

A TECHNO-ECONOMIC ANALYSIS OF ETHANOL PRODUCTION FROM HYDROLYSIS
OF CELLULOSE WITH NANOSCALE MAGNETIC SOLID ACID CATALYSTS

by

TREVOR JOSEPH AULT

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Major Professor
Dr. Keith Hohn

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TREVOR AULT

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Abstract

Acid catalysts have been shown to be very successful in the pretreatment of cellulosic biomass to improve glucose yield and improve overall yield of ethanol. This report presents the results of a techno-economic study that looks into the use of nanoscale magnetic solid acid catalysts for glucose production. Magnetic solid acid catalysts are an improvement over using diluted acid due to eliminating acid-waste generation and corrosion hazards. Their magnetic nature also allows them to be easily separated from reaction products by an external magnetic force. After the technology is analyzed, a series of unit operations is proposed to go from the laboratory scale to the industrial plant scale.

The next step was to develop material and energy balances using HYSYS process simulation software. Capital and operating costs are estimated and all the information is combined into a discounted cash flow economic model. The economic portion of the report uses a probabilistic cost assessment. It is used to quantify the range of risks in the project from swings in feedstock costs, differences in yield from catalysts, and any other significant variables. Both capital costs (initial equipment & construction investment) and operating costs (feedstock supply, chemicals, and personnell) are included with ranges of error based on databases and expert opinion. This method of evaluating investment efficiency can be helpful for predicting the cost benefits of proposed future research.

The yield and percent catalyst magnetically recovered is assumed based on laboratory research to simplify the model. A 2000 metric tons of biomass per day facility was analyzed. Using the magnetic solid acid catalyst technology, the capital costs are estimated to be \$160 million and this technology saves around 10% of capital costs compared to ethanol plants that uses conventional acid hydrolysis. The yield of the magnetic solid acid catalysts should be around 75% to compete with existing ethanol technologies. The metric used for this report is the discount profitability index (DPI) which is the ratio of future cash flows divided by investment. A DPI "hurdle rate" of 1.3 is used, which is similar to industry economic metrics of projects that include new process plants. The calculated DPI for the project is 1.38 DPI which is higher than using conventional cellulose treatment technologies. The recommendation is continue to study this technology's large scale applicability before attempting any plant pilot studies.

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Chapter 1 - Introduction

Renewable energy has received significant interest in recent years both at the industrial and academic level. Governments realize that with the draining of petroleum, natural gas, and coal reserves it is advantageous to have a source of energy that is sustainable, creates domestic jobs, and can be produced independently by a country so that it does not require energy imports. During the mid-1990s, cost analysis showed that taking into account carbon credits, plant productivity, and operating costs the cost to produce biofuel oil is around \$59-186/barrel (Sheehan, 1998). But due to the unsustainable nature of fossil fuels and the ever increasing advances in science & engineering, biofuels are becoming more economically competitive with fossil fuels. Cellulose is the primary structural component of green plants and has a huge potential to be converted to fuels on the same scale as fossil fuels are currently consumed worldwide (Perlack, 2005). Since glucose, and other cellulose products, can be efficiently converted into fuels and other chemicals, the hydrolysis of cellulose into products represents an important step in solving worldwide energy problems.

Ethanol also has many advantages over other potential replacements of fossil fuel. It currently is produced in a fairly large quantity. It is estimated that the production of ethanol in the United States was just under 14 billion gallons per year in 2011 (RFA, 2012). There are many facilities for ethanol production throughout the United States (and as such has an experienced labor pool for operations and engineers) (RFA, 2012) and ethanol is able to be combined with gasoline into internal combustion engines (combines in existing engines and already used as 10% ethanol/90% gasoline blends and with flex fuel vehicles and 85% ethanol blend can be used). It is used currently in the United States to supplement the volume of gasoline with a renewable component and as an oxygenate for fuel to promote cleaner burning. Ethanol addition increases the octane rating of the fuel and reduces carbon monoxide (CO) and volatile organic compounds (Jacobson, 2007).

Ethanol is a colorless, volatile, flammable liquid. The properties of ethanol differ considerably from the other products historically stored and handled in transportation vehicles. Ethanol has a slightly higher specific gravity than gasoline (.794 vs. .72 - .78 for gasoline), a much lower Reid Vapor Pressure (2.3 psi at 100° F vs. 8 – 15 psi at 100° F for gasoline) and a

very high affinity for water, whereas water is only negligibly soluble in gasoline. Water will not separate from ethanol by gravity and sufficient water can be absorbed by the ethanol already blended into the base gasoline to cause it to separate from the gasoline (phase separation). Table 1 summarizes the key differences between ethanol and gasoline fuels. (Green, 2007)

Property	Gasoline	Ethanol
Specific Gravity	.72 - .78	.794
RVP (at 100 °F)	8 – 15 psi	2.3 psi
Affinity for Water	Low	High

Table 1: Properties of gasoline & ethanol

The most common way to produce ethanol is from biomass. Pretreatment (the initial pulverizing, heating, and mixing with water), hydrolysis, and fermentation are the three major steps for ethanol production from lignocellulosic biomass. Other methods can be used to produce ethanol such as from gasification followed by chemical reactions or more fermentation. But this report focuses on the pathway of lignocellulosic hydrolysis and fermentation due to its compatibility with the technology analyzed (catalysts used for the hydrolysis of lignocellulosic biomass). Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. The carbohydrate polymers (cellulose and hemicelluloses) are bound to the lignin. Lignocellulosic biomass includes agricultural residues, energy crops, wood, and paper waste. This represents a large amount of potential feedstock for ethanol production that could potentially replace the amount of fossil fuels consumed yearly.

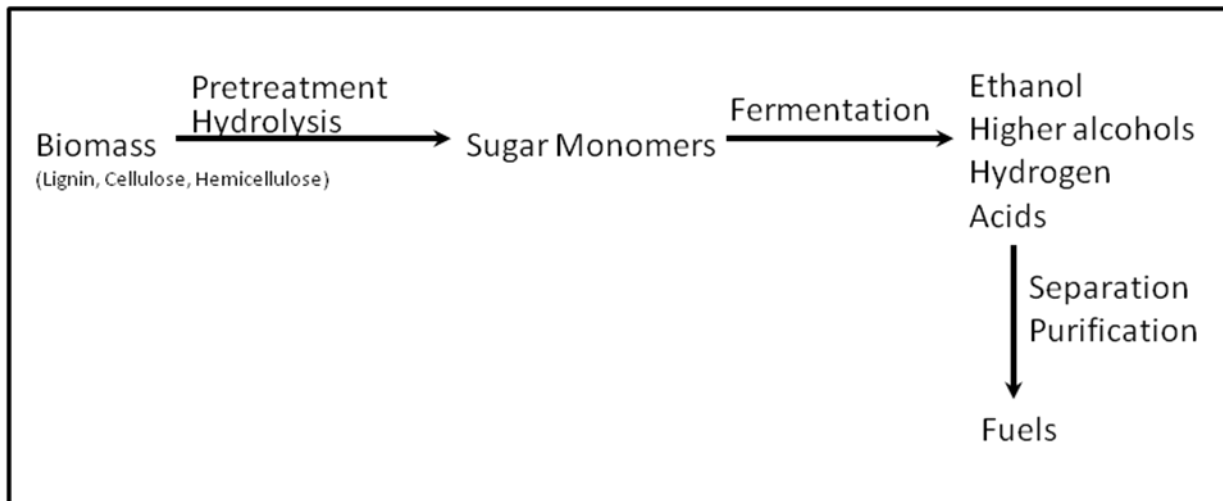


Figure 1: Schematic of the conversion of lignocellulosic biomass to fuel (modified from Kumar et al 2009)

With all the advantages of using ethanol to replace fossil fuels there are a large set of challenges for it to replace fossil fuel use. It is difficult to economically compete with a fuel source that has over a hundred years of industrial use and one in which the feedstock is currently pumped out of the ground as stored energy. The thermodynamic constraints of biofuel from biomass, i.e. by any fuel derived from photosynthesis, are necessarily limited by the solar energy which can be exploited by plants. Fossil fuels still are incredibly hard to replace due to their nature of being stored energy in reservoirs. They are also still very cheap compared to alternative energy sources and biofuel derived from plants.

This study analyzes a new technology for ethanol production and gives a techno-economic evaluation of its use. The audience of this report is people interested in this technology for large scale use: policy makers, scientists, researchers, industrial leaders, and any other stakeholder that will make informed decisions on this technology's potential and future use. The work also serves as a starting point for engineering and operating companies to begin design work beyond the high level process flow diagrams (PFDs) to develop the more detailed engineering work needed be done to take this technology to an industrial setting. The chapters also include results of a scaled down ("scan level") life cycle assessment and safety topics are meant to give readers a starting point for future work before implementing this technology. Performing a life cycle assessment on its large scale use will determine the environmental

impacts of this technology and will hopefully determine if it has any negative effects once produced on an industrial scale.

The focus on this report is the use of nanoscale magnetic solid acid catalysts (M-SACs). These catalysts perform hydrolysis and make up only a small portion of the biomass to ethanol conversion process. For the study, the complete process design is studied from biomass collection and transport to ethanol production and sales. This is done in an effort to help benchmark the technology versus other biofuel technology (i.e. how much does it lower the typical cost of a \$/volume ethanol production compared to competing technology). The sensitivity analysis is also done for that reason as well. The biomass hydrolysis catalyst affects the process only by changing the yield of glucose (and other useable products) from lignocellulosic biomass. But the holistic view of the ethanol plant is included to see what hurdles remain to implement this technology: if it be internal challenges (cost to produce catalyst, yield of glucose, and recovery of magnetic catalyst) or external challenges (capital costs, waste water treatment, operating costs). With this holistic view one might be able to know when to implement the technology (high fossil fuel energy prices), where to direct research (if it is on increasing catalyst yield or magnetic recovery), or when to refresh the study (when assumptions made on pricing are no longer valid).

The high-level approach used for this analysis was meant to follow other techno-economic models that analyzed technology at the research stage. It requires information from many different fields (cost estimates, thermodynamics, catalyst yields, economics, etc). The general approach was to develop a set of engineering assumptions based on the technology to be studied. In the case of magnetic solid acid catalysts (M-SACs), their yield and other unique qualities is taken from existing studies. The magnetic recovery (also unique to future use of this technology) data is also used from separate reports. From the initial analysis of the technology, a general process configuration is used for the proposed plant (in this case an ethanol fermentation plant). From this process layout, material and energy balances are developed from the process flow diagrams (modeled with HYSYS software). Capital and operating costs are then estimated based on the data obtained from the plant design and flow model. From this a discounted cash flow model can be created and, by varying process parameters, one can develop a sensitivity analysis (Excel with Monte Carlo/Crystal Ball software). The sensitivity analysis approach

provides a clear idea that the real contingency for this specific project is based on its uncertainties rather than relying on arbitrary values, historical databases, or estimator judgment.

This techno-economics evaluation methodology order is summarized here:

- 1) assumptions on technology based on laboratory data
- 2) process design and flow diagram creation
- 3) material and energy balances development
- 4) capital and operating cost estimate
- 5) discounted cash flow model
- 6) sensitivity analysis

The results of this study will potentially lead to future research, more rigorous studies, pilot studies, and debates on its accuracy. As technology improves and economics change, this report may need to be refreshed to include an updated analysis. Therefore, whenever possible, the assumptions are listed to aid future work.

Chapter 2 - Technology Background

Magnetic Solid Acid Catalysts for Cellulose Hydrolysis

Renewable biomass consists of trees and other plants that are grown throughout the year. The structure of lignocellulosic biomass is very complex and meant to be durable to outside conditions. Cellulose is the major component of plant biomass. Cellulosic materials consist of lignin, cellulose, and hemicellulose. The purpose of hydrolysis is to break the glycosidic bonds and create soluble sugars. Hydrolysis represents a very critical step in the overall process of ethanol creation and any industrial process that utilizes bulk plant biomass as a feedstock. The yields achieved during hydrolysis translate into how much ethanol can be produced per unit of biomass feedstock. This yield during biomass hydrolysis often determines the economics of the process. The hemicellulose portion of the feedstock creates primarily xylose, mannose, arabinose, and galactose. Glucan in the hemicellulose and cellulose are converted to glucose. The assumptions made for the products of the reaction are based on previous studies and listed in the appendix and design sections of report.

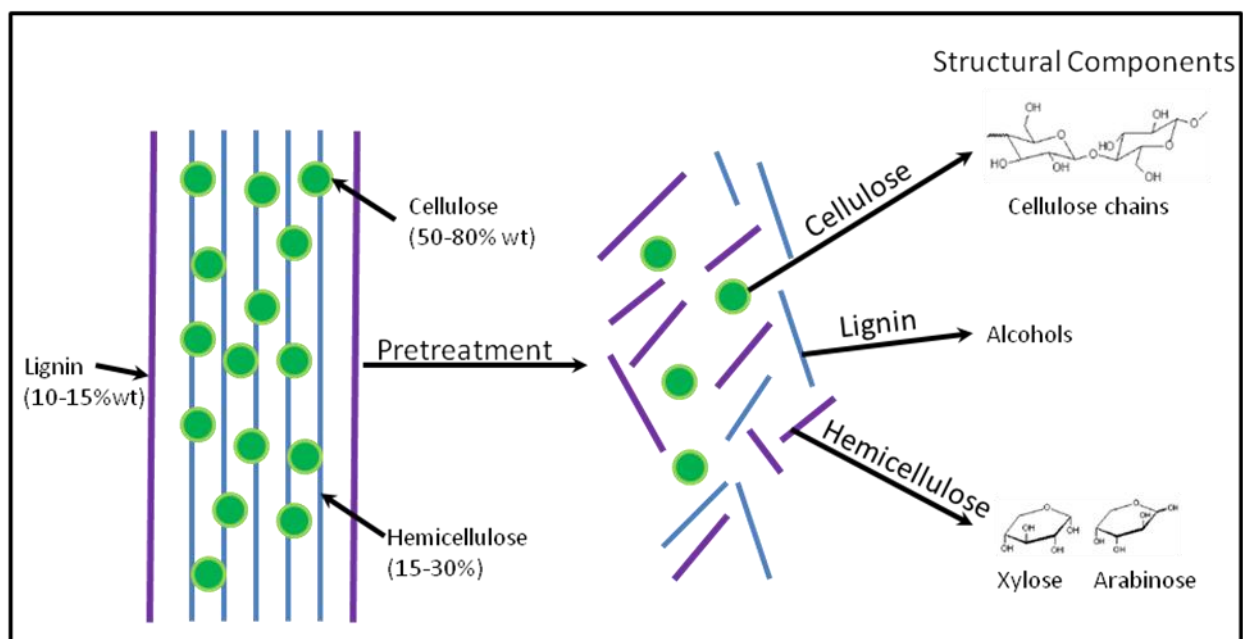


Figure 2: Schematic of the role of pretreatment in the conversion of biomass to fuel. (Modified from Hsu et al 1980 and Iborra et al. 2006)

The study of the hydrolysis of cellulose has been studied and over time the analysis has been refined. Theoretical pathways of cellulose hydrolysis reactions have also matured over time to be able to model the appearance of individual products of cellulose hydrolysis versus other models that group reactions for simplicity. Also, the strategy to catalyze the reaction has also seen improvements. Early on two distinct different strategies were used to catalyze the hydrolysis of cellulose. The first strategy was using low (ambient, 20-50° C) temperatures and very high concentrations of acid (31-70 % wt H₂SO₄). But the high operating costs, inability to recover the acid and need for expensive material to handle the high concentration of acid made this process not practical for large scale use. Secondly, a great deal of effort has been put into researching enzymatic degradation of cellulose due to the high selectivity of enzymes and the moderate reaction conditions needed. But costs of enzymes are considered a bottleneck to large scale use of enzymes on cellulose to produce biofuels (Aden, 2002). Therefore, dilute acid hydrolysis is being considered a more economic process for cellulose hydrolysis compared to using enzymes. Researchers have shifted to using dilute acid hydrolysis at elevated temperatures to have high conversion of cellulose to biofuel precursors. But using dilute acid hydrolysis still has similar challenges as using strong acid hydrolysis. Both require storage of concentrated acid (dilute acid system would require a concentrated acid storage tank) and special design steps to be taken to prevent corrosion or misdirected flow in plant that would disrupt plant conditions.

A recent advance in biofuels is the hydrolysis of cellulose using a solid acid catalyst. To aid the in recovery of catalyst and improve the costs of the process the catalyst can be mounted to a small magnet. The hydrolysis yields of cellulose to glucose can be very high using solid acids, with glucose yields from cellulose being reported as high as 74.5% (Da-ming, 2011). Solid catalysts offer the advantages of potential catalyst recovery, less or even no corrosion, and milder reaction conditions. Magnetic solid acids were developed to further aid in the recovery with the catalyst after the reaction. Using an external magnetic force, the magnetic solid acid can be recovered. This presents the added benefit of being able to recover the catalyst and not use a very acidic environment (which reduces the chemicals and the amount of waste water treatment needed).

Da-ming and co-workers have studied the hydrolysis of acid-functionalized magnetic nanoparticles and their results formed the design basis of the catalyst used in the techno-

economic evaluation. (Da-ming, 2011) The catalyst was synthesized using a modified synthetic method (a modification of Stucky's method) to create the mesoporous silica and magnetic acid-functionalized nanoparticle catalyst. Da-ming et al carried out several experiments to test the properties of the catalysts that were synthesized. Nitrogen adsorption/desorption isotherms were measured to determine the average pore diameter, Barrett-Emmet-Taller (BET) method was used to determine the surface area, and Barrett-Joymer-Halenda (BJH) method was used to determine pore size and volume. The results show that for a typical compound they created, $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$, it has a pore diameter of 4.8 nm, a pore volume of $0.49 \text{ cm}^3 \text{ g}^{-1}$, and a surface area of $464 \text{ m}^2 \text{ g}^{-1}$. X-ray powder diffraction (XRD) was carried out and showed at high diffraction angles, the typical diffraction peaks of pure magnetite (Fe_3O_4) can be observed, indicating the nanoparticle is within the mesoporous channel. Also, X-ray photoelectron spectroscopy (XPS) was carried out and showed only one peak at 169.01 eV, which corresponds to all sulphur groups being converted to sulfuric acid. All the results imply that the embedding of the magnetic nanoparticles into the catalyst has been achieved and the mesoporous structure is intact (see Figure 3).

To measure the activity and yield, Da-ming et al used cellobiose and microcrystalline cellulose as the model compounds for the reaction. All the catalytic experiments were carried out in an autoclave. For a typical experiment, 1.5 g catalyst and 1.5 g substrate were added into 15 ml water. Then the mixture was heated to the desired temperature within 20 min with vigorous stirring (typical temperatures ranged from 150-200°C). To recycle the magnetic catalyst, Da-ming et al used a glass tube equipped with a magnet. The concentration of glucose was analyzed by a HPLC (high performance liquid chromatography) system consisting and refractive index detector. The amount of total reducing sugars was determined by reaction with color formation. The color formation was monitored at 510 nm using a spectrometer. The results indicate the yields (depending on the temperature, acid catalyst, and type of cellulose) can range from 30-95%. The Da-ming and co-worker's results generally indicated that two factors affected yield the most: the structure of the cellulose and which catalyst used. For example, using $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ with starch resulted in a 95% yield while using $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ with cellulose resulted in a 30% yield. Other factors that appear to influence the yield appear to be concentration of the substrate, amount of catalyst, temperature, and amount of acid sites per gram of catalyst. Other authors have performed similar experiments to Da-ming et al. With

sulfonated carbons at 250°C, Pang et al showed cellulose is selectively hydrolyzed into glucose with the glucose yield as high as 74.5%. Pang et al, while not using magnets in their experiments, showed similar catalyst properties to Da-ming et al and the ability to achieve high yields. (Pang, 2010) These specific reaction conditions such as the yield ranging from 30-95%, the temperature of reaction, and the concentration of cellulose in the aqueous solution, went into the basis of the assumptions of the catalysts performance on the industrial scale.

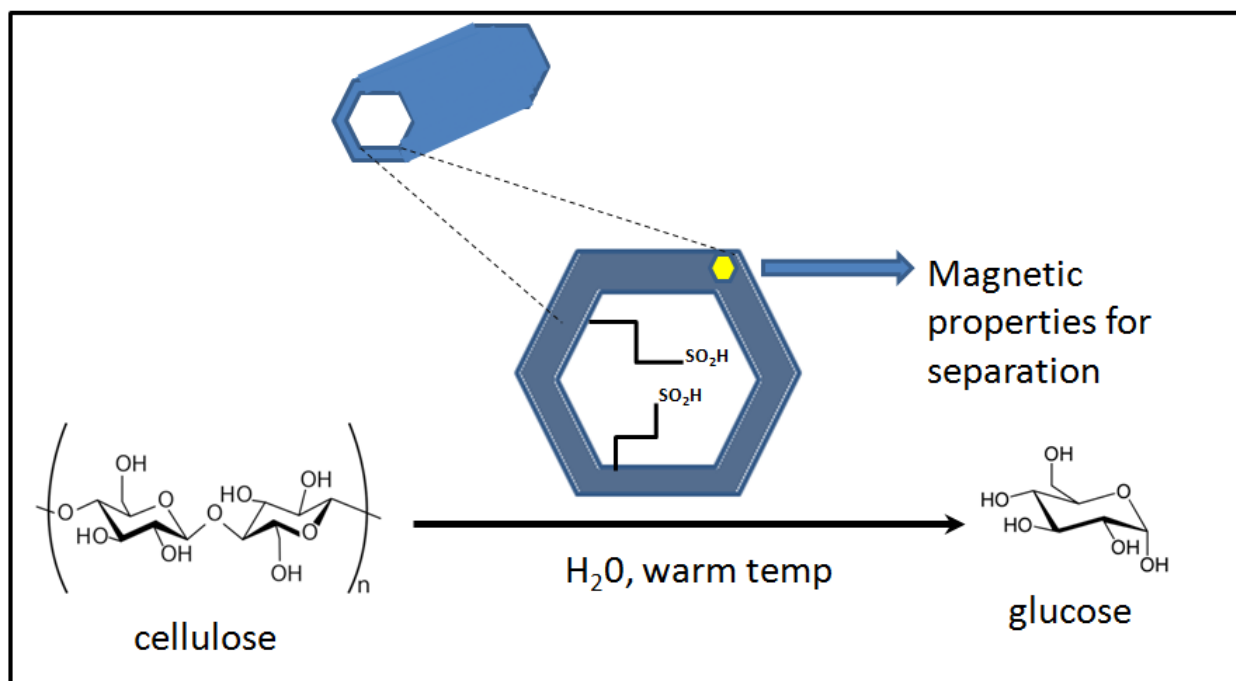


Figure 3: Magnetic solid acid catalyst used for the hydrolysis of cellulose chain to glucose (modified from Lai et al 2011)

But laboratory environments don't always translate into industrial results. High yields are often achieved by using very low concentrations of cellulose. Using a low concentration of cellulose and high amount of aqueous solution would not fit a plant process well due to lower overall production of product and the higher costs associated with separation equipment. In other words, the tradeoffs for high glucose conversion from cellulose would be lost on costs for processing equipment. Low glucose concentrations (but high yield) result in higher energy demand downstream. So catalysts that can handle high concentrations of cellulose but achieve high yields should be developed and used for this process.

