necessary based on a 12

hour cycle of ethanol production. The annual cost of operating the plant was \$746,190. While currently the process does not appear to be economically favorable, this does not include any government financial support for eliminating greenhouse gas emissions, or money saved from carbon tax credits. Detailed explanations of cost estimates and calculations can be found in Appendix F.

13. Cost Estimates

Most of the design project is process design and simulation which results in little actual cost since nothing will be built. No prototype will be pursued because the process is infeasible at small scales. The only item in the budget is a contingency fee of \$100 for printing costs or cost for any reference materials needed.

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