Some authors though have achieved yields between 50-70% using elevated cellulose concentrations such as 1:10 wt% (in other words for every one lb, of cellulose, there is ten lbs. of water) cellulose to liquid (compared with papers that used 1:100 wt% cellulose to liquid to achieve high glucose yields) (Da-ming, 2011). To account for the large variability in both yield achieved and concentration of cellulose to aqueous solution, two major assumptions are made about the catalyst's properties:

1. The ratio of dry cellulose to aqueous solution is 1:10 in the hydrolysis reactor
2. For sensitivity analysis, yield is varied to determine what yield must be achieved to make the process economic.

The ratio of cellulose to aqueous solution matches other process plant conditions proposed by other groups and used in current ethanol plants (Aden et al, 2002). Table 2 gives examples of magnetic solid acid catalysts that can be used and properties for catalyst used in techno economic evaluation.

Catalyst	Substrate	Yield (mol %)	Amount of Acid Sites (mmol/g)
Fe ₂ O ₄ -SBA-SO ₃ H	Cellobiose	96	1.09
Fe ₂ O ₄ -SBA-SO ₃ H	Starch	95	1.09
Fe ₂ O ₄ -SBA-SO ₃ H	Corn cob	45	1.09
M-SAC (used generic properties similar to other reported catalysts)	Cellulose	Varied for study (see sensitivity analysis varied from 30%-95% yield)	N/A

Table 2: Examples of magnetic solid acid catalysts, reported yields, and generic catalyst used for techno economic evaluation (table adapted from Da-ming Lai et al 2011)

The yield depends on the condition of the cellulosic biomass entering the reactor. Cellulobiose, (cellulobiose is a disaccharide of two glucose molecules linked by a $\beta(1\rightarrow4)$ bond) can see very high yields (96%) but using more ordered and complicated analogues of cellulosic biomass in the reaction results in lower yields. For example, using amorphous cellulose (an ordered structural arrangement of glucose molecules) the yield drops to 50%. This could be

caused by insolubility of amorphous cellulose and steric hindrance of undissolved sections entering catalyst sites. Similarly, when microcrystalline cellulose (more tightly packed molecular glucose chains) is used the yield drops off to 26%. This shows one of the limitations of using magnetic solid acid catalysts versus acidic solutions. The glycosidic bonds of cellulose (the bonds cleaved by this catalyst) are blocked from the reaction site if the cellulose is not dissolved into smaller or unpacked arrangements. (Da-Ming 2011)

There are two currently accepted methods to degrade cellulose in ethanol plants that could be replaced by nanoscale magnetic solid acid catalysts. The two current methods are enzymatic hydrolysis and acid hydrolysis. Both of those methods have their tradeoffs including high costs for enzyme production and higher equipment and water treatment costs for using acid hydrolysis. The use of magnetic solid acid catalysts offers some improvements to using enzymes or acidic solutions. These advantages include being easily separable by applying a magnetic field and very high yields. In contrast to using acidic solutions, their mild nature does not require one to invest heavily in corrosion resistant piping and water disposal methods. The downside to this technology is that it is unproven in an industrial setting. Glucose yield data is based on laboratory results and might not translate into process plant conditions. All this considered, the potential of not designing for acid conditions and having to treat highly acidic water for disposal offers a huge capital and expense savings for large scale use of this technology. Another challenge is that while these catalysts have a means to be separated by a magnetic field, the separation of magnetic objects is still limited to much larger scales (micron and tenths of micron size particles) and only has recently been examined on the nanoscale for separation.

High Gradient Magnetic Separation (HGMS) of Nanoscale Magnetic Catalysts

The next unique technology used for this analysis is the separation/purification stage of the process using magnetic separation. Several other techniques were considered for separating the magnetic solid acid catalysts from the solution. Sedimentation of the catalysts could be an option due to magnetic particles tendency to form aggregates (Zhang 2008) but because of the

flow rates expected for fuel production, it was eliminated as a candidate. Sedimentation would be a slow process, and the settling velocity for the magnetic particles would require having excessively large tanks to accommodate the expected flow rates. For our design, it was calculated that for around 75,000 kg/hr (density of water 1kg=1 liter) would require a sedimentation volume of very large tanks (calculated to be in the range of 9,000 m³). Some things can be modified to increase the settling velocity such as adjusting pH, but even then under the most favorable conditions the settling velocity is around 1ft/sec (Stolarski 2007). The capture efficiency of the catalyst is also well below 100% and would result in continual replenishment of catalyst or damage to downstream equipment (as magnetic catalysts pass through to rest of the plant). Other technologies were also considered for the separation of the magnetic nanoscale catalyst. These included chemically destabilization (Zhang 2008) and expanded bed absorption (Hubbuch 2008). Each had different disadvantages such as requiring very large processes to remove the catalyst or not achieving a very high amount of recovery. These options were not considered for this project.

What appears to be the best way to separate and purify the catalyst under this application is high gradient magnetic separation (HGMS). High gradient magnetic separators are designed to recover weakly magnetic material from non-magnetic matter and are currently used industrially for many applications including the processing of iron ores, rare earths and industrial minerals.

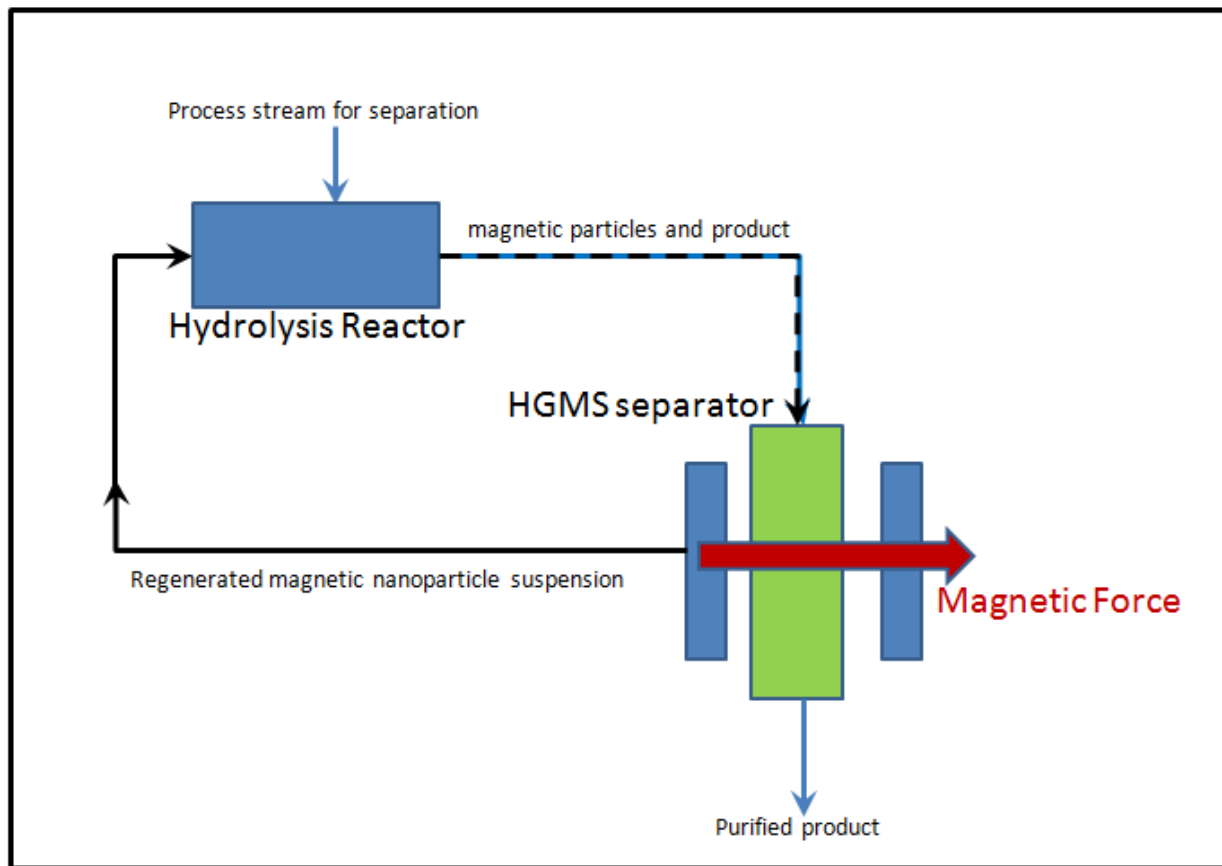


Figure 4: A general flow diagram of high gradient magnetic separator (HGMS) used for cellulose hydrolysis (modified from Moeser et al 2004)

Recently, research has shown very high capture efficiencies (up to 99.8%) of HGMS (Owings, 2011). The magnetic force is proportional to the volume of the object so smaller objects require a larger magnetic force to separate. A rough power demand can be calculated from correlations based on the magnetic principle that force is proportional to the volume of the particle (Mular et al, 2002). Therefore, nanoscale particles would require a large amount of energy to separate. The results show that roughly 800 kW of power is required for the entire plant HGMS section. The particles can be recovered by using a back wash of basic solution (pH of 10 to 11). Basic backwash is the proposed method to remove the magnetic solid acid catalyst from the filter after a cycle is completed (Owings 2011). The operation of these separators would be similar to industrial softeners where there would be a regeneration stage following the separators being saturated with magnetic particles. Also, as velocity increases, the capture efficiency decreases due to turbulent forces of particle and fluid. In experiments, the capture

efficiency can still be greater than 90% for velocities up to 4cm/s in very small columns (14cm). This corresponds to residence times of around 4 seconds. Also experimental results show that HGMS in series greatly increase the capture efficiencies (Owings 2011).

Owings (2011) recommended several general design parameters when designing a HGMS for nanoscale magnetic particles. His work shows that gravity fed filters provide higher capture efficiencies than other methods and will facilitate industrial use. Steel wool is also recommended as an efficient means to capture nanoscale magnetite. The design recommendations are summarized in table 3.

Parameter	Value	Units
Column Length	0.5	meters
Column Diameter	1	Meters
Slurry Flowrate	1790	Gallon per min (gpm)
Packing Fraction	0.68	g/ml
Induced Magnetism	2	Telsa (T)
Power Required	800	kW (Mular, 2002)
Backwash Flowrate	2980	gpm
Backwash pH	10.5-11	

Table 3: Recommended design parameters for recovery of mangetic solid acid catalysts (data from Owings 2011).

Combining these parameters with the estimated design rate of the plant we can get enough information to estimate the capital cost to construct and operating costs for a series of HGMSs for our economic evaluation. Because the current technology for HGMS for nanoscale particles have only been applied on a laboratory scale, several assumptions for design parameters are used to get it to the industrial scale. The sparing philosophy for the entire plant was assumed to be one vessel down for repairs and one vessel as sparing. Combining the design parameters above, to achieve the flow rates for the plant and the desired capture efficiency the plant will contain a primary HGMS followed by a polishing HGMS (to further remove any catalyst).

The operational requirements in addition to routine monitoring are preparation of the regenerate and conducting the regeneration of the magnetic filter. Often these are automated through a set of control valves, sensors, and logical programming. Operators typically are able to change set points for volumes of water to be used, timing of steps, and pH levels to handle

upset conditions. Experience has shown that over time operating procedures shift to using excessive amounts of basic solution and larger than needed volumes of solution to regenerate the magnetic solid acid catalysts. With this in mind, larger amounts than the laboratory results were used for all the scaled up plant design parameters (+20% volumetric flow of basic solution was chosen from laboratory scale to plant scale as an assumption). Oversight and management controls should be considered in design. In addition to routine maintenance of valves and pumps, periodic filter cleaning and vessel inspection will be required. The cleaning agents are hazardous and may be incompatible with the column materials. Cleaning agents can be replaced with other methods to remove the fouling of the vessel. Vessel internals (metal fibers, etc) were assumed to be replaced around every 10 years. The vessel itself was assumed to have a 30 year life which is consistent with vessels that are properly coated. Shorter life of the material can be expected where the water fouls the material or an excessive amount of basic solution is used and a variety of other operational parameters are considered.

Sometimes, spent backwash using basic solutions has been disposed to the sanitary sewer system. For small laboratory scales, the impact on the wastewater treatment plant will not be significant due to the small volumes for personal research use. For larger industrial plant use, the problem is much more significant. Deep well injection into a saline aquifer is one alternative as is evaporation; this system is often used by oil and gas industry to dispose of spent basic water at remote locations. All of these options are highly site specific. Because the issue of waste water disposal is significant, the examination of the option of HGMS as a treatment technology should consider the disposal alternatives and costs very early in the design process. Depending on the location and access to the correct land, the treatment of the spent basic solution fluid has a large impact both on the sustainability and the feasibility of removing metals from water HGMS. Depending on the exact design of the system and where the fluid is disposed to, it would affect the quantitative results of analyzing the system from an economic perspective.

For the design of the plant, it will be assumed that backwash water will be sent to a storage location where the magnetic solid acid catalysts can be purified and sent back to the front of plant for reuse in cellulose hydrolysis. It is also assumed that the waste water from the process will be combined with other process streams and sent to an aerobic digestion and sludge treatment area. In other words, the treatment of the HGMS backwash water will occur in a

central plant location. In summary, the following assumptions are made for the HGMS technology for the isolation of the catalysts after the hydrolysis reaction:

1. 99.8% capture efficiency base case (this will factor into how often the catalyst needs to be replenished) but it is varied in sensitivity analysis
2. 30 year life for vessel
3. 10 year life for vessel internals
4. Backwash water is treated with other waste water process streams in plant
5. To process 2000 metric tons/day of biomass (which corresponds to 120,000kg/day of aqueous solution handling) one must use 12 total HGMSs (6 trains each with one primary and one polisher HGMS: 2 in use, 2 in backwash, 1 down for repair/inspection, 1 spare) based on processing rate of 1790 gpm.

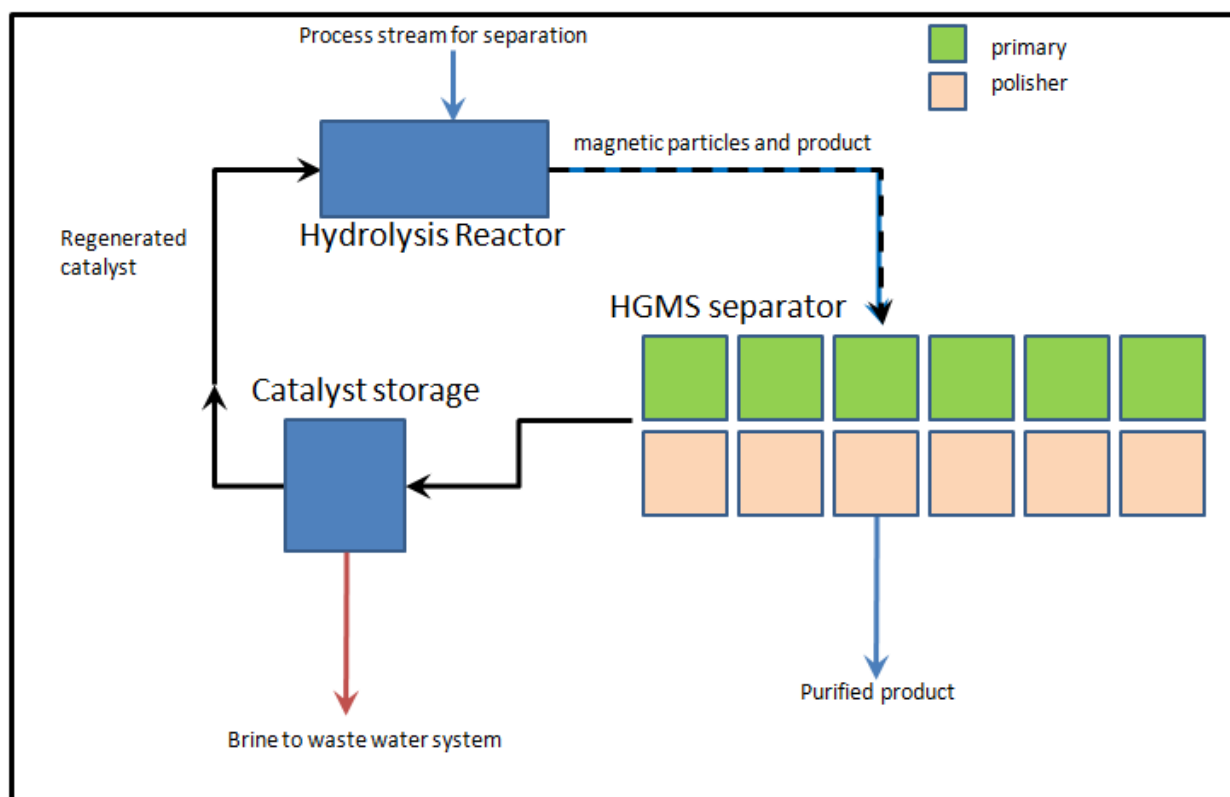


Figure 5: Proposed layout for HGMS with magnetic catalyst

This is a very high level assessment of the HGMS and future work should determine the feasibility of taking the laboratory results to a larger scale. This analysis should examine times between regeneration and capture efficiency towards the end of the HGMS cycle. In other words, the concern is how the capture efficiency is affected when the separators becomes saturated with catalyst. Also, if one is going to apply it to a large scale, engineering work should also include vessel spacing and safety requirements of using high powered magnets.

Summary of the Assumptions on Technology and Future Work

The basic assumptions of the model are to have yields and catalyst recoveries that match laboratory results. This report will analyze the ability of the technology that is currently at the laboratory level to be applied to large scale industrial settings. This is easier said than done and much work needs to be done to scale up the technology of magnetic solid acid catalysts and their use with high gradient magnetic separation to the large scale. Future work should follow the recommendations of previous authors (Da-ming, Duque, and Owings) on ways to close the gap between the laboratory and industrial scale. Some of the recommendations to continue the research include study of the thermal stability and water affinity of the catalyst to determine how much may be lost during pretreatment conditions (elevated temperatures and aqueous conditions).

The big advantage of this technology is the recyclability of the catalysts and it should be studied long term, after several regenerations, to determine the long term catalyst properties and ensure there are no changes during reactions. Also, the study is based on a % yield of glucose only. The heterogeneous nature of the catalysts could also be studied to determine what mass transfer limitations may be present. So in other words, the reaction kinetics should be evaluated to determine retention time necessary for reactor sizing and more precise numbers for yield. Selectivity of the catalyst needs to be improved to further maximize the yield of glucose and limit unwanted byproducts (Da-Ming, 2011).

In future work it may also be worth exploring the use of magnetic separators to separate the magnetic solid acid catalysts. As stated in previous section, other options exist that may prove to be better options. The recovery method does not necessarily have to be magnetic for the catalysts; any metal core catalysts could work due to the differences in density of solutions (Duque, 2009). But it is crucial to get high recovery of the catalyst to prevent constant replacement or equipment damage downstream of the process.

If the use of high gradient magnetic separation is pursued, more work needs to be done on comparing velocity of fluid and capture efficiency in the filter. Smaller particles result in decreased stability so while the laboratory results look promising, more work should be done to

determine if the smaller size results would result in lost catalysts on a large scale (Moeser, 2004). Also, loading of the magnetic separator and diffusion limitations may have a significant effect on large scale application. If this technology is pursued, a shaping plan should be established to show the current state of the technology and critical steps to go from laboratory scale to the large scale. This report shows it is very promising but strategic investment and research work need to be done to get some of the uncertainty down and propose scaled up version of it.

Until those uncertainties are resolved though and detailed process design takes place the following assumptions were used for the techno economic report:

Assumption	Value	Reference
capture efficiency	99.8%	Owings (2011)
life of vessel	30 year	used for this report
total HGMSs to process biomass amount	12	used for this report
Ratio of dry cellulose to aqueous solution	1:10	Da-ming (2011)
Glucose Yield (P10:P50:P90)	50%/75%/90%	Da-ming (2011)

Table 4: Summary of technology assumptions

Chapter 3 - Process Design

Design Basis

The design basis chosen for this plant design was a feedstock of corn stover and a daily rate of 2000 metric tons of biomass to be processed. The size was selected based on reports of optimum ethanol plant size with regards to transport costs (Aden, 2002). After the size of the plant was established, a typical flow of the biomass and associated unit operations were input into the simulation software. A comprehensive process model was then developed for biomass saccharification, fermentation, and distillation in the HYSYS process simulator. The HYSYS model was used for two main reasons: 1) To get flow streams of each component needed to estimate operating costs and revenue from products & 2) To get an overall plant layout so that a capital cost can be estimated. With the exception of the use of the magnetic solid acid catalysts,

the design of the plant is very similar to other proposed or already functional cellulosic ethanol plants. (Aden 2002)

The thermodynamic basis used for the simulation was non-random two liquid (NRTL) model. The selection of the thermodynamic model is the biggest decision that went into the design that could greatly affect distillation performance, separation of fluids, and amount of vapors that are produced. Several other models were weighed that could affect the quality of the results. The components expected in the mixture are going to be a combination of polar component (ethanol, glucose, water) and ideal behaving gases (methane, carbon dioxide at low pressure and moderate temperature). So therefore an activity coefficient model was selected due to their rigor in focusing on the liquid state and assuming ideal gas behavior. Systems that contain water and ethanol are generally considered well suited for activity coefficient models (Prausnitz 1999). Of the binary interaction parameter activity models, the NRTL and Wilson equation are most commonly used. The binary interaction parameter models calculate activity from empirical data of two components (binary) and extrapolate them to other mixtures. Both NRTL and Wilson are considered acceptable for polar liquids, nonideal liquids, and ideal vapors. Eventually NRTL was chosen as the thermodynamic model to use in the HYSYS process simulation due to its improved ability to model electrolyte solutions (which would be encountered when minerals are added or in other process streams that use basic solutions). But both Wilson and NRTL were tried in the HYSYS simulation and there was not a significant difference between the two.

The feedstock was assumed to be corn stover due to its wide scale use in current ethanol facilities and the amount of corn stover produced in the Midwest of the United States. “Stover” is a term that refers to the rest of the corn plant: everything above ground except the kernels (leaves, stalk, cobs, husks, etc) (Perlack 2005). The feedstock type and composition is very crucial to the overall plant design and economics due to increases or decreases in products due to the composition change. For example, cellulose could result in requiring a new design for handling an increase in certain products or affect the overall yield of the plant. In future studies it would be interesting to take the process simulation and vary the inlet composition of the biomass to see how it would affect the operation of the plant. There may be a wide variety of plants that could be used and, similar to crude pricing in oil refineries, one can purchase biomass based on price and expected products. But to simplify the model only corn stover was used and its feedstock composition can be seen in table 5.

Feedstock Compositions (Aden, 1999):	
Cellulose (Glucan)	37.4%
Xylan Fraction	21.1%
Arabinan Fraction	2.9%
Mannan Fraction	1.6%
Galactan Fraction	2.0%
Lignin Fraction	18.0%

Table 5: Feedstock composition used for study based on corn stover

After the overall design of the plant (which technology to apply to other portions of the plant), thermodynamic package, and feedstock composition were determined, the next steps were to begin to develop the process flow diagram of the plant. For each of the reactors the kinetic data were not used, but the reactor performance is based on published numbers for yields for ethanol plants. This was considered an acceptable assumption to make since it has been done before in other techno-economic evaluations (Humbird 2011). Also, for the new technology of separating the nanoscale magnetic solid acid catalysts with high gradient magnets, the simulation software used a typical reactor but separated all the solids out of the system, recycled and put

them back into the front of the plant. So in other words, for the simulation software no attempt was made to apply the physics of the magnetic force, reactor retention time, and capture efficiency to designing the system. The hydrolysis reactors simply apply the yield from published reports and later downstream the catalysts are manually separated from the process simulation (user defines that all catalyst leaves unit operation for recycle) and then recycled to front of plant. The magnetic separators (denoted HGMS-primary & HGMS-polisher) only removed a 1% of the catalyst in each stage (95% removal in the HGMS-primary & the remaining 5% HGMS-polisher). So the HGMS reactors are treated as a “black box” and the operating costs (mostly from filter replacement and energy costs to apply the magnetic force) were input manually.

The distillation tower for the ethanol was treated rigorously and the entering stream of ethanol is distilled in the tower. The process flow diagram has the feed entering the plant and mixing with several other streams (chemicals). To estimate the costs of chemicals used the daily feed rate was used and the necessary chemical feed rates were then calculated into the daily operating costs. Heating, cooling, pumping, and compression costs were also calculated on a kilo-watt hour basis so the energy costs so that energy costs of the plant can be incorporated into the design.

Another important aspect of the plant is the treatment of the vapors off the top of the tanks. As seen in the process flow diagram of the plant (Fig 6 & Appendix H) each stream is separate and appears to go to atmosphere. Typically vapors are not allowed to vent to atmosphere in many air regulatory areas. The streams appear to go to atmosphere and are totaled later in a separate stream (“compression-1”) and feed to a fired boiler for electricity and heat generation. This was done because combining the 7+ streams of gas/vapors that come off each unit operation and sending them to compression sites and then to waste gas incineration caused the process flow diagram to become very cluttered and unreadable. Instead, each vapor stream was taken off the top of each unit operation. Then a single stream was created to account for all the excess gas and then this stream is combusted. Ethanol vaporizes in air less readily than gasoline. When it is loaded into a truck compartment it generates approximately half of the vapor that a similar volume of gasoline would generate (RFA, 2009). Ethanol vapor is compatible with both vapor combustors and carbon adsorption units and does not adversely affect the capacities of these units. There are however, components of each of these systems that will require

additional attention when ethanol vapor is introduced beyond the requirements for straight gasoline and distillate.

Also, some of the operations that are in a typical ethanol plant are not included. A large portion of existing plants is the trucking/conveyor system at the inlet of the plant. This was not included in the HYSYS model because there were no existing unit operation to model it. Similarly laboratory facilities and a control room were not included. The costs of each of these facilities was estimated later and not included in the process simulation but included in the cost estimate. So the process simulation only includes pumping, hydrolysis, fermentation, distillation, and other necessary unit operations to accurately model the mass balance of the system.

Another major portion of the plant that was not included in the process simulation was a filtration area to remove particulates from the product. Ethanol filtration is required by the Ethanol Product Integrity Standard (RFA, 2009). Filtration is especially important for ethanol because of its strong solvent properties. While being transported to the plant, inside the plant and within the sales terminal, there are numerous opportunities for the ethanol to encounter and become contaminated with particulates. These include tanks and piping within the terminal & process plant. Similar to other necessary unit operations that were not included in the HYSYS simulation, the filtration of ethanol was accounted for in the cost estimate. The cost of the ethanol compatible filter elements is very close to that of the elements that are only compatible with petroleum products. It is important to note that even though filter elements rated for ethanol service are usually compatible with gasoline and distillates, conventional filters used in gasoline or distillate service are not compatible with ethanol. Ethanol will dissolve the glue holding the filter element together in a non-alcohol rated element causing a catastrophic failure. (API 2003) It is recommended that ethanol compatible filter elements be used for all products in the terminal so as to eliminate any possibility of this occurring. This hazard would cause a leak and significant fire hazard. Because of this, the filter costs were based on filters rated for ethanol service only and not on filter costs for petroleum products. Whenever possible, cost estimates were based on equipment suitable for biofuel/ethanol use only.

Another exercise was done to make sure the results were accurate. After the mass and energy balance was completed, it was compared to other studies to see if it was accurate or not. Tables 6 & 7 shows the major inputs and outputs of an ethanol plant in comparison with each

other. Table 6 shows the results for this study that took 2000 metric tons/day of and calculated all the inputs (stover, water, and energy) and outputs (dried grain, waste water, carbon dioxide). The results were then normalized to a per ton basis to compare to the study completed by Mai et al (2005). The original study looked at a similar corn to ethanol conversion. The similarities support the accuracy of the process simulation done for the ethanol plant that uses the magnetic solid acid catalysts. It is also reassuring that the overall yield of the plant is below the theoretical yield of glucose to ethanol. The theoretical yield, or the maximum possible amount of ethanol that can be produced from glucose, is for every 1 ton of glucose produces 0.5 ton of ethanol (based on equation $\text{Glucose} \rightarrow 2\text{ethanol} + 2\text{CO}_2$). It is less that the max theoretical yield in this process simulation due to conversions less than 100% in many cases. Also there are losses due to vapor production and losses in waste streams (see table 7).

This report: Magnetic Solid Acid Catalyst Plant		
Inputs		
Component	Amount	Per ton basis
Corn Stover	2000 mt/day	1.0
Water	5000 mt/day	2.5
Energy	10,000 MMJ	5 MMJ ($\times 10^6$ J)
Outputs		
Component	Amount	Per ton basis
Dried Grain (solids)	800 mt/day	0.40
Waste Water	5,300 mt/day	2.65
Carbon Dioxide	480 mt/day	0.24
Ethanol	760 mt/day	0.28

Table 6: Mass & Energy balance for proposed ethanol plant

Mei et al (2005)		
Inputs		
Component	Amount	Per ton basis
Corn Stover	3125 mt/day	1.0
Water	8380 mt/day	2.7
Energy	19,000 MMJ	6 MMJ ($\times 10^6$ J)
Outputs		
Component	Amount	Per ton basis
Dried Grain (solids)	1040 mt/day	0.33
Waste Water	8500 mt/day	2.72
Carbon Dioxide	970 mt/tons	0.31
Ethanol	1000 mt/day	0.32

Table 7: Mass & Energy balance for study completed by Mei et al 2005

The full mass & energy balance of the process is in Appendix E. The nutrients refer to the nutrients required for *Z. mobilis* growth. These nutrients are Corn steep liquor (CSL) and Diammonium Phosphate (DAP). These are both nitrogen and energy sources and are added to the fermentation reactor to sustain the bacteria that ferments the glucose into ethanol. The ratios of enzyme and nutrients are based on stoichiometric relationships for maintaining the bacteria (Aden, 2002). The mass and energy balances in the appendix match table 6 and are similar to published work for mass & energy balance in published work in table 7 (Mei et al, 2005). One will notice in energy balance (Appendix E) that there is a error of around 3% between the inlet and outlets of the plant. It was calculated that the energy input is 10,000 MMJ/day versus an output of 9,690 MMJ/day. This was assumed acceptable due the size of the error (3% was assumed small enough to be acceptable) and the overall assumptions used in the design of the process simulation.

The HYSYS model is rigorous & accurate but it is not perfect. Many operations, such as the separation of catalysts and hydrolysis reactor yield, were modeled either based on fixed laboratory results or on known values. Stoichiometric relations capture the mass and energy balance but don't account for other reactor design considerations such as retention time and heterogeneous catalyst effects. This may affect the results of the over yield of products, cost estimate, and therefore the overall project economics. But one must weigh the trade-offs of effort and increased quality of information in all techno-economic evaluations of new

technology. If readers find the results intriguing, more detailed process simulations can be done. One must keep in mind that with any process simulation, it simulates based on assumptions and no simulation can ever fully predict real world results.

Basis of Plant Size & Utilization

The plant size was fixed at processing 2000 metric tons a year of biomass. The size is based on past studies that have looked at the optimal way to design a plant based on transportation costs and availability of biomass in rural areas (Gnansounou, 2010). Simply put, the larger the plant the higher the transportation costs due to having to travel further to collect biomass. In 1991, NREL (National Renewable Energy Laboratory) undertook a study to evaluate the trade-offs of a typically designed ethanol plant and varying the capacity of the plant. The trade-offs (cost to increase plant capacity, operating costs, revenue from sales) indicate that the optimum plant size is 1750 metric tons per day of biomass (Ruth, 1999). Other reports have used varying values for this size though. A value of 2000 metric tons per day of biomass though was settled on due to other studies that have used it and it is reasonably close to the NREL study's optimal feed rate of 1750 metric tons per day. Some techno-economic evaluations of ethanol plants used values as high as 2500 metric tons per day of biomass (Humbird, 2011) so this set value for the plants throughput seemed accurate and reasonable.

It was assumed that the run time of the plant is 350 days/year based on recommendations for plant operating time per year (Brealey 2003). This is 15 days of down time per year, which seems like a conservative estimate (safe) even when considering the complexity of the process and use of new technology. Due to the multi train nature of many processes this in reality could be much less considering the driving force for a plant shut down would only be single train operations (distillation columns & waste gas combustion). Distillation columns typically take one week for a full maintenance turnaround, so 15 days of downtime is probably on the high end of expected yearly maintenance plant down time.

Process Flow of Ethanol Plant

The process simulation flow can be seen in figure 6 and a larger version in Appendix H. Biomass enters the plant assumed to be already pulverized to small enough form for the pretreatment. As mentioned in the previous section, the truck off loading and conveyor system is neglected in the process simulation but in reality this would be an important part of plant design. The feedstock storage and handling would need to be specified from scales for sales to spacing of biomass for storage. While it was not included in the simulation; its costs are included in cost estimate and based on similar studies. A value for energy was assumed for the crushing of the biomass into smaller sizes for initial treatment and this was included in the electrical energy demand.

The biomass enters the simulation environment and is immediately mixed with steam for the purpose of increasing temperature and getting into an aqueous solution. When this moderate temperature mixture (~150 C) is mixed with the nanoscale magnetic solid acid catalyst in V-101 it creates a mixture of soluble sugars (xylose, mannose, arabinose, and glucose). Vapors are collected from the mixture, compressed, and combusted later as waste gas. Since the process simulation software does not have a chemical to represent the catalyst, a user defined one was input into the system where the properties of iron were used, and it was specified that the compound is a solid for all conditions that would be encountered in the plant. From there the mixture travels through the high gradient magnetic separators (HGMS-Primary & HGMS-Secondary). During this stage, the separators remove 95% of the user defined solid (the nanoscale magnetic solid acid catalyst) in the first stage and then the remaining 5% in second stage polishing separator. This section of the plant represents the unique part of the technology. Other groups in the saccharification/hydrolysis stage typically perform hydrolysis with strong/dilute acids or enzymes. The major goal in this stage is to take the cellulose (representing a large % mass of the feedstock) and other sugars from its chain structure into individual glucose molecules. To model this reaction with the nanoscale magnetic solid acid catalysts, only yields were input for glucose yield. This number is based on published reports for glucose yield from these catalyst in a laboratory environment. The base case of the simulation was 75% for glucose yield from cellulose but was varied from 50% to 90% in the sensitivity analysis (see Chapter 5). All deterministic results are based on a yield of 75% such as the

material balance and economic results in Chapter 4. From there the solution (the monomer sugars) travel into storage tanks where vapors are again removed.

From here the solution enters the fermentation tanks where the sugars are converted to ethanol. Similar to other techno economic evaluations of biomass to ethanol plants, the enzyme selected was *Zymomonas mobilis* because it is a publically known enzyme and its costs are known and can be factored into the operating expenses (Humbird 2011). As with the hydrolysis reaction, the yields were input into the process simulation. The added benefit of *Z. mobilis* is its ability to convert both xylose and glucose to ethanol (Aden 2002). Some authors have decided to grow the bacteria and use their enzymes all within plant, but for the process simulation a separate stream of enzymes were put into the reactor and an estimated yearly use was estimated. This cost was factored into the cost estimate. The nutrients needed to grow *Z. mobilis* were also included in the operating costs as well (see mass balance in Appendix E). Future, more detailed, process simulations may need to account for how bacteria are produced. Volumes of the size of the vessel were estimated based on other techno economic reports and factored to account for the different estimated volumetric flow rates. (Aden 2002, Humbird 2011) The total size of fermentation tanks required is around 1 million gallons which in reality can be broken into smaller tanks in parallel. The fermentation tanks were cooled by air coolers and cooling water heat exchange (cooled to 40°C to prevent enzyme/bacteria damage). The required amount of energy to cool the reactor was input into the process simulation to calculate the operating expense of keeping the reactor temperature at steady state. Once again, the vapors from the fermentation process are collected, compressed, and used for waste gas heat & power generation. Most unit operations assumed a certain amount of heat lost due to ambient conditions and throughout the process heat or cooling was input into the system. This is done to get an accurate amount of the heating costs of the plant (see E-101).

From here the mixture of products from the fermentation beer are sent to the purification portion of the plant. Following other existing plant designs and published reports, the two methods of purification are molecular sieve adsorption and distillation. (Aden 2002, Humbird 2011) The beer column removed CO₂ produced during the fermentation reaction (this is seen in vapors-7 stream) and sends it to the atmosphere. After the beer gas is removed, it enters the distillation column. The bottom of the column are sent to the solid handling section (solids

removal-2) and a portion of the un-reacted mixture from there is recycled back to the front of the plant (stream RCY-2).

Molecular sieve adsorption and distillation are used to purify the ethanol to sales specification. For the design, a sales specification of >99.3% ethanol purity was assumed. From this the distillation column can be sized based on the entering components. Other product take offs were also estimated for side products and unwanted by-products such as acids (lactic acid, acetic acid, etc) and other compounds (xylitol).

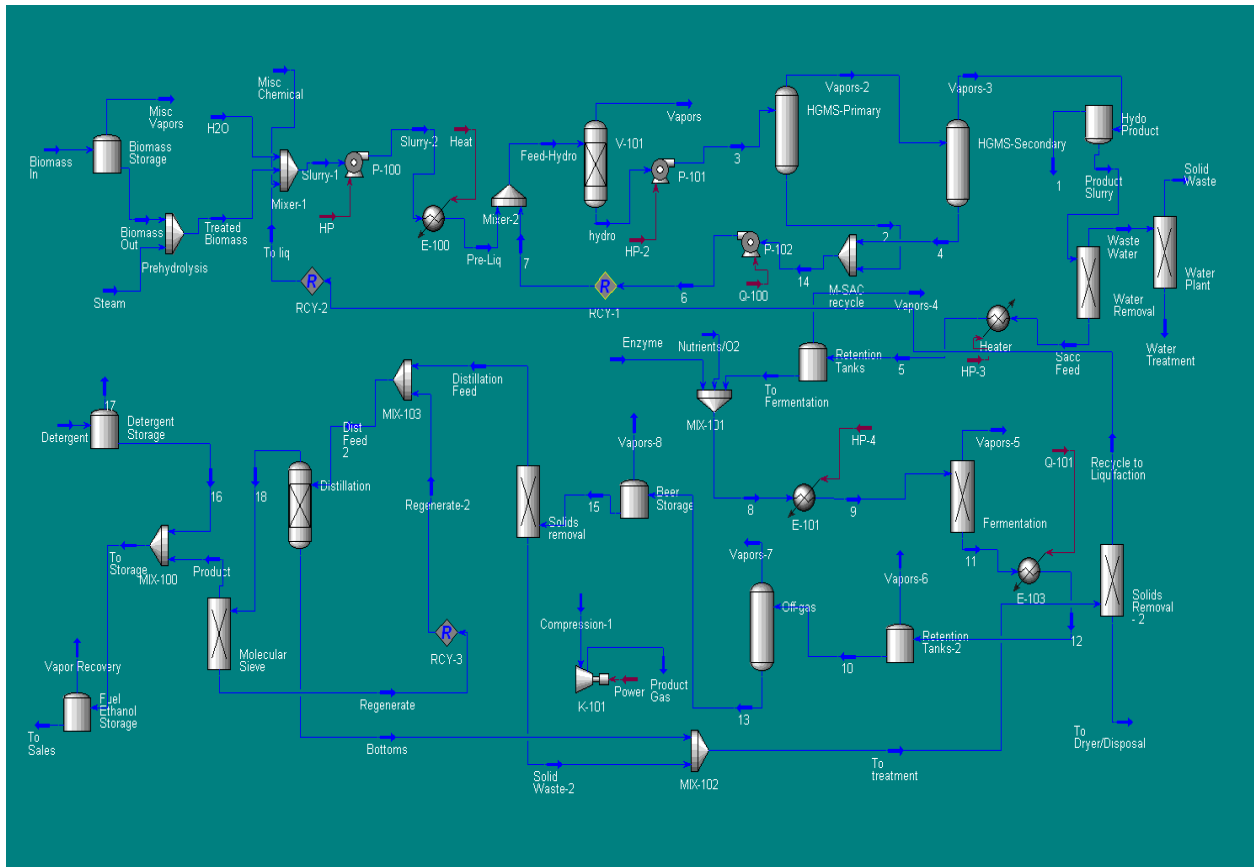


Figure 6: Process flow diagram (PFD) of ethanol plant with magnetic solid acid catalysts using HYSYS software

The amount of silage and other waste products from the process warrants careful attention to the solids handling and water treatment facilities. The amount of waste water is calculated, its chemistry known, and therefore one can design a high level water treatment facility. The major sources of waste water are non-recycled water from the process, condensate

from vapor recovery and compressor system, and water from the solids removal system. The typical first step for water treatment is the removal of dissolved solids and for this the technology a walnut shell filter and dual pass bag filters were used to get the total dissolved solids in water down to solids of <1micron in size. The other process needed is to remove any organic matter. This was done by anaerobic digestion and aerobic digestion. After removing the solids and organic matter, the water was considered treated and sent in local utility waste water for municipal treatment.

The final stage of the process simulation was the ethanol storage. For the final stage a small amount of methanol was added to follow similar process simulation designs (Aden 2002). The methanol acts as a denaturant for the ethanol. In other words, in order to make ethanol not suitable for drinking or to be used in other purposes (eg. medical purposes), methanol is added to it to make it more poisonous and unpalatable. Methanol was used because it is cheap, unpalatable, and extremely poisonous. Other chemicals to consider for a safer design might be ammonia or gasoline. This portion of the plant does not represent a huge cost impact so methanol was chosen without much consideration to the trade-offs of other chemicals. Similarly to the front of the ethanol plant, no simulation work was done on the loading racks for trucks that ship ethanol out of plant.

Several other systems could be potentially modeled but were not for the sake of simplification of the process simulation. In reality, there are several smaller systems that could be included. The utility water system may be needed to be included if the municipal water is of poor quality. For example, if it is high in metal ions such as calcium and magnesium (the water is hard) a softening system may be needed to be included. Also, it was assumed the design of the instrument control system would be based on an instrument air system and programmable logic controllers (PLCs) control the plant operation. This, and any other minor systems that were not necessary for the energy and mass balance, was not included in the simulation but its capital and operating costs were included in the cost estimates. Air control systems and conveyor systems were not included because they are essentially utility system and don't affect the reaction yield. This allows for us to design the system in HYSYS and account for these systems in the cost estimate and the results would reflect an accurate cost estimate and yield.

Comparisons to Other Reports

There are many ethanol plant techno economic reports that exist and it should be noted that some of the design decisions that went into this process flow diagram and simulation were different from what other authors chose. Future work may choose to include different designs in the work that will affect the cost estimate and therefore the overall project economics. A major difference is that this process chose to use corn stover as the feedstock which is considered a relatively easy feedstock to produce economically. Other studies (US DOE, 2004) have used wood chips as a feedstock which has a less favorable composition than other feedstocks. Sassners et al (2008) directly compared the economic performance of lignocellulosic to ethanol conversion by three different feedstocks: softwood (spruce), hardwood (salix), and agricultural residue (corn stover). In that study it was found that the chemical composition (notably the differences in the amount of hexose and pentose) affected the overall process economics. Changing the feedstock was not done in this study but may impact the results in real world plant designs. It was considered for the sensitivity analysis, but changing the chemistry resulted in large changes in the process design and affected the capital costs. With so many variables, it was chosen to keep the feedstock constant.

Many other authors have also significantly varied the feed rate of the plant well beyond the “optimum levels” chosen for the design basis of our plant. In reality, this may be an option if the plant is located with a higher amount of available biofuel or has easy transportation access that would lower transport costs (such as near railroad or water way). These detailed design decisions (such as plant location) should go into more detailed future work.

Most studies have used pretreatment of biomass with either dilute or strong acid. This is the major difference between this study and existing techno economic evaluations. Most studies differ on how the fermentation enzyme is produced. Aden (2002) had on-site production of enzyme while others (Wooley 1999) did not include it in the process design but assumed a value for the costs and use. Also, on a totally different pathway, many authors have compared the thermochemical ethanol (via indirect gasification) with lignocellulosic ethanol production (Phillips, 2007). So while this technology may appear to be an improvement over conventional methods to produce ethanol, it should be kept in context with different pathways that can produce ethanol from biomass.

One of the biggest differences in this report compared to other reports is the material used for the plant construction. Carbon steel, from a corrosion standpoint, is generally considered compatible with fuel ethanol and all other anticipated chemicals in the plant that uses nanoscale magnetic solid acid catalysts. The big trade off (as seen in Chapter 4, section Capital Investment) of using this technology is the ability to avoid using stainless steel. Traditional ethanol plants must use stainless steel (or other metal that is corrosion resistant such as Hastelloy or Incoloy piping) due to the acid streams. The fermentation stage equipment for both designs can be either be stainless steel or carbon steel. If carbon steel is used, it is with a thicker wall to take into account corrosion allowance so the costs savings of using carbon steel versus stainless steel for this stage is negligible. Authors have used both in their analysis (Aden, 2002 & Humbird, 2011). Capital costs are similar for a stainless steel reactor and one made out of extra thick carbon steel. So in the case of the fermentation stage, it was assumed to be carbon steel but the reactor costs are similar for both cases.

Carbon steel is used as this plant's design basis for simplification even though the fermentation stage may be stainless steel. Carbon steel has been used in ethanol service for many years and is the preferred material because of its strength and lower cost. While carbon steel is susceptible to SCC (stress corrosion cracking: the growth of cracks in a corrosive environment), this phenomenon has rarely been seen in piping. SCC occurs more frequently in the plate steel associated with storage tanks especially on the tank floors and to a lesser extent in the lower areas of the tank walls. (RFA, 2009) In order for SCC to occur there must be a stressed area within the steel. This is common in the steel plates of a tank floor where cyclical filling and emptying of the tank constantly change the level of stress in the floor panels and welds as they flex under the varying weight of the fluid in the tank. The stresses induced by the flexure are added to the stresses already present in the heat affected zones around the welds. Part I of API Technical Report 939-D (2007) identifies high mechanical loads, stress concentration and flexural loading (dynamic stressing/straining) as mechanical factors associated with promoting SCC. In piping applications these stress fluctuations are less pronounced because of the higher rigidity inherent in the pipe. This could factor into the lower incidence of SCC that has been observed in piping. So with this in mind, carbon steel was selected as the piping material for the plant, and all tanks that were assumed to be susceptible to SCC, were assumed to

be protected with an internal coating or constructed out of an alloy material (see cost estimate breakdown in Appendix B).

Almost all other techno-economic reports use stainless steel as around 50% of their plant piping due to the acid streams used in the hydrolysis section (Aden, 2002). Stainless steel offers the advantage of being less susceptible to SCC but introduces other considerations including higher material costs and special welding procedures and is therefore not generally recommended for plant design unless necessary. The most common grade, 304, is susceptible to exterior surface corrosion and, in coastal areas, chloride corrosion cracking. This is a consideration for marine environments where chlorides from the salt air and moisture from humidity can combine to cause corrosion over the entire surface area of the pipe and/or concentrated corrosion in areas where chloride deposits can accumulate without being washed away periodically. Acid piping must be constructed out of some form of corrosion resistant material. Stainless steel has been used in most techno-economic reports because it provides the corrosion resistance but is not as expensive as other options.

Other authors (Wingreen, 2008) have varied the plant configuration to determine the best design of an ethanol plant. But the results of the study seemed to be offset by the overall uncertainty of early design economics. For example, studies looked at integrating stripping sections with evaporators and different ways to handle the waste gas. The differences in the design seemed offset by the overall error introduced when doing high level economic evaluations. In other words, it is difficult to base a decision to implement a design that saves \$10 million dollars when the overall uncertainty in the cost estimate is \$60 million. So only one design was used in this study and the glucose yield (which is the largest uncertainty in the use of magnetic solid acid catalyst technology) was varied to see the potential of the technology to be adopted in industrial ethanol plants. The previously mentioned variations such as daily tonnage of feedstock and feedstock composition are worth studying but were not included in this report. Also, the plant and technology selection was based on existing technology and no attempt was made to pair this technology with new or emerging technology.

Chapter 4 - Economic Analysis

Methodology

Using an unbiased way to evaluate potential projects is essential to a successful business. Mostly companies have a longer list of potential investments than available funds to spend them on. So ranking investments in terms of an overall, normalized rate of return is important to help determine which investments to make and where to spend money. Economic analysis is a systematic process for evaluating and examining alternatives and information using economic measures, methods, and statistical tools to assist in selecting the best alternative/opportunity. It combines the use of cash flows and financial theory with financial statistical analysis. It is generally accepted by organizations that the proper way to evaluate potential investments is by using a discounted cash flow basis.

In order to compare the attractiveness of investment alternatives with cash flows that occur at different times in the future, the cash flows must be adjusted to account for both the time value of money and the risk associated with the cash flow. All project economics, forecasts, and resultant economic parameters should be computed on a cash basis.

Why does one discount the future value of money? The timing as well as the amount of the cash generated by or expended by an investment alternative are key drivers of its financial attractiveness. Timing is important because funds received today are worth more than funds received in the future. This time value of money principle is included in the investment analysis by discounting future net cash flows at appropriate rates to reflect their present value.

U.S. and foreign tax considerations can influence the results of an evaluation significantly by reducing the project's cash flow. Tax treatment for revenue, operating costs, and capital investments may differ. In addition, the tax treatment for interest payments, overhead costs, R&D expenditures, and state income taxes requires special handling.

The basic concept of discounting cash flows is that of compound interest. The formula for compound interest:

$$\text{Future Value} = \text{Present Value} * (1 + i)^n$$

where

i = a return (discount rate) expressed as a percent

n = the number of periods in the future

In order to compare projects with cash flows occurring at different points in time, a return standard is needed, which should account for both the time value of money and the project risk. Since projects are exposed to different risks, in theory, they should have different return standards, meaning they should use different rates to discount their cash flows to calculate present values. The project to install a biofuel plant that utilizes a new technology is assumed to be of significant risk and a discount rate of 10% was used. This value is comparable to the risk associated with drilling a new petroleum well or other “first of its kind” new technology project. Other reports review used 4% discount rates for their proposed ethanol facilities, so this will make the economic analysis more conservative and include risk associated with the project. Table 8 lists a few of the economic parameters used to model this ethanol plant. It is important to note a few of them that may be up for debate. As mentioned earlier, the discount rate/cost of capital is 10% due to technological risk. This is often called shareholder's required return on a portfolio of all the company's existing securities. So while other ethanol reports have used as low as 4% (Gnansounou, 2010), I feel 10% accurately captures the risk of the project.

For the depreciation, a 10-year cycle was used. The Modified Accelerated Cost Recovery System (MACRS) is the current tax depreciation system in the United States. Under this system, the capitalized cost (basis) of tangible property is recovered over a specified life by annual deductions for depreciation. A 10 year property was used for the assessment. A ten year property includes assets used in “petroleum refining and vessels and water transportation equipment” (US IRS, 2011). There were other options to handle the depreciation of the plant capital costs but a 10 year cycle was chosen because its definition matched closely to the plant being installed. Depreciation can affect the financial results significantly so future work should include a more rigorous review of the proposed location’s tax code and even include a financial analyst on the project team due to the complexity of the problem.

Summary of major economic parameters used		
Parameter	Value	Reference
Cost of Capital	10%	Brealey (2003)
Depreciation	10 year cycle	Luenberger (1998)
Tax Rate	33%	Brealey (2003)
Equipment/Project Life	30 years	Hertz (1968)
Design Allowance	5%	Hertz (1968)
Sales Tax	8.5%	Hertz (1968)

Table 8: Major economic parameters used

Along with net present value (NPV), the economic metric used to evaluate the results was the discounted profitability index (DPI). The DPI of a project is the ratio (also referred to as the benefit-cost ratio) is the present value of future cash flows divided by the initial investment. Net present value can give results that favor larger projects. The DPI attempts to normalize projects and compare them on an equal basis. Larger projects may have a higher NPV but this does not reflect the investment efficiency of the project.

The formula for DPI is:

$$DPI = 1 + NPV / [Inv_n / (1 + i)^{n-0.5}]$$

where:

NPV = net present value

Inv = Before tax investment in period n

Using DPI gives a normalized look at how efficient an investment is. Larger projects usually have higher NPVs due to their size (and increased revenue generation) but using DPI gives a look at how efficient an investment is. For ethanol plants this is important because many

different designs with varying feedstock rates are used in industry and economic proposals. For example, one ethanol plant may cost \$1 billion and have a net present value of \$100 million while smaller designs have capital costs of \$200 million and a NPV of \$50 million dollars. The preferred alternatives would be to build 5 smaller facilities with the available capital because it would increase value to the corporation (\$200 million NPV for smaller design versus \$100 million NPV for larger design). This is essentially what DPI does: it normalizes investments regardless of size to determine which one is more capital efficient. It is used in this report to compare this design with several other plants that used dilute acid hydrolysis for ethanol production.

Capital Investment

Capital cost estimates become more accurate with additional front-end loading and engineering. It is important to include all capital costs related to the useful life of the project (including maintenance capital). To address uncertainties, capital cost estimates include both allowances and contingency. Allowances are included in the base cost estimate for the defined scope to cover known requirements that cannot be efficiently estimated. The capital cost estimate of the proposed ethanol plant includes allowances. Some typical allowances are; design, material take off, waste and trim, pipeline routing, underground, and expected weather. The allowance used for the project is based on recommended general allowances for plants where the location has yet to be determined (Dixit, 1994).

Contingency was also added to the cost estimate of the ethanol plant. Contingency is an amount added to a cost estimate to allow for unknown items, conditions, or events that experience shows will likely occur (for example, typical minor design development). Contingency is different from allowances. Allowances should be included in the base cost estimate and not be duplicated in the contingency. Every project cost estimate should evaluate risk and include identifiable contingency costs in the cost estimate to get the funding cost target at an acceptable risk level (that it will not overrun). Adding contingency does not improve the accuracy of the cost estimate; it just reduces the likelihood of overrun and increases the likelihood of an under-run. Similar to the allowance added to the project, a general value for the

contingency was added for the project since little is known about the specifics of the site (Dixit, 1994).

Cost estimates should encompass all the incremental capital expenditures associated with making the investment. Not only is it important to consider the current investment requirements, but also the known capital investments that may be required later in the useful life of the asset (van Groenendaal, 1998). The life of the facility was selected to be 30 years and it was also when the economic analysis was stopped. It is convenient that for typical design it is specified that the life of the equipment is 30 years and using a 10% discount rate causes the economic evaluation to not consider future replacement of equipment. This is due to future cash flows (30+ years) not having a significant impact to the current NPV of the project. Assessing revenue and cost changes into the future (escalation rates) is essential to determine the cash flow associated with an investment decision. Although in the long-term, escalation rates tend to track background inflation rates, in the short term, one should not assume revenues and costs track inflation without a thorough assessment of the appropriate drivers of revenue and cost. Feedstock price, margin, and cost guidelines include inflation and escalation assumptions. For this analysis a 4% inflation was used for all future sales and purchases. This caused the economic results to be similar each year. More exact models may have higher escalation for certain goods than others.

Cost estimation is full of potential pitfalls and often is the largest uncertainty to the projects. Also, an accurate cost estimate is the most crucial to a project's success because it is often the largest factor going into if the economic results are accurate or not. (Sweeting, 1997). The cost estimate was developed from the HYSYS process simulation unit operations and known equipment that would be needed at the facility. From the list of equipment that was generated, "cost curves" were used to determine a capital cost estimate for the equipment. From that the cost for the construction of the facility can be determined based on factored estimates for costs such as engineering, piping, and instrumentation. A cost curve estimate is based on finding the costs and capacities of plants similar to the one being estimated. The estimator adjusts that data for date, location, and common facilities, calculates the new cost, and makes further adjustments to develop the estimate for the new facility. The equation for cost curves is:

$$y = a * (x)^b$$

where:

y = cost

a (coefficient) = specific to plant type

x = capacity

b (exponent) = specific to plant type (close to 0.6 but can range from 0.3 to 1.0)

To make a curve estimate of the cost of a new plant, one needs to gather data on the capacity of the new plant and the cost and capacity for two or more similar plants. Data for the cost curves have been collected over several years by me from other existing cost curves and other cost estimation work. The curves were applied to all major equipment expected to be encountered in the plant. The process flow diagram served as a good guide for what major unit operations would be expected, but for other equipment not seen in the process simulation (such as motor control centers, electrical distribution, and laboratory facilities) were estimated based on a reasonable amount expected during for construction. For example, the size of the motor control center equaled the anticipated horsepower load of the facility (so if 1000 hp was needed for plant, a cost estimate for a MCC for 1000 hp was generated). Things like a control room, laboratory, and trucking station were assumed to need only one for the newly constructed plant.

Graphically, this cost curve equation will plot as a straight line on log-log paper. In practice, the curve may not be smooth but may be stepped at certain points, such as when limitations of equipment size require pairing equipment (using a parallel piece of equipment) or adding a second train. This method is considered suitable for geographically confined plants, such as process plants and some utilities. It is considered unsuitable for new technology plants that do not have cost histories. What makes this method applicable to this situation of evaluating an ethanol plant is that the majority of this plant is using existing, mature technology. After the major equipment needed to construct the ethanol plant is categorized, the specifics of the new technology (using the solid magnetic acid catalysts) are accounted for in the design. There are several key differences between the material used and the process flow diagram for the proposed plant with those of the reference plant and these differences result in the differences in the cost estimate from this plant (see Chapter 4, section “Comparisons to Other Technology & Ethanol Plant Designs”).

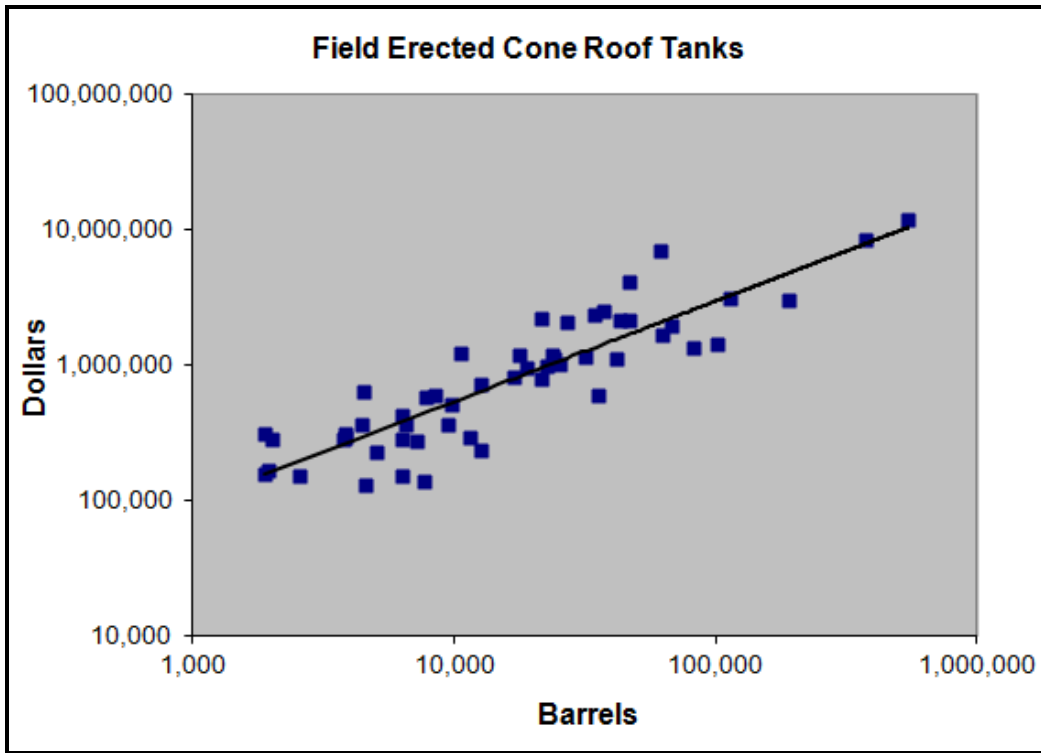


Figure 7: Cost curve used for fixed roof tanks

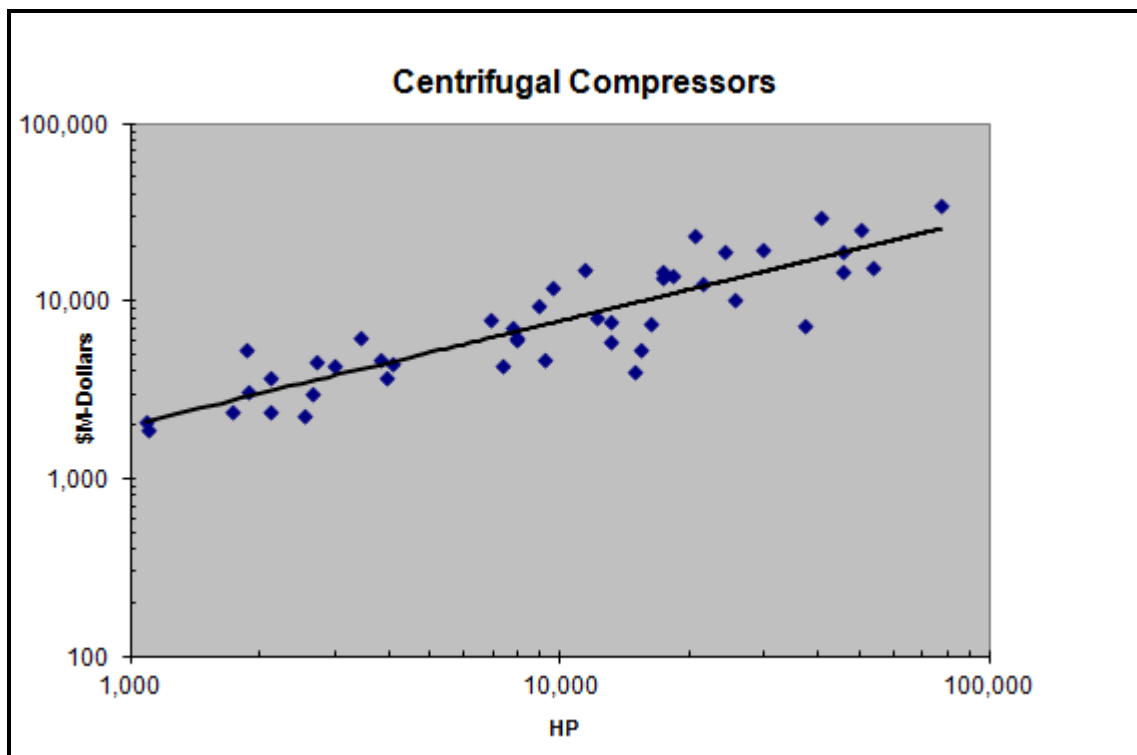


Figure 8: Cost curve used for estimating centrifugal compressor costs

After all the information is include, the cost estimate is considered +/- 40% of the expected capital costs. From experience, cost estimates and economic analysis that include the methods used in this report (cost curves) are 15-40% accurate. This means the cost estimates include process flow diagrams, preliminary process design, and preliminary major equipment sizing. For +/- 40% accuracy, the cost estimates can be based on cost curves, vendor quotes, and recent purchases. For the sensitivity analysis, +/- 50% was used as the variability of the expected cost estimate to include another level of conservatism in the economic results. Future work to increase the accuracy of the cost estimate will require more work and eventually a mutli-discipline team (several engineers, cost estimators, accountants, etc). It is generally accepted that to achieve 15% capital cost accuracy one requires almost completed process & instrumentation diagrams (P&IDs), electrical one line drawings, complete site survey (including soils analysis), environmental compliance plan, sized equipment quotes, and a long list of rigorous project deliverables that would require months (or even years) of work to assemble. For the purposes of analyzing if using magnetic solid acid catalysts, 40-50% accuracy is

acceptable, and the large swings for capital costs that could be encountered during construction were handled in the sensitivity analysis in chapter 5.

Comparisons to Other Technology & Ethanol Plant Designs

In typical ethanol plants, the pipe specification is stainless steel (304SS, 316L, etc) for the pretreatment, saccharification, and solids handling area due to the high amount of acid in the water. But with the use of magnetic solid acid catalysts, the pipe specification can be modified for that section to use typical carbon steel. The savings would be significant and this material can be used for the majority of the rest of the plant such as the distillation tower and ethanol handling. Most existing techno-economic reports for ethanol plants use dilute or strong acid for the hydrolysis reactions; but in the case of using the solid catalyst, these corrosive conditions can be avoided and traditional carbon steel can be used for the hydrolysis reaction section (specification similar to 1CS12). The use of this carbon steel would be for temperatures between -20F and 450F, all expected corrosion conditions (used a corrosion allowance of 0.063 in which will allow for 30+ years of operation) and up to 450 psi (pounds per square inch) pressure. This would make it suitable throughout the plant. Therefore, the piping in the hydrolysis, pretreatment, and other sections will be significantly cheaper in the magnetic solid acid catalyst plant versus a traditional plant, which would have to use stainless steel. The pumps and reactor will be significantly cheaper as well. One example is that a typical pump for a given flow rate of 50 gallon per minute (gpm) costs around \$3000/pump when using carbon steel. That same pump constructed out of stainless steel parts would cost around \$16,000/pump (Wooley 1999). This cost savings per pump is multiplied throughout major sections of the facility and translates into much cheaper construction costs for the plant that utilizes the magnetic solid acid catalyst technology.

To give an idea of the capital savings for using the magnetic solid acid catalysts compared to traditional methods Figure 9 was constructed that shows how the cost estimate compares for the magnetic catalyst compared to other detailed techno-economic evaluations of ethanol plants (Aden, 2002 & Humbird, 2011). Typically these reports breakdown cost estimates based on each section of the facility. Here it is seen that the capital costs of the pretreatment section are much less compared to other reports. Granted, there are slight

variations of the feedstock composition, feedstock rate, and other variables that make direct comparisons between the reports difficult, but based on a total percent cost to construct the plant, the magnetic solid acid catalyst causes a large savings in the pretreatment and other sections of the plant. Other savings would be from not having to include the lime softening stage or any other controls (such as to monitor pH). On a very high level and assuming laboratory yields and be achieved in a process plant, comparing the use of magnetic solid acid catalysts to traditional methods would save capital costs of around \$19.2 million dollars of capital construction costs and around \$0.30/gallon of operating cost margin for ethanol production (due to much less chemicals being used). Appendix F lists some of the capital and operating costs improvements on using the magnetic solid acid catalysts versus conventional dilute acid hydrolysis. Beyond the improvements in capital costs, significantly less chemical costs are required as well. It is estimated that the chemical savings is close to one million dollars per year. This was calculated by taking existing economic evaluations of ethanol plants and normalizing it to 2000 metric tons/day and comparing it to operating costs for this report.

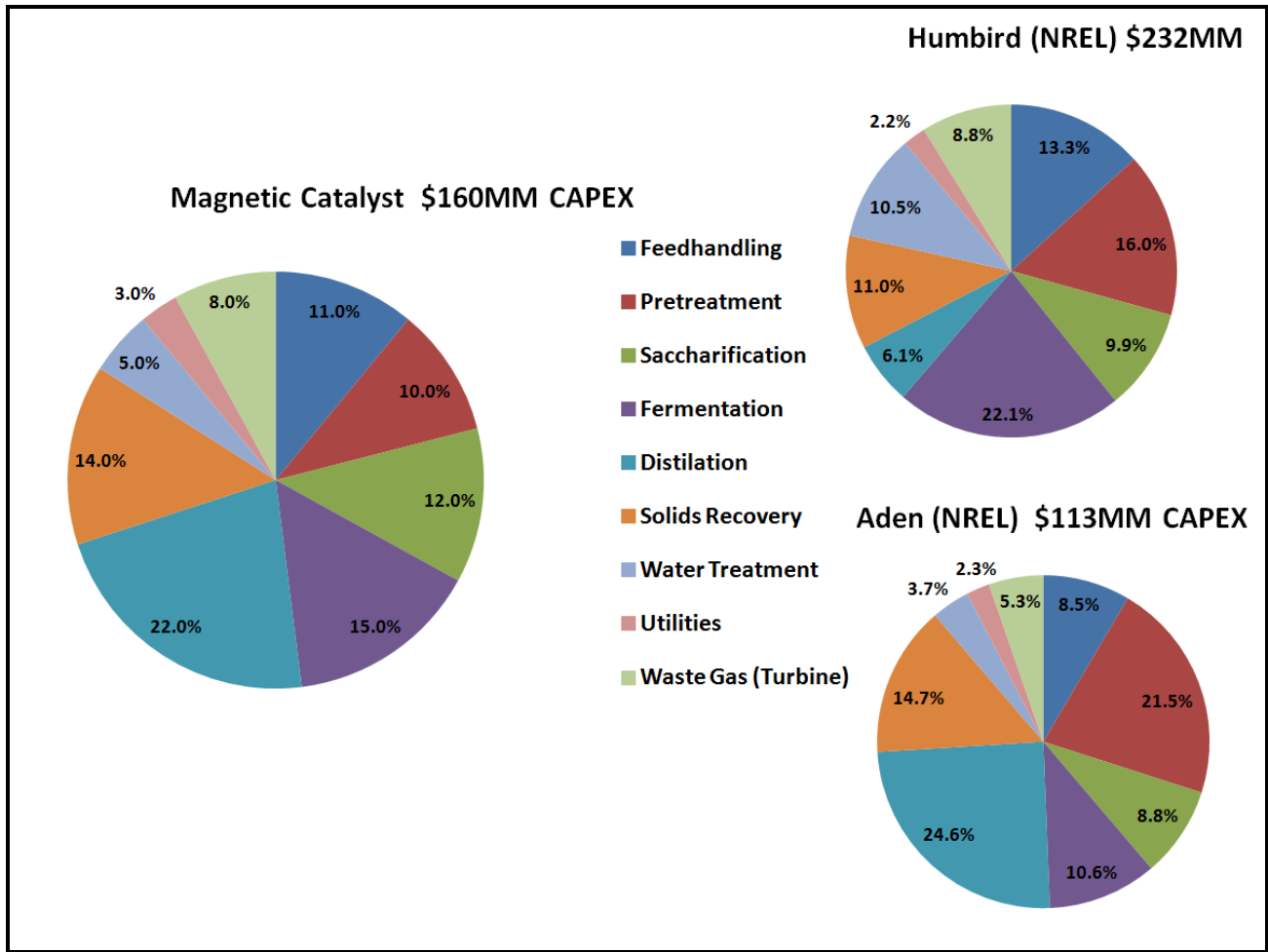


Figure 9: A comparison of magnetic solid acid capital costs versus other reports

There are also intangible environmental and safety drivers to use this technology in future design such as using inherently safer design (concentrated acid tanks present a variety of safety risks such as tank rupture and personal exposure). Also, high pH (basic conditions) can cause glucose to go to unwanted byproducts such as HMF. Eliminating these chemicals eliminates the risks of over liming and the need for pH control.

As part of the research for this project, a high level life cycle assessment (LCA) was performed on the catalyst by taking all the material used in its preparation. CMLCA software was used with four impact categories analyzed: global warming, acidification, ozone depletion, and eutrophication. But it was based on taking a laboratory scale process and assuming that the large scale production of the catalyst would be the same (same chemicals & amounts used in preparation) but this is a very large assumption. The results show that for 1 kg of magnetic solid

acid catalyst produced, it leads to 470.5 kg of CO₂, 0.66 kg of SO₂, 0.01 kg of CFC-11, and 0.33 kg of PO₄ (phosphate ions) which is similar to other published works on catalyst life cycle impacts. But to truly examine the environmental trade-offs one should do a full comparative study of traditional ethanol product versus using magnetic catalyst to assess the trade-offs quantitatively. But on a high level, the avoidance of concentrated sulfuric acid used in the process, less unit operations, and less risk to the environment due to spills indicated that beyond economic improvements, this technology also improves the health and safety of the workers and as well as improve environmental impacts.

There are also negative effects associated with use of the catalysts. The saccharification section is much more expensive in this plant design due to the use of the high gradient magnetic separator and their associated equipment. The multi-train and primary/polisher design is required to get the capture efficiency high enough so that catalyst is not being replaced regularly. The use of high gradient magnets has some safety considerations as well such as personal with pacemakers or carrying metal. But this can be sufficiently mitigated by knowing the field strength, placing access controls to the area, and other safeguards for industrial magnet use. Concentrated acid has been the cause of many industrial accidents, much less than industrial magnet use. The comparison of using concentrated sulfuric acid and magnets indicate that magnets are the inherently safer design for ethanol plants.

Some similarities exist with the use of magnetic solid acid catalysts in the design; both traditional ethanol plants and this design require elevated temperatures (~150C) for the hydrolysis process. And with the exception of the pretreatment, hydrolysis, solids handling, saccharification sections, the two plant designs are almost identical. The use of magnetic solid acid catalyst is probably only one step to a future next generation ethanol plant that might incorporate many potential improvements over their current design.

Deterministic Economic Results

Similar to other techno-economic study results, the ethanol production costs are driven largely by two large factors: 1) capital investment and 2) feedstock costs. Fixed and variable operating costs play a minor factor in the overall process economics. Similar to mass balance results, the economic results were similar to other techno-economic evaluations of ethanol plants

(similar capital costs, net present value, and discounted profitability index). Other reports have also remarked that the major risks to economic success for building ethanol plants are capital required to construct facility and feedstock costs (Aden, 2002 & Humbird, 2011). Figure 10 shows the non-discounted cash flows per year to illustrate the large initial investment and future expected profit in future years. For this particular plant, the yield of glucose from the magnetic solid acid catalysts is also a risk but it was assumed to be 75% as a base case and varied in sensitivity analysis (chapter 5).

The project cash flows are measured and discounted for 30 years. It was assumed that after an investment decision is made it would take one year to complete detailed engineering and one year to construct. The economic analysis was stopped after 30 years because it was assumed at this point major upgrades would be needed at the plant (equipment at end of life) and a major capital investment would be needed at that time with its own set of economic decisions to be made. Also, 30 years is when other ethanol reports stop the assessment as well (Aden 2002, Humbird 2011). The discount factor (the amount at which future cash flow is reduced) at 30 years is 0.092 which means that it cuts off cash flow for 30+ years but the plant can still produce a profit. The discounting of cash and accounting for longer term cash flows is a topic that receives a lot of debate and their handling should be considered in more rigorous economic evaluations. These longer term cash flows are not included in the net present value (NPV) of the facility.

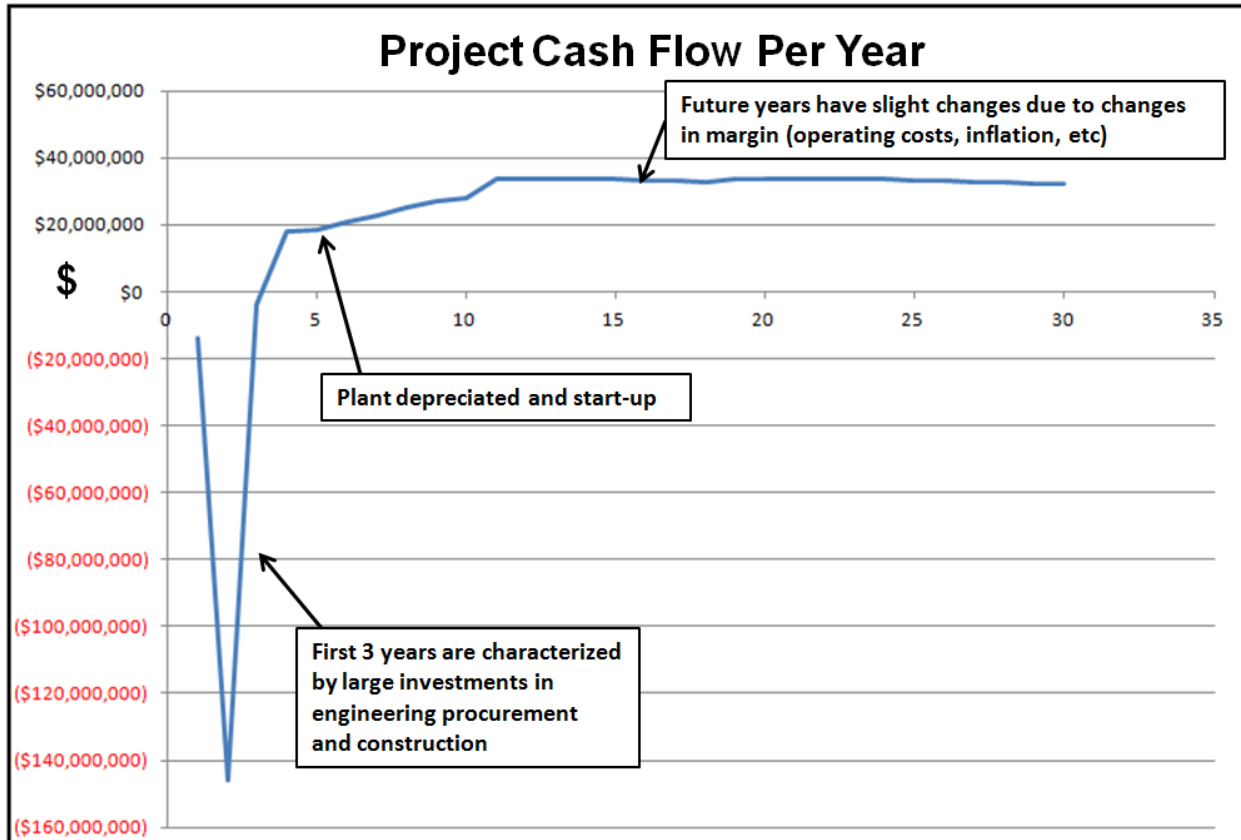


Figure 10: Non-discounted yearly cash flow for project

The results of the deterministic evaluation show that for a capital investment of \$160 million dollars it will result in a net present value of roughly \$60 million dollars. This translates into a DPI of 1.38. This compares with other proposed ethanol plants that have a DPI that are typically just below 1.3 (Aden 2002, Humbird 2011). The major difference is the less capital costs required to construct the facility and minor improvements in operating costs. Figure 11 shows how the net present value of the project was calculated over the life of the project. Similar to the cash flows, there is a large use of money to pay for engineering, procurement, and construction. Using 10% discount rate, the plant pays for itself after 15 years. The results indicate a moderately attractive project that is an improvement over traditional ethanol plants. For large projects, a company's hurdle rate is typically around 1.3. A hurdle rate is the DPI that a company sets as the cut off for projects to ensure that only projects that maximize value for the company. A DPI of 1.0 means the capital invested is equal to the amount of money to be

returned. Projects with $DPIs = 1$ are considered uneconomic because even the safest of investments (such as bonds, stocks with high yields) return a higher rate of return and free capital should be invested in them first. $DPIs$ range from as high as 1.8 to 1.1 depending on how economic the project is. A 1.38 indicates that project is both economic and adds value to a company by completing it compared to other projects. Typically at this point the next step would be to study the major risks to the project further, develop more accurate cost estimates, and other steps to improve the accuracy. Sensitivity analysis helps address which areas have the largest risk and therefore should be studied.

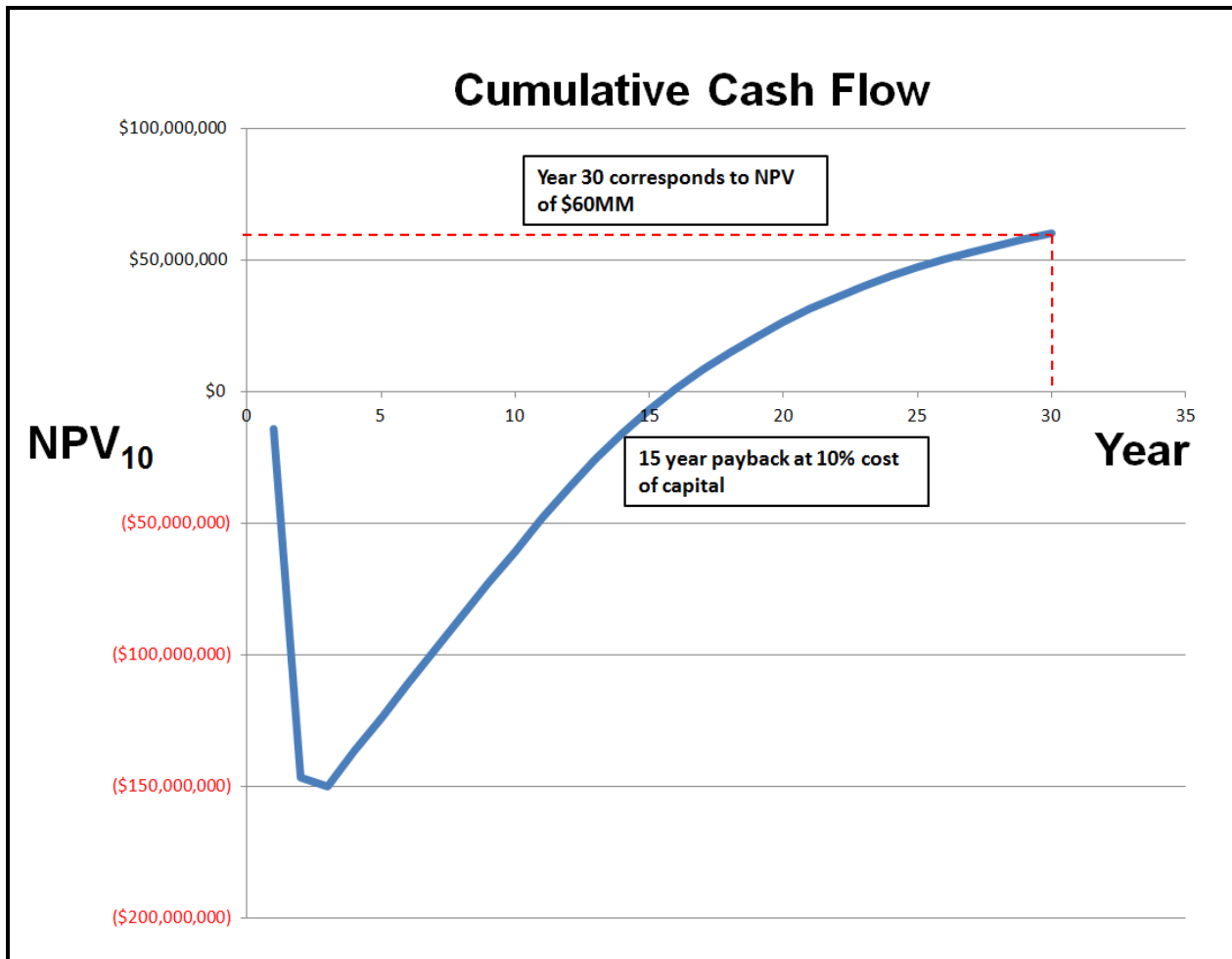


Figure 11: Cumulative net present value (NPV) for project

Chapter 5 - Sensitivity Analysis

Methodology

At the center of our ability to manage, understand, and analyze uncertainty and risk are our level of understanding and the availability of information and data. In this final chapter, the document the uncertainty of the ethanol project and analyze it to understand the risk both qualitatively and quantitatively. The use of the range of values of the capital cost estimate and key cash flow drivers (e.g., price and margin forecasts) were used to develop probabilistic assessments. For other cash flow drivers (such as catalyst yield & recovery) data was used from laboratory results.

A sensitivity analysis is performed to determine if selecting the P10-P50-P90 range in escalation rates changes key investment decision—either the go, no-go decision, or the selection of alternatives. P10-P50-P90 refers to the % likelihood an event is going to happen. In other words, if the P10 yield of the catalyst is assumed to be 50%, then there is a 10% chance that the catalyst will have that yield. These probabilities can be used for any cash flow driver in the economic assessment and, with probabilities, can be combined into an expected value for the project. Deterministic economic results are as the name implies: only deterministic and sensitivity analysis is crucial to understand the risks of a project. For example, deterministic results might show a successful project but if there is a 25% chance the technology will not work, this should be incorporated into the final expected value of the project.

Earlier in Chapter 3, it was emphasized the importance of well thought out and explicitly defined assumptions for the investment alternatives and technology performance, which form the basis for cash flow calculations. These assumptions represent the best estimates about what will happen in the future. However, from experience that despite our best efforts, our ability to predict the future is limited and the assumptions used in previous sections most likely have a significant amount of error associated with them. Actually, each variable in our analysis has a range of values with different probabilities of occurrence at any future date. When the actual values differ from the assumptions, the economic outcome of the investment is usually different from what is anticipated.

Sensitivity analysis is a process for testing how much the economic outcome of the investment will vary if the assumptions about the future are changed. The purposes of sensitivity analysis are to (van Groenendall 1998):

- 1) Identify the uncertain variables or assumptions that are most critical to the success of the project (i.e., the value drivers).
- 2) Determine which variables merit additional study.
- 3) Understand how much the economics of the investment may change with appropriate changes in the assumptions and observe whether the relative magnitude and direction of the outputs are reasonable.
- 4) Show stakeholders (in this case government, industry, researchers) how much the economic outcome of the project could differ from the value of the project with all the other variables at their P50 estimates.

The first step in sensitivity analysis is to estimate the range of values that apply to assessments for each potentially significant variable. Sensitivity analysis is important because it focuses attention on the uncertainties that are critical to the decision, and provides insights about which alternatives are best and when.

Sensitivity Inputs

Probabilistic analysis is a structured approach of using statistically based tools and methods to deal with uncertainty. (van Groenendall 1998) Realistically assessing the range of uncertainty is the foundation for generating a useful probabilistic forecast that appropriately reflects our knowledge. Typical sources for estimating these ranges include in-field or external analogue data, history matching, and expert opinion. Regardless of how the ranges are developed, it is important they be performed in a statistically valid manner. To avoid bias, it is recommended assessing minimum and maximum values first and defining the most likely case

from the perspective of the endpoints. It is important to remember that the shape of a data parameter's distribution is usually less important than the range, and most experts tend to overestimate the degree of accuracy to which they can estimate a variable. In this report, a normal distribution is used for uncertainties. (Brealey, 2003)

Revenue generated in fuel production investments is strongly linked to the raw material cost, such that cash flow development typically involves development of forecasts of gross margins. In many cases, volume assumptions and gross margin assumptions are strongly linked (dependencies) and must be assessed together. So in this case I assessed the variability of the feedstock costs and this translated into a different NPV for upper and lower limits of the feedstock costs.

Table 9 lists the major variables used for the sensitivity analysis. The cost estimate was assumed to be +/- 50% so the upper level is \$240 million dollars and the best case is \$80 million dollars. The two most crucial aspects of the technology of using nanoscale magnetic solid acid catalysts are the yield and the ability to capture and reuse the catalyst with a magnetic force. For this I assumed that for the yield the base case is a yield of 75% and upper/lower yields are 50% and 90%. The catalyst recovery was assumed to be between 98%-100%. This was accounted for in the process economics that the lower the recovery would result in higher operating costs as the catalyst is replaced. All variables that were used in the sensitivity analysis were translated into either a higher or lower NPV. For example, the higher costs for feedstock result in less gross margin for processing the ethanol, less profit, and ultimately a lower estimated NPV for the project.

Sensitivity Analysis			
Variable	P10	P50	P90
Capital Investment	\$80MM	\$160MM	\$240MM
Hydrolysis Yield	50%	75%	90%
Feedstock Costs	\$40/ton	\$50/ton	\$70/ton
Catalyst Recovery	98%	99.8%	100%
Availability	330 days/year	350 days/year	365 days/year
Operating Costs (Δ /gal)	\$0.30	\$0	\$-0.30

Table 9: Variability studied in sensitivity analysis

In analyses that look only at uncertainties and not sequential decisions, Monte Carlo simulation is a way of generating probabilistic results that approximate the expected values generated from decision trees. Monte Carlo simulation is a process of sampling a range of possible values from several uncertainties according to their individual uncertainty distribution, then using the sampled values in a mathematical equation to calculate a dependent uncertainty. Sample size and statistical significance need to be considered and the data checked for quality control. The appropriate distributions can then be estimated using Monte Carlo simulation tools (the tool used was Crystal ball add-on for Excel). The amount of iterations chosen was 10,000 for this report's Monte Carlo simulation. So using the probabilities and ranges in table 9, 10,000 economic models were generated and each occurrence for NPV was tabulated. From there a probabilistic result for the project economics is generated.

Sensitivity Analysis Results

By varying each variable, one at a time, within its specified range of values while holding all other variables at their P50 value, the effect of this variable on the economic results of the project can be observed. A tornado chart (Figure 12) is a graphical means of describing the swing or impact of each variable compared to the case when all other variables are at their P50 value. The tornado diagram indicates which uncertainties should receive additional focus to gain the greatest benefit in understanding the value of a decision alternative. Less critical uncertainties are set at their base values for the analysis. Figure 12 is the tornado diagram generated from the inputs. As you can see, the largest risk to project economic results is the capital costs of the plant. This is due to the large range of uncertainty and how much it impacts the project. Hydrolysis yield is the second highest risk to the economic results. The catalyst recovery plays a significant but not overwhelming factor in the results. This may be due to the generous catalyst recovery (98-100%) that was used. The results from the tornado diagram indicate that future work should be dedicated to refining the capital costs of the plant and the hydrolysis yields. It should also be prudent that the assumptions for the catalyst recovery can be confirmed in a plant system before a final investment decision is made. In other words, I assumed that the worst case scenario is 98% recovery for each cycle. If it is indeed lower than

this, say 50%, it would greatly impact the project as catalyst would be continually replaced during each hydrolysis cycle. Operating costs were varied based on the base case. This was done in similar techno economic evaluations of ethanol plants. To vary personnel costs (payroll), chemical, transportation costs individually would make a very long tornado diagram and each of those variables are fairly each to predict. So all the operating costs were lumped into the “operating costs/expense” category and the base case was varied symmetrically for +/- \$0.30/gal of ethanol.

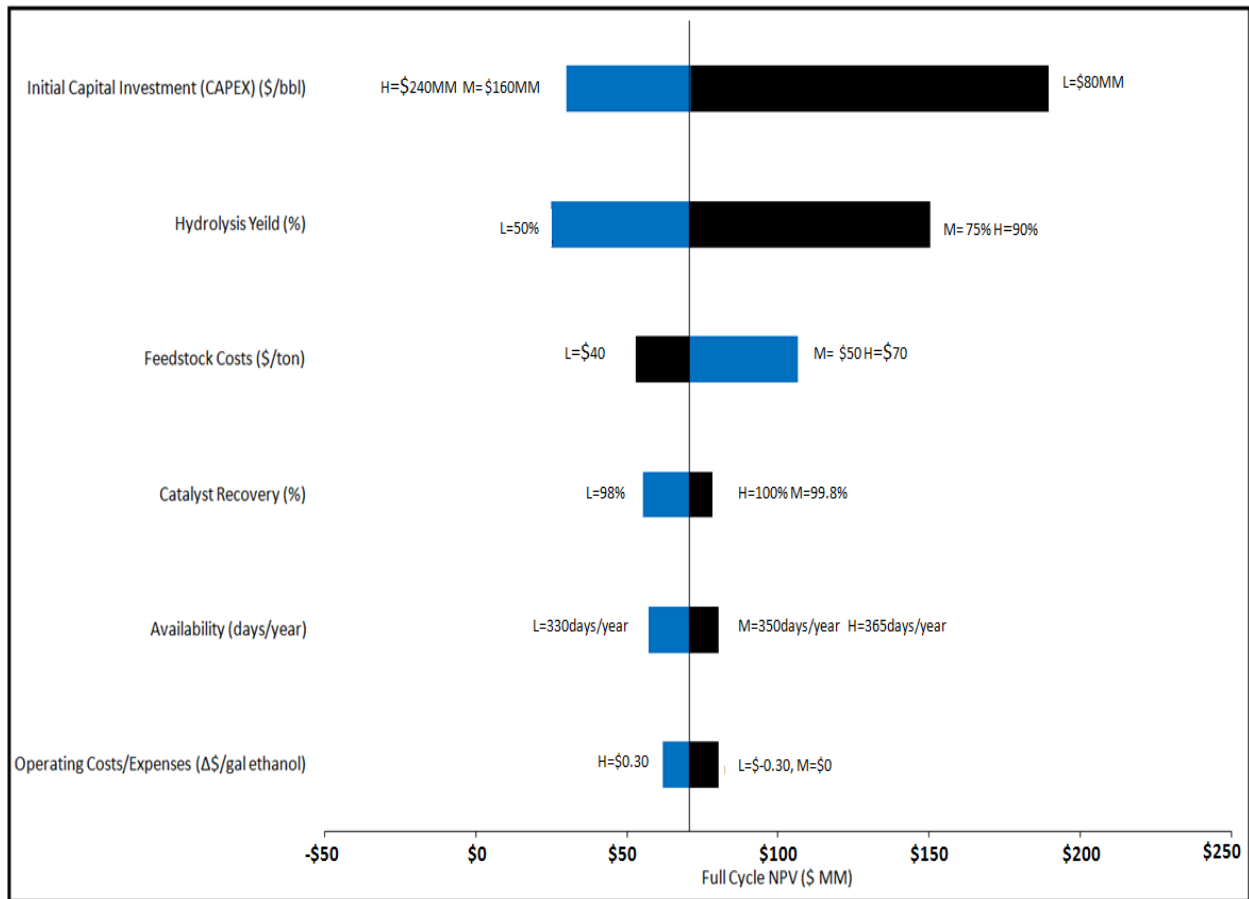


Figure 12: Tornado diagram for project economics

From the Monte Carlo simulation, a cumulative probably distribution graph can be created that shows the likelihood of getting a certain economic result for the project. So for 10,000 iterations and each P10-P50-P90 probability included, the graph can be generated base on the likelihood of a result and the project NPV. Figure 13 shows the graph which shows net present value versus probability generated from the simulation. There are a few key points to

the graph. First, there is a 10% chance that the project can have a negative NPV. This would be from not just a single issue but could be a combination of factors. For example, the negative NPV could be caused by a low hydrolysis yield, higher than anticipated capital costs, and long shutdowns for maintenance. The next important point on the graph is the 50% probability line. This represents the expected value from the project. Since all the variability is assumed normal (i.e. symmetric), the expected value from the probability analysis is the same as in the deterministic case. If there was anything analyzed in the simulation that was not normal distribution it would result in the deterministic results not equal the probabilistic results. That is the key behind doing analyses this way: it is a way to include risk into the project. The sensitivity analysis is a way to include all of the project risks and develop a truly holistic view of the proposal. Lastly, often times decision makers want to see the upper 10% project economics. In this case it is around \$134 million NPV which would be a DPI of around 1.8.

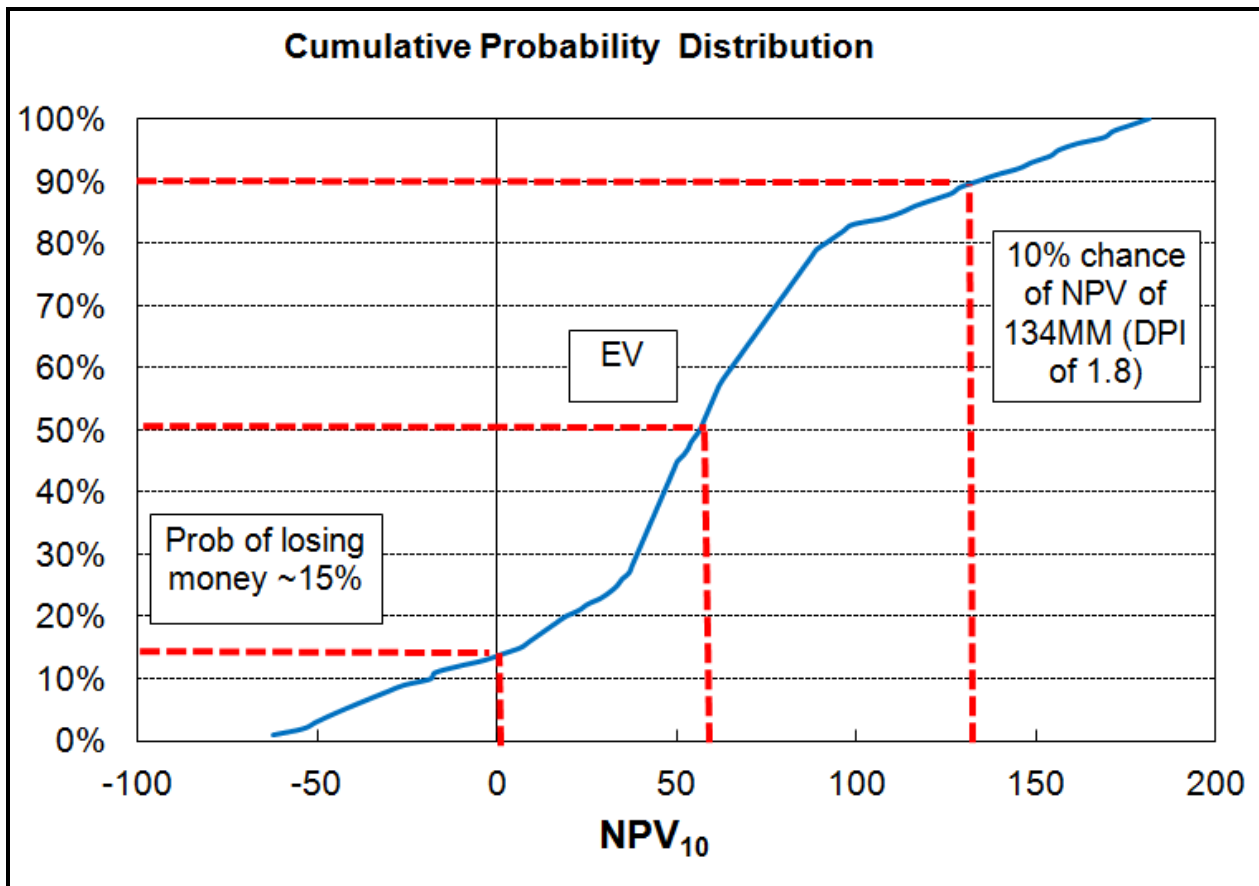


Figure 13: Cumulative probability distribution for net present value of project

An investment efficiency chart, as shown below in Figure 14, is a plot of NPV versus discounted investment at 10%. Given that DPI is a ratio of NPV to discounted investment, the slope between any alternatives [i.e., $(\text{NPV Alt C} - \text{NPV Alt A}) / (\text{Inv Alt C} - \text{Inv Alt A})$] is a representation of their incremental DPI. This slope can be compared visually to the slope of a designated DPI hurdle rate (1.3 in this case) for insights as to which alternative is preferred. If the slope from one alternative to another is greater than the DPI hurdle rate slope, the implication is that the higher investment alternative is warranted, at least on a capital efficiency basis. Discounted NPV is on Y axis and Investment (discounted) on X axis. By drawing a 1.3 DPI line through a point of interest (alternative) one can quickly determine if the incremental value for another alternative is worth the incremental investment. Alternatives below the line, lose value. Other alternatives above the line gain value. Since most likely future ethanol plants will be modular (ethanol plants will have similar designs similar to refineries), this graph shows that for each time a plant is built using magnetic solid acid catalysts, it saves around \$20 million dollars of NPV compared to other plants designs. The alternatives used were all plants that use dilute acid hydrolysis. Only 3 data points were used because it required finding the discounted cash flow from the report and manipulating the data for a 10% discount rate. That amount of work had to be done to ensure the data is normalized for all the cases. So “Alt-C” appears to be the best conventional hydrolysis project but the “M-SAC” project (magnetic solid acid catalyst) shows that it is a better investment choice compared to the other alternatives and above the economic DPI hurdle rate chosen for this project. In summary, the investment efficiency chart shows that compared to three examples of plants that use acid hydrolysis, the use of magnetic solid acid catalysts represents a better alternative to pursue.

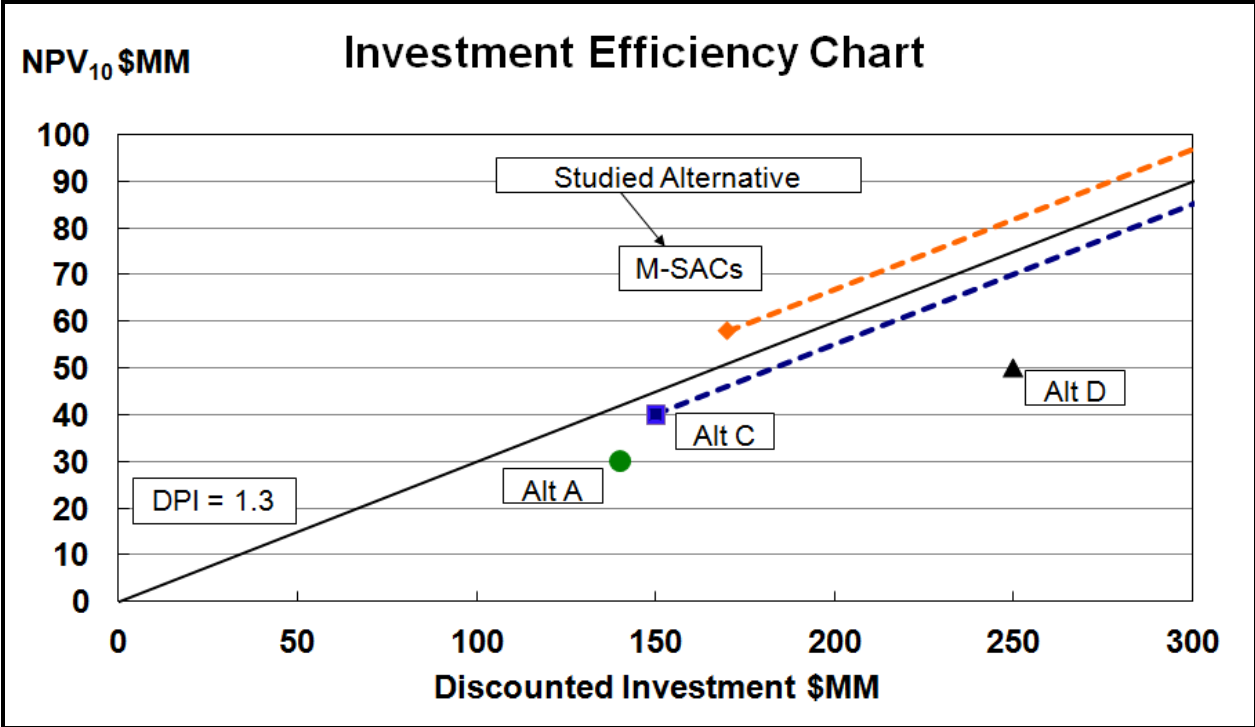


Figure 14: Investment efficiency chart for project (data from Aden 2002, Humbird 2011, and Gnansounou 2010)

As part of the analysis, the variability of the hydrolysis was studied specifically. During this analysis, the hydrolysis yield was varied from 20-100% to see how it would affect the economics. During this variation of the yield, all other factors were held constant. Figure 15 shows the NPV versus yield for catalyst. This graph is used to show how the most crucial aspect of the technology can affect project NPV. If 40% yield is achieved, the project loses money. 60% yield the project meets the report's (and industry) chosen DPI hurdle rate of 1.3. The case, 75%, matches the probabilistic and deterministic economic results of a \$60 million dollar NPV.

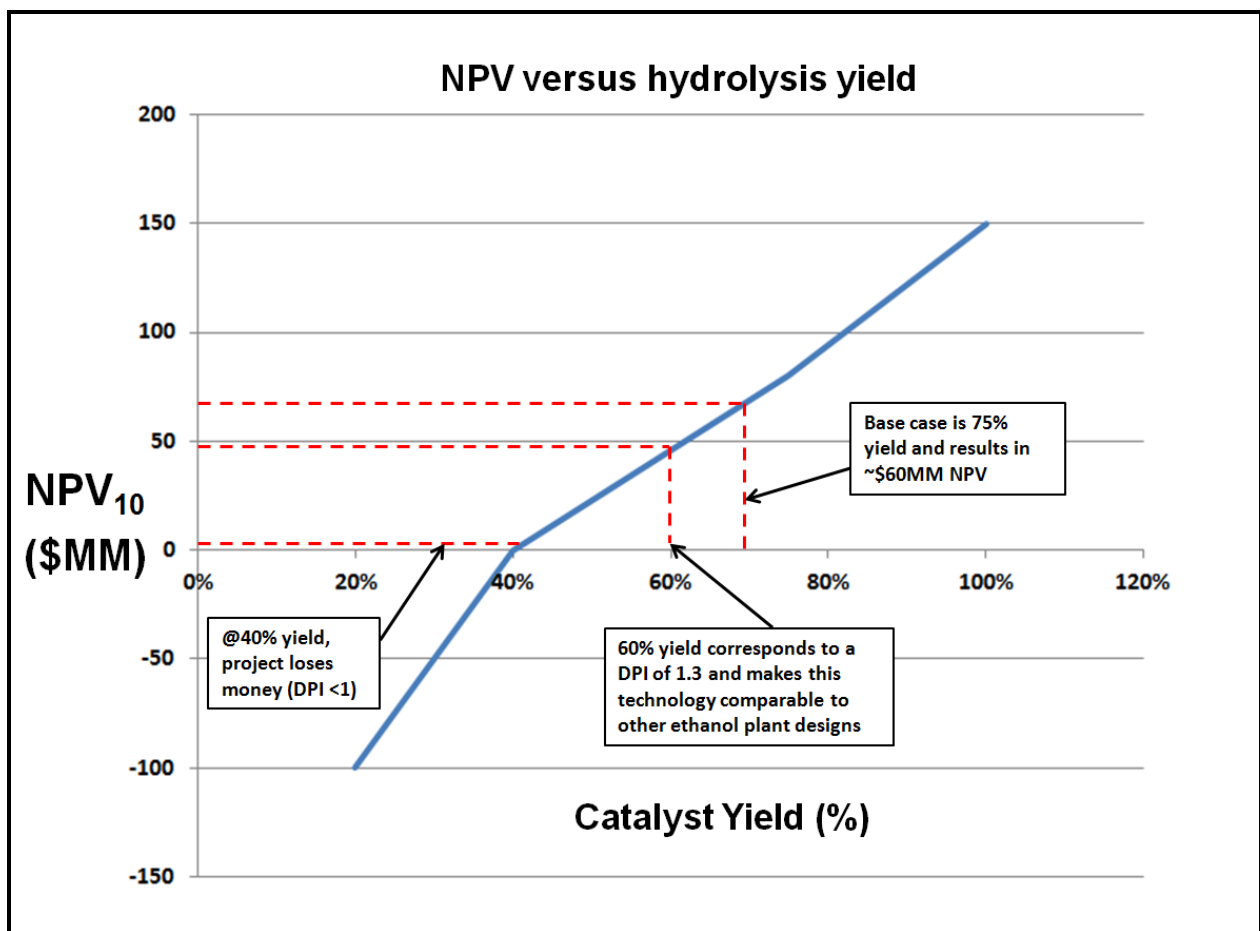


Figure 15: NPV versus magnetic solid acid catalyst yield

The sensitivity analysis indicates that the largest risks come from the accuracy of the cost estimate and the hydrolysis yield of the catalyst. This would lead future groups to continue to study these two in more detail to refine the results and decrease the risk to project. The results

can also be used as knowledge of the technology improves. If it can be guaranteed that hydrolysis yield will be above 60% (through a pilot project or some other scaled experiment to match industrial settings) it will show that a full scale implementation should be studied further.

Chapter 6 - Conclusions

Table 10 shows some of the advantages and disadvantages of the technology today but many of the gaps can be closed with further research such as laboratory scale pilots and simulations of the magnetic catalyst recovery. The biggest risk to the economic results is the plant capital costs, but the next steps should not be to refine the cost estimate but to continue work to understand the technology and its feasibility to be installed in an industrial scale plant. The biggest challenge before going to an industrial scale is almost always that it has never been done before and investors are always hesitant to endorse the risks of new technology that can either have poor performance or completely not work at all. But if we reject potential technological improvements because they involve large changes, we will probably have none left that are worth pursuing. Refineries today look much different than the ones that were first built. Each change represents a technological improvement that took time and money to develop and implement.

<u>Advantages</u>	<u>Disadvantages</u>
<ul style="list-style-type: none"> ▪ Inherently safer design that removes concentrated acidic and basic streams from process plant ▪ Overall improved environmental impacts ▪ Saves an estimated 10% on plant capital costs ▪ Catalyst can be improved and yields can increase (potential upside to technology) ▪ DPI is greater for using this technology compared to existing designs for ethanol plants 	<ul style="list-style-type: none"> ▪ Unproven at large scale ▪ Currently all data is from laboratory experiments ▪ Biofuel projects still are below petroleum projects for economic performance (upstream oil projects typical have DPIs >1.4) so still must compete with fossil fuels ▪ Requires much more additional time, money to develop technology

Table 10: Advantages and disadvantages of implementation

The next work that should be undertaken might be to further plan the unit operation and design a laboratory scale reactor that utilizes the magnetic solid acid catalyst and a smaller high gradient magnetic separator to continue to test the technology. To continue to refine the cost estimate and HYSYS process simulation would not add much value because ultimately the question will be asked if the technology has been proven. A shaping plan should be developed for the technology which would identify each technological uncertainty and a plan put in place to close the gaps strategically over several years. The technology shaping plan would include things like characterizing all the catalyst properties, model the magnetic separator, and complete a laboratory scale continuous reactor and separation equipment. The final part of the shaping plan may be to install the system as a small scale pilot project inside an existing ethanol plant. This way all of the major risks to the project can be resolved. At this point, then a more detailed process simulation, cost estimate, and techno-economic report can evaluate the technology. This future work would have the goal of getting initial approval to construct a ethanol plant that is based on the use of nanoscale magnetic solid acid catalysts.

Whatever the next steps taken, the results of the techno economic evaluation of these catalysts indicate that they are an improvement over existing methods to perform hydrolysis of biomass. It might not represent a way for biofuels to completely replace fossil fuels. But improving the technology and understanding of biofuels slowly and incrementally may allow them to one day become the preferred investment alternative not only for environmental reasons but from a strictly investment perspective as well.

References

A. Aden et al. "Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover", NREL, NREL/TP-510-3248 (2002)

API 939 D (2003) SCC-CS in Fuel Grade Ethanol-Study

Bare, J.C., D.W. Pennington, and H.A. Udo de Haes. "Life cycle impact assessment Sophistication", International Workshop, International Journal of LCA, 4: 299-306. 1999.

Brealey, R.A. and S.C. Myers, "Principles of Corporate Finance," 7th ed., McGraw-Hill, New York NY, 2003.

Brown, S.P.A and M.K Yucel, "What Drives Natural Gas Prices," Federal Reserve Bank of Dallas, Research Note, 2005.

Da-ming Lai, et al. "Hydrolysis of Cellulose into Glucose by Magnetic Solid Acid", ChemSusChem, 4, 55-58, 2011.

Dixit, A.K. and R.S. Pindyck "Investment Under Uncertainty," Princeton Univ. Press, Princeton, NJ, 1994.

Gnansounou, Edgard and Dauriat, Arnaud "Techno-economic analysis of lignocellulosic ethanol: A review" Bioresource Technology 101, 4980-4991, 2010.

Green, D. and Perry R. "Perry's Chemical Engineers' Handbook" 8th edition McGraw-Hill New York, NY, 2007

Hertz, D.B. "Investment Policies That Pay Off," Harvard Business Review, 46, pg 96-108, 1968.

Hsu, T. A. Ladisch, M. R. and Tsao, G. T. “Alcohol from cellulose”, Chem. Technol. 10 (5), 315–319, 1980.

Hubbich, Jurgen J.; Matthiesen, Dennis B.; Hobley, Timothy J.; Thomas Owen R.T. “High gradient magnetic separation versus expanded bed adsorption: a first principle comparison” Bioseparation, Vol 10, No 1-3, 99-112, 2001.

Humbird D., Davis R., Tao, L, C. Kinchin, Hsu D. and Aden A. “Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover” National Renewable Energy Laboratory Technical Report, 2011

Iborra, S., A. Corma and G. Huber. “Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering” Chemical Reviews 106(9): 4044., 2006

ISO 14044: Environmental management – Life cycle assessment – Requirements and guidelines, International Organisation for Standardisation (ISO), Geneve, 2006.

Jacobson, M. “Effects of Ethanol (E85) vs. Gasoline Vehicles on Cancer and Mortality in the United States”, ACS Publications, 2007.

Kawamura, Susumu and McGivney, William T. “Cost Estimating Manual for Water Treatment Facilities”, John Wiley & Sons Inc, New Jersey, 2008.

Lai, Den, Guo, and Fu. “Hydrolysis of biomass by magnetic solid acid Energy” Environ. Sci., 201, 4, 35-52, 2001.

Luenberger, D.G., “Investment Science,” Oxford Univ. Press New York, NY, 1998.

McJunkin Red Man Corporation “Pipe Fittings Flanges Handbook”, Houston, TX, 2010.

Mills, E. et al, “From Volatility to Value: Analyzing and Managing Performance Risk in Energy-Saving Projects,” *Energy Policy*, 34, pp 188-199, 2006.

Moeser, Geoffrey D et al. “High-gradient magnetic separation of coated magnetic nanoparticles” *AIChE Journal* Vol. 50, No. 11, 2000.

Mular A.; Barratt D.; Halbe D, “Mineral Processing Plant Design, Practice, and Control: Proceedings”, Volume 2, Bench Scale and Pilot Testing Society for Mining, Metallurgy, and Exploration, Inc, 2002

Norgate T.; Lovel R., “Sustainable water use in minerals and metal production. Proceedings of the Green Processing Conference”, 5-6 June, Newcastle, Australia, 2006.

Owings, Paul C; “High Gradient Magnetic Separation of Nanoscale Magnetite” Master’s Thesis, Kansas State University, 2011.

Pang J et al; “Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures” *Chemical Communications*, 46, 6935–6937, 2010

Perlack, R; Wright, L.; Turhollow, A; Graham, R; Stokes, B; Erbach, C; “Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-ton Annual Supply”, United States Department of Energy (DOE) Oak Ridge National Laboratory, 2005.

Phillips, S., et al “Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass”. National Renewable Energy Laboratory (NREL), 2007.

Prausnitz, John; et al “Molecular Thermodynamics of Fluid-Phase Equilibria 3rd Edition”, Prentice Hall, New Jersey, 1999.

Renewable Fuels Association (RFA), “E85 Fuel Ethanol Industry Guidelines, Specifications, and Procedures” Renewable Fuels Association, Washington D.C., 2009.

Renewable Fuels Association (RFA), “Accelerating Industry Innovation: 2012 Ethanol Industry Outlook”, 2012.

Ruth, M., “Large Scale Ethanol Facilities and Short Cut for Changing Facility Size,” Internal Report, National Renewable Energy Laboratory Technical Memo, 1999.

Sheehan J, “A Look Back at the U.S. Department of Energy’s Aquatic Species Program: Biodiesel from Algae”, 1998.

Stolarksi, Mathias, Eichholz, Christian; Fuchs, Benjamin; Nirschl, Hermann. “Sedimentation acceleration of the remanent iron oxide by magnetic flocculation” China Particuology, Vol 5, 145-150, 2007.

Sweeting, Jack; “Project Cost Estimating: Principles and Practice, Institution of Chemical Engineers”, 1997.

T. Norgate, N. Haque, “Energy and greenhouse gas impacts of mining and mineral processing operations”. Journal of Cleaner Production, 18, 266-274, 2010.

T. Norgate, et al, “Assessing the environmental impact of metal production processes”. Journal of Cleaner Production, 15, 838-848, 2007.

U.S. Energy Information Administration “Short Term Energy Outlook,” U.S. Dept. of Energy. 2010.

U.S. Internal Revenue Service Publication 946, “How to Depreciate Property”. Washington, DC: U.S. Government Printing Office. 2011.

US DOE, 2004 “Biomass Feedstock Composition and Property Database”. Biomass Program, Energy Efficiency and Renewable Energy (EERE), US Department of Energy (DOE), 2009.

van Groenendall, W.J.H “Estimating NPV Variability for Deterministic Models,” European Journal of Operational Research, 107, pp. 202-213, 1998.

Wooley, R., Ruth, M., Sheehan, J., Ibsen K., Majdeski, H., Galvez, A. “Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Cocurrent Dilute Acid Prehydrolysis and Enzymatic Hydrolysis: Current and Futuristic Scenarios”. National Renewable Energy Laboratory (NREL) 1999

Zhang, Yang; Chen, Yongsheng; Westerhoff, Paul; Hristovski, Kiril; Crittenden, John C. “Stability of commercial metal oxide nanoparticles in water”. Water Research, Vol. 42, 2204-2212, 2008

Appendix A - List of Economic Variables and Definitions

Nomenclature:

(developed from Mills et al, 2006 and Luenberger, D.G., 1998)

$ATCF_i$	incremental after-tax cash flow in period i years generated by investment
CoV_{n+1}	Continuing value of the investment in period $n+1$
IC_i	Capital investment in year i
IC_{ci}	Cumulative capital investment through year i
M_i	maintenace costs in year i
n	number of financial evaluations periods for the investment
NPV	net present value
OD	days of operations per year
OE_i	change in operating earnings in year i
P_j	Price of fuel j (such as \$/MBtu or \$/kW)
Q	Energy Demand (MBtu/h or kW/hr)
r_c	corporate weighted-average after-tax cost of capital

r_d	depreciation rate for the investment %/100
r_r	risk premium to be applied to the expected returns for a particular investment
r_t	incremental tax rate for earnings %/100
y	cost
$a(\text{coefficient})$	specific to plant type
x	capacity
$b(\text{exponent})$	specific to plant type (close to 0.6 but can range from 0.3 to 1.0)

Definitions

A/T	After Tax
ATCF	After-Tax Cash Flow
Before Tax (B/T)	Cash flow or income before payment of income taxes
Capital	Money that a company uses to fund its various activities or investment proposals. Obtained either from stockholders who invest in the company (equity capital) or by borrowing money from lenders (debt)

Cash Flow	The set of cash payments associated with an investment. The net cash flow is the sum of positive and negative cash flows in any given time period
Depreciation	A method of <i>writing down</i> or spreading the cost of an asset over its life as it wears out. Depreciation is a non-cash charge used only to calculate book income or to calculate taxable income
Deterministic	Said of a model where all parameters are fixed or determinate
DPI	Discounted Profitability Index: The profitability index (also referred to as the benefit-cost ratio) is the present value of future cash flows divided by the initial investment. DPI is an expanded version of the profitability index and discounts also the initial investment, which may not always be incurred in the first period of the project. A ratio of 1.0 is logically the lowest acceptable measure on the index. Any value lower than 1.0 would indicate that the project's PV is less than the initial investment and therefore not economic. As values on the profitability index increase, so does the financial attractiveness of the proposed project.
Discount Rate	The rate used for present value discounting
Discounted Cash Flow	A method for evaluating cash flows, which recognizes the time value of money. Future cash flows are adjusted to their equivalent present values by discounting at an appropriate rate, usually the cost of capital or a reference discount rate
Expected Value (EV)	The probability weighted average of all possible outcomes represented in a probability distribution.

FEED	Front End Engineering and Design
Incremental Analysis	A method of analysis that compares the results of an investment to projections of what would occur without the investment, i.e., the change in expected cash flows as a result of the investment.
Interest Rate	The rate of money growth when the return is expressed in then-current dollars before any tax considerations.
Monte Carlo Simulation	A process for modeling the behavior of a stochastic (probabilistic) system. A sampling technique is used to obtain trial values for key uncertain model input variables. By repeating the process for many trials, a frequency distribution is built up which approximates the true probability distribution from the system's output.
NPV (Net present value)	The dollar value today of expected net cash flow discounted at an appropriate discount rate.
Probability (Bayesian)	Bayesian or subjective Probability is a personal assessment of likelihood based on judgment and state of information. The state of information or judgment is not the same for everybody.
Probability (Classical)	Classical or objective Probability is a known probability like a coin flip, casino games, and lotto.
Rate of Return (ROR)	The discount rate that the present value of a project's future cash return to the present value of a project's investment outlays or, in other words, the discount rate at which the cumulative cash flow equals zero. Also known as the Internal Rate of Return (IRR) and Return on Investment (ROI).

Reliability	Measure of the agreed or expected performance of a mechanical or production system. Reliability depends on the overall system configuration and incorporates assessments of factors including the time between failure (MTBF) at the equipment and system level as well as operating and maintenance protocols and assumptions.
Sensitivity Analysis	An analysis that measures the impact of uncertainties on the value of the opportunity in order to determine which uncertainties are critical to the evaluation.
Tornado Diagram	A sensitivity graph showing the output value range produced by the range of each key uncertain input variable, arranged in decreasing magnitude of effect.
Uneconomic	Not meeting an economic hurdle rate or index required for profitability under current economic and operating conditions, or a project not capable of returning cost of capital from all future investments.

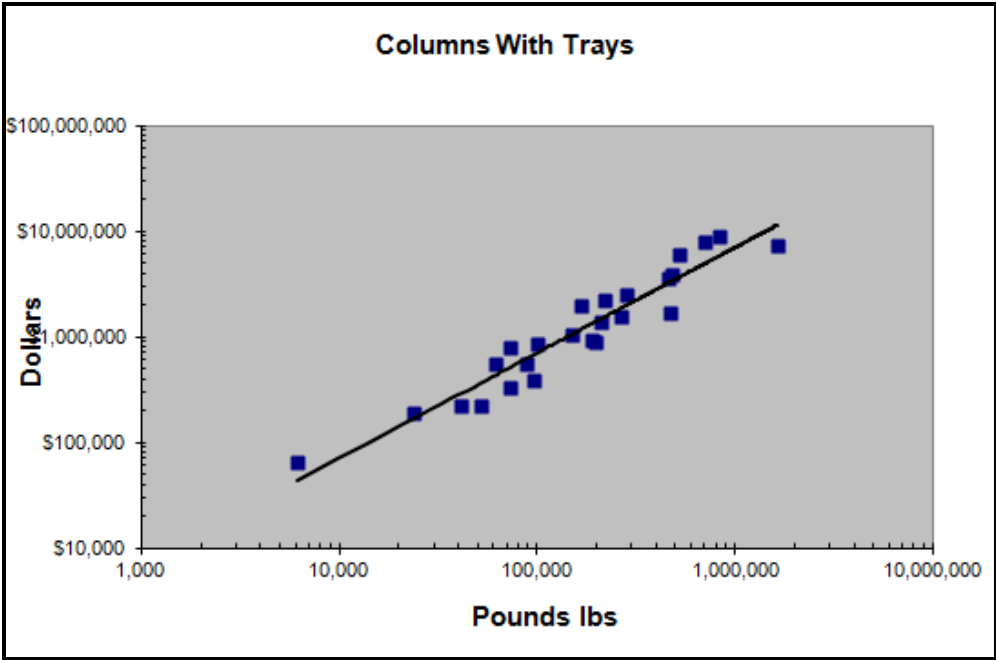
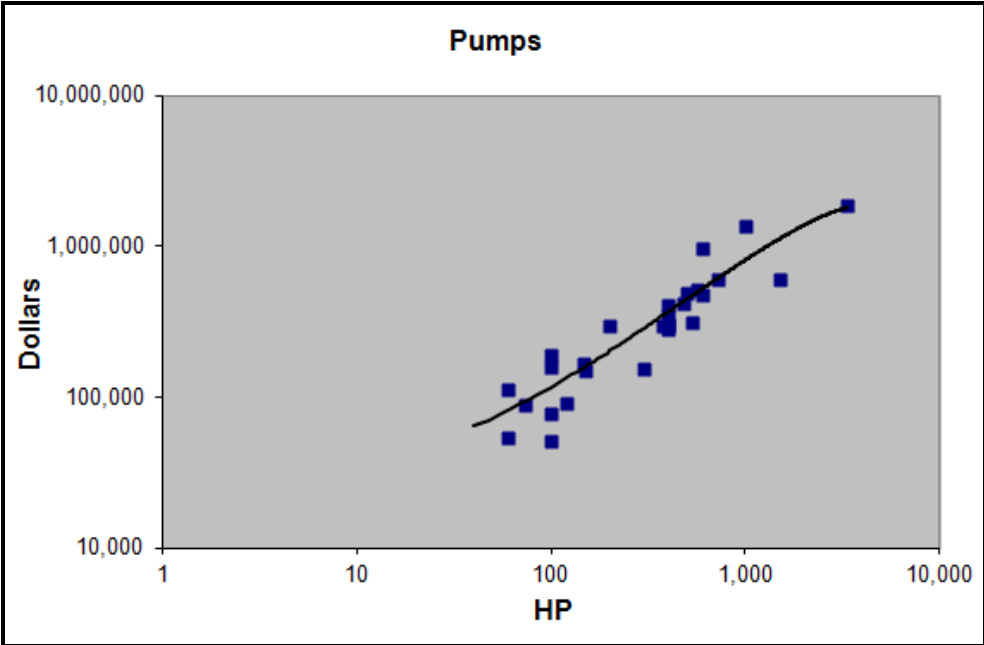
Appendix B - Major Equipment List

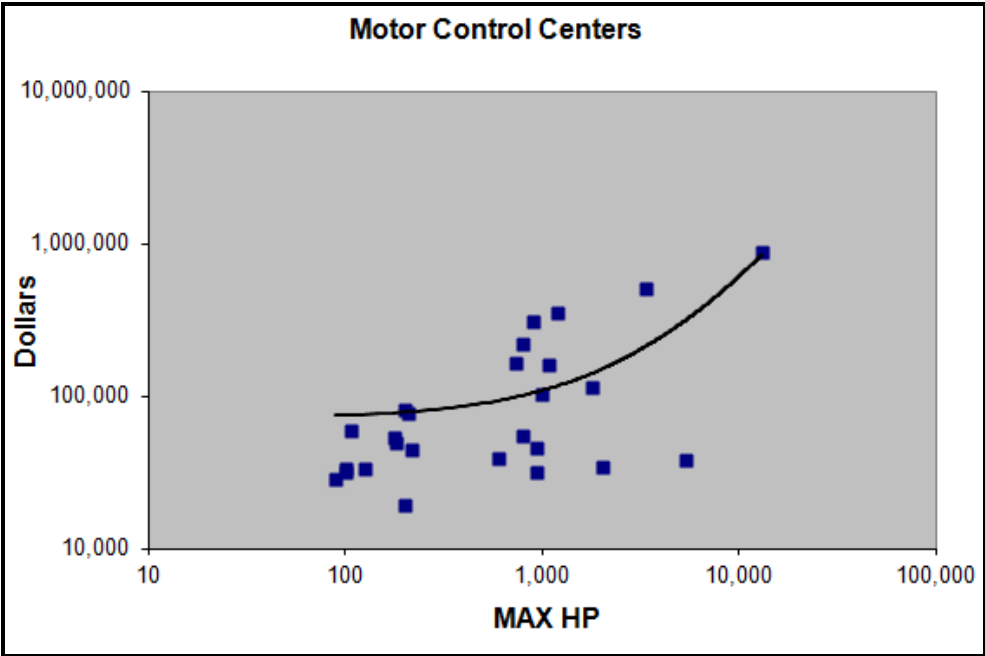
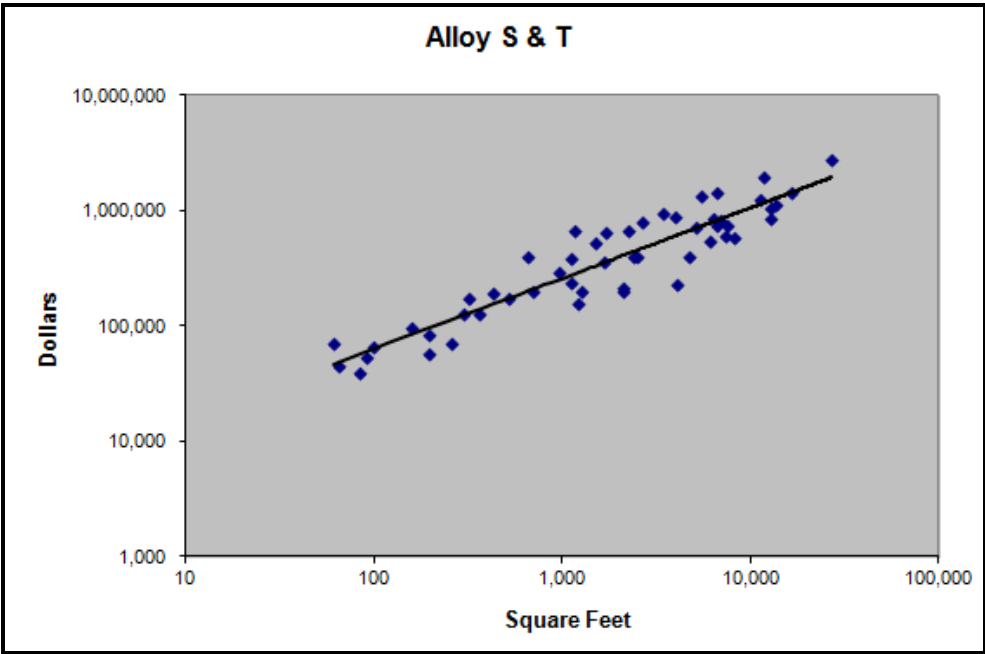
(Note: this is list only includes major equipment used in plant, other items such as valves, instrumentation, and other misc items were omitted) \$M denotes 1,000 & \$MM denotes 1,000,000

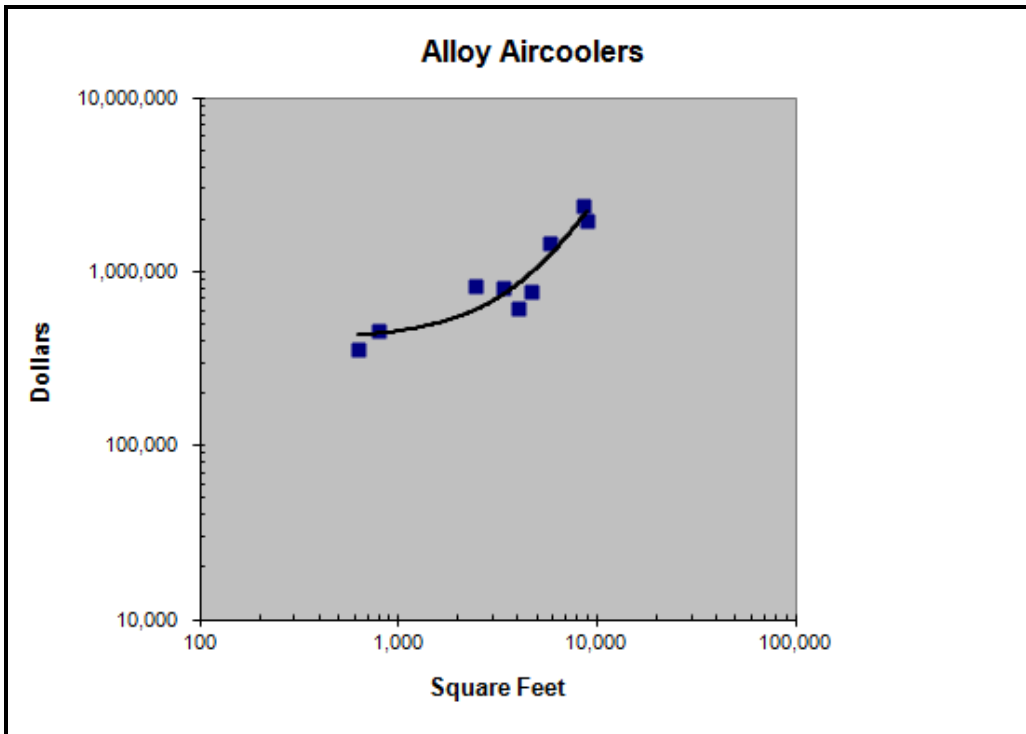
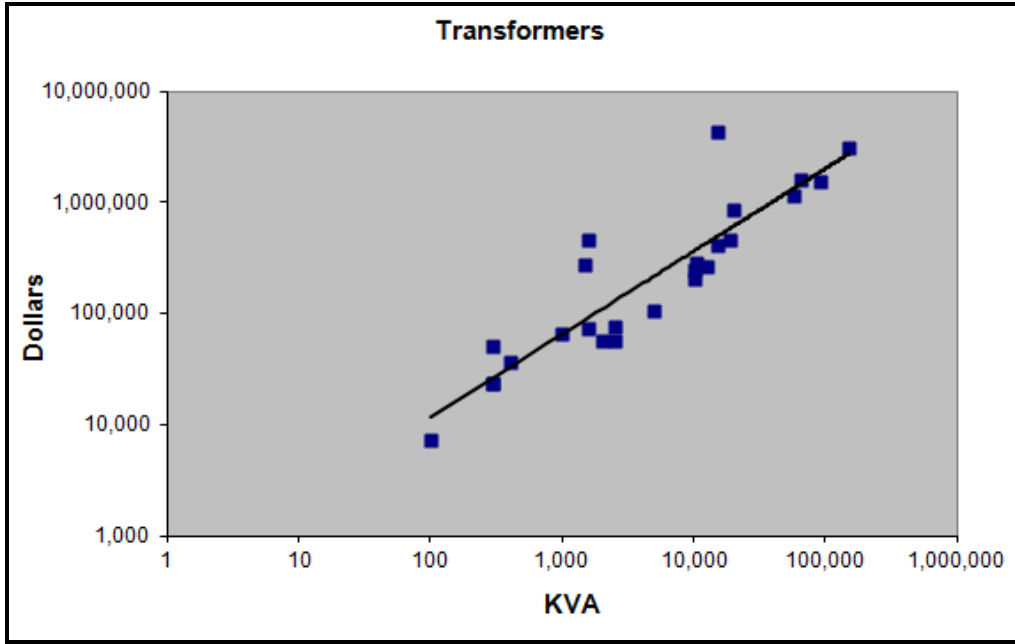
Equipment	Cost	Quantity	Comments
Motor Control Centers	\$100M	5	hp from equipment
Turbine/Generator	\$10.2MM	1	burn waste gas from tanks/vessels
Centrifugal Compressors	\$100M	2	charge to HP for turbine
Rotary Compressors	\$100M	6	gas compression from vapor rec.
Vessels	\$120M	6	misc for scrubbing gas
Laboratory	\$1MM	1	water testing
Transformers	\$500M	1	electrical distribution
Pumps	\$50M	48	Assume pumps pump each HYSYS op and 3x50% sparing philosophy, sized based on flow rate. Almost all pumps are carbon steel
Control Room	\$2.2MM	1	based on quote from project
Instrument Air Dryer	\$50M	6	for each air compressor
Alloy Air Cooler	\$500M	5	cooling process streams
Boiler (steam)	\$11.1MM	1	To generate steam/electricity
Aerobic Digester Blower	\$1.9MM	1	feed air to bacteria
Bioreactor	\$5.2MM	1	for enzyme production
Reverse Osmosis System	\$2MM	1	high quality water for stream gen
Centrifuge	\$7MM	1	based on quote, flowrate, and medium
Anaerobic Basin	\$17MM	1	based on quote, flowrate, and medium
Aeration Digester	\$2.7MM	1	water treatment
Evaporator System	\$3.8MM	1	water treatment
Pressure Filter System	\$3.5MM	1	filter out for water treatment
Ethanol Filter	\$100M	1	treatment of ethanol product

Saccharification Tank	\$3MM	1	large volume due to amount of fluid
Magnetic Seperator	\$350M	12	primary and softeners, based on alloy vessels
Pretreatment System	\$5MM	1	based on reports of cost
Solid Liquid Seperator	\$4MM	1	based on reports of cost
Nut Shell Filters	\$500M	2	remove TDS from water
Bag/Cartridge Filters	\$40M	6	remove TDS from water
PLCs	\$75M	8	logic controllers, feed into control sys
Electrical Distribution	\$500M	1	10 kV lines etc
Cooling Tower System	\$1.5MM	1	based on HYSYS results
Beer Column	\$3.7MM	1	based on HYSYS results
Inst. Air Compressor	\$20M	6	assume 5 instruments/unit operation
Misc Tanks	\$250M	5	2xdrain, 2x condensate collection, and 1 overflow tank
Conveyor System	\$4.1MM	1	truck off loading
Biomass Storage	\$4.5MM	1	large cost due to need for large volume and vapor controls (assume 1.3 million gallons)
Fixed Equipment Totals		\$96.1MM	
Discipline	%	Total	Comment/Reference
pipng/instrumentation	0.08	\$7.69MM	Kawamura (2008)
construction	0.2	\$19.2MM	Kawamura (2008)
FEED	0.15	\$14MM	Kawamura (2008)
Structural	0.05	\$4.8MM	Kawamura (2008)
Contingency	0.05	\$4.8	Dixit (1994)
Allowance	0.05	\$4.8	Dixit (1994)
Overhead	0.085	\$8.17MM	Dixit (1994)
Misc Construction Costs		\$63.9MM	
Total Capital Investment		\$160MM	

Appendix C - Selection of Cost Curves Used







Appendix D - Misc Parameters

Financial Parameters

(Note: This value was used at year zero, but inflation was used to forecast price increases)

Parameter	Value	Reference
Equipment Utilization	90%	van Groenendaal (1998)
Cost of Capital	10%	Brealey (2003)
Depreciation	10 year cycle	Luenberger (1998)
Tax Rate	33%	Brealey (2003)
Equipment Life	30 years	Hertz (1968)
Annual Operation	350 days/year	Brealey (2003)
Personal Costs	\$80M/personal	Brealey (2003)
Ethanol Selling Price	\$2.05/gallon	Brown (2005)
Inflation	4%	Brealey (2003)
Overhead costs	5%	Brealey (2003)
Design Allowance	5%	Hertz (1968)
Sales Tax	8.5%	Hertz (1968)

Process Parameters

Process	Unit	Reference
Feedstock Flow	2000 (metric tons/day)	chosen for report
Feedstock Compositions:		
Cellulose	37.4%	corn stover, Aden (2002)
Xylan Fraction	21.1%	corn stover, Aden (2002)
Arabinan Fraction	2.9%	corn stover, Aden (2002)
Mannan Fraction	1.6%	corn stover, Aden (2002)
Galactan Fraction	2.0%	corn stover, Aden (2002)
Lignin Fraction	18.0%	corn stover, Aden (2002)
Pretreatment:		
Xylan to Xylose Yield	90%	Adan (2002)
Mannan to Mannose Yield	90%	Adan (2002)
Galactan to Glucose Yield	90%	Adan (2002)
Arabinan to Arabinose Yield	90%	Adan (2002)
Saccharification:		
Catalyst Recovery	99.9%	Based on HGMS
Cellulose to Glucose Yield	75% (base case, varied in study)	Zhang et al (2008)
Co-Fermentation		
Glucose to Ethanol Yield	95%	Adan (2002)
Xylose to Ethanol Yield	85%	Adan (2002)
Arabinose to Ethanol Yield	85%	Adan (2002)
Mannose to Ethanol Yield	85%	Adan (2002)
Galactose to Ethanol Yield	85%	Adan (2002)
Contamination Loss	3%	Adan (2002)

Appendix E - Mass & Energy Balance

Mass Balance (water & carbon)	Total Flow (metric ton/day)	Non-water/solids (mt/day)	Water Flow (mt/day)
Process Inlets			
Feedstock (Stover)	2352.9	2000.0	352.9
Chemicals & Nutrients	163.8	13.7	150.1
Enzymes	173.7	173.7	0.0
Water	4479.6	0.0	4479.6
Inlet Total	7170.0	2106.2	5063.8
Consumption/Generation (consumption is -, generation is +)			
Pre-hydrolysis	-66.9	0.0	-66.9
Saccharification	-65.7	0.0	-65.7
Combustion	480.8	0.0	480.8
Wastewater Treatment	8.9	0.0	8.9
Consumption/Generation Total	303.6	0.0	303.6
Process Outlets			
Ethanol Production	800.0	800.0	0.0
Evaporation/Vents to Atmosphere	480.0	480.0	0.0
Waste Water	5300.0	0.0	5300.0
Solids (Landfill/dried grain)	893.6	826.2	67.4
Outlet Total	7473.6	2106.2	5367.4

Appendix F - Incremental Savings of Dilute Hydrolysis and Magnetic Solid Acid Catalysts

Summary of Significant Changes between dilute acid and magnetic acid catalyst designs			
Incremental Operating Costs			
	Dilute Hydrolysis Rate (operating costs)	Magnetic Solid Acid Catalysts	Reference
Sulfuric Acid	2988kg/hr (\$0.66MM/year)	0 kg/hr (\$0/year)	Aden, 2002 & Humbird, 2011
Lime (basic solution)	2095 kg/hr (\$1.23 MM/year)	113 kg/hr (\$0.1MM/year)	Aden, 2002 & Humbird, 2011
Electrical Costs	0 kg/hr (\$0/year)	800 kW (\$0.55MM.year)	Mular 2002, \$0.08/kWh
Est. Costs/day **	\$1.89MM/year	\$0.56/year	
Reactor Costs			
	Dilute Hydrolysis	Magnetic Solid Acid Catalysts	Reference
Pretreatment System Material	Hastelloy C-2000 / Incoloy 825 Reactor	Carbon Steel (A106 Grade)	
Pretreatment System	\$17.1MM	\$3.1MM	Aden, 2002
Hydrolysis Reactor Design	Hastelloy C-2000 / Incoloy 825 Reactor	Carbon Steel (A106 Grade)	
Hydrolysis Reactor Costs	\$3.6MM	\$1.5MM	Aden, 2002
Saccharification Reactor Design	Hastelloy C-2000 / Incoloy 825 Reactor	Carbon Steel (A106 Grade)	
Saccharification Reactor Costs	\$2.9MM	\$1.3MM	Aden, 2002
Total Reactor System	\$23.6MM	\$5.9MM	
Piping Costs			
	Dilute Hydrolysis Amount (Costs)	M-SACs Amount (Costs)	Reference
Pretreatment Hydrolysis Saach. Piping	Hastelloy C-2000 / Incoloy 825 clad steel	Carbon Steel (A106 Grade)	McJunkin, 2010
Pretreatment Hydrolysis Saach. Piping Cost	2560 ft (\$1.64MM)	2560 ft (\$0.66 MM)	McJunkin, 2010

**** Note:** Chemical costs used are \$.37/gallon for sulfuric acid & \$1.10/gallon for hydrated lime.
Reference: Chemical Industry News & Chemical Market Intelligence <http://www.icis.com/> (2012)
Reed Business Information Limited

Appendix G - Discounted Cash Flow Summary

Year	1	2	3	4	5
Capital Investment	(\$14,010,000)	(\$145,990,000)	\$0	\$0	\$0
Ethanol Sales	\$0	\$0	\$73,100,000	\$84,100,000	\$84,111,000
By-product Credit	\$0	\$0	\$1,500,000	\$2,700,000	\$2,700,000
Total Sales	\$0	\$0	\$74,600,000	\$86,800,000	\$86,811,000
Feedstock Costs	\$0	\$0	\$15,100,000	\$17,000,000	\$17,003,800
Operating Costs	\$0	\$0	\$18,620,000	\$19,820,000	\$19,821,200
Total Costs	\$0	\$0	\$33,720,000	\$36,820,000	\$36,825,000
Depreciation	\$0	\$0	\$44,800,000	\$32,000,000	\$22,400,000
Taxable Income	\$0	\$0	(\$3,920,000)	\$17,980,000	\$27,586,000
Income Tax	\$0	\$0	\$0	\$0	\$9,103,380
Years Cash Flow	(\$14,010,000)	(\$145,990,000)	(\$3,920,000)	\$17,980,000	\$18,482,620
Discount Factor	1.000	0.909	0.826	0.751	0.683
Year Net Present Value	(\$14,010,000)	(\$132,719,509)	(\$3,239,488)	\$13,508,374	\$12,623,629

Year	6	7	8	9	10
Capital Investment	\$0	\$0	\$0	\$0	\$0
Ethanol Sales	\$84,113,201	\$84,115,403	\$84,117,605	\$84,119,808	\$84,122,011
By-product Credit	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000
Total Sales	\$86,813,201	\$86,815,403	\$86,817,605	\$86,819,808	\$86,822,011
Feedstock Costs	\$17,004,561	\$17,005,322	\$17,006,084	\$17,006,845	\$17,007,608
Operating Costs	\$19,821,440	\$19,821,680	\$19,821,921	\$19,822,161	\$19,822,401
Total Costs	\$36,826,001	\$36,827,002	\$36,828,004	\$36,829,006	\$36,830,009
Depreciation	\$19,200,000	\$16,000,000	\$12,800,000	\$9,600,000	\$8,000,000
Taxable Income	\$30,787,200	\$33,988,401	\$37,189,601	\$40,390,802	\$41,992,002
Income Tax	\$10,159,776	\$11,216,172	\$12,272,568	\$13,328,965	\$13,857,361
Years Cash Flow	\$20,627,424	\$22,772,228	\$24,917,033	\$27,061,837	\$28,134,641
Discount Factor	0.621	0.565	0.513	0.467	0.424
Year Net Present Value	\$12,807,568	\$12,854,923	\$12,787,421	\$12,624,347	\$11,931,901

Year	11	12	13	14	15
Capital Investment	\$0	\$0	\$0	\$0	\$0
Ethanol Sales	\$84,124,215	\$84,126,418	\$84,128,623	\$84,130,828	\$84,133,033
By-product Credit	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000
Total Sales	\$86,824,215	\$86,826,418	\$86,828,623	\$86,830,828	\$86,833,033
Feedstock Costs	\$17,008,370	\$17,009,133	\$17,009,896	\$17,010,659	\$17,011,423
Operating Costs	\$19,822,642	\$19,822,882	\$19,823,122	\$19,823,363	\$19,823,604
Total Costs	\$36,831,012	\$36,832,015	\$36,833,018	\$36,834,022	\$36,835,026
Depreciation					
Taxable Income	\$49,993,203	\$49,994,404	\$49,995,605	\$49,996,806	\$49,998,007
Income Tax	\$16,497,757	\$16,498,153	\$16,498,550	\$16,498,946	\$16,499,342
Years Cash Flow	\$33,495,446	\$33,496,250	\$33,497,055	\$33,497,860	\$33,498,664
Discount Factor	0.386	0.351	0.319	0.290	0.263
Year Net Present Value	\$12,912,494	\$11,740,436	\$10,672,162	\$9,704,330	\$8,820,198

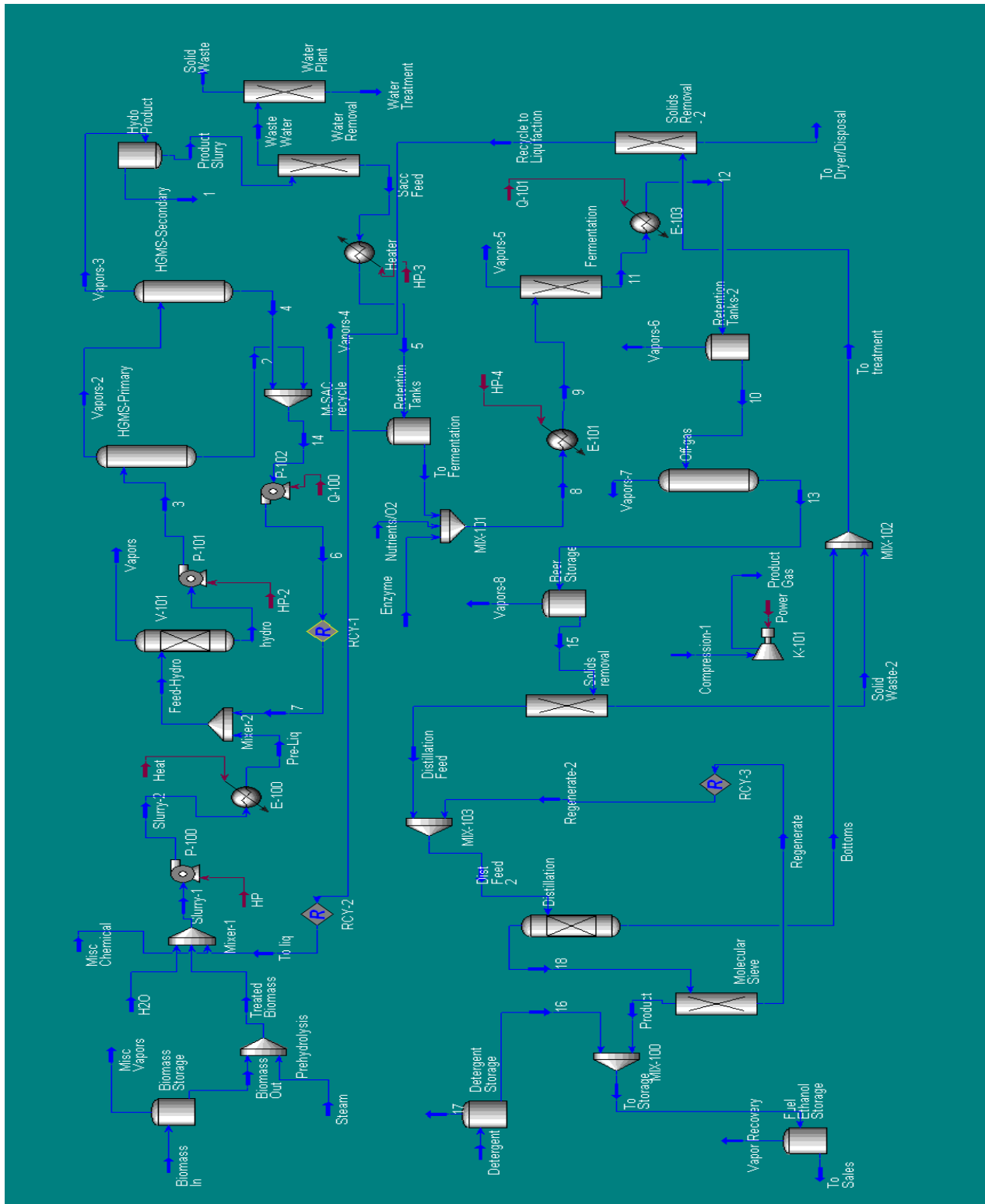
Year	16	17	18	19	20
Capital Investment	\$0	\$0	\$0	\$0	\$0
Ethanol Sales	\$84,213,807	\$84,227,277	\$84,240,749	\$85,669,968	\$86,007,750
By-product Credit	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000
Total Sales	\$86,913,807	\$86,927,277	\$86,940,749	\$88,369,968	\$88,707,750
Feedstock Costs	\$17,175,497	\$17,341,403	\$17,351,825	\$17,362,254	\$17,372,688
Operating Costs	\$20,014,801	\$20,207,842	\$20,414,989	\$20,636,637	\$20,873,209
Total Costs	\$37,190,298	\$37,549,245	\$37,766,815	\$37,998,890	\$38,245,897
Depreciation	\$0	\$0	\$0	\$0	\$0
Taxable Income	\$49,723,509	\$49,378,032	\$49,173,934	\$50,371,078	\$50,461,853
Income Tax	\$16,408,758	\$16,294,750	\$16,227,398	\$16,622,456	\$16,652,411
Discount Factor	0.239	0.218	0.198	0.180	0.164
Cash Flow	\$33,314,751	\$33,083,281	\$32,946,536	\$33,748,622	\$33,809,441
Year Net Present Value	\$7,975,551	\$7,198,922	\$6,516,825	\$6,071,377	\$5,527,844

Year	21	22	23	24	25
Capital Investment	\$0	\$0	\$0	\$0	\$0
Ethanol Sales	\$86,144,997	\$86,330,271	\$86,515,944	\$86,702,017	\$86,888,489
By-product Credit	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000
Total Sales	\$88,844,997	\$89,030,271	\$89,215,944	\$89,402,017	\$89,588,489
Feedstock Costs	\$17,383,129	\$17,393,577	\$17,404,030	\$17,414,490	\$17,424,956
Operating Costs	\$21,125,162	\$21,392,987	\$21,677,209	\$21,978,387	\$22,297,123
Total Costs	\$38,508,292	\$38,786,564	\$39,081,239	\$39,392,877	\$39,722,079
Depreciation	\$0	\$0	\$0	\$0	\$0
Taxable Income	\$50,336,705	\$50,243,707	\$50,134,706	\$50,009,139	\$49,866,410
Income Tax	\$16,611,113	\$16,580,423	\$16,544,453	\$16,503,016	\$16,455,915
Discount Factor	0.149	0.135	0.123	0.112	0.102
Cash Flow	\$33,725,592	\$33,663,284	\$33,590,253	\$33,506,123	\$33,410,495
Year Net Present Value	\$5,011,623	\$4,547,910	\$4,124,883	\$3,742,634	\$3,391,165

Year	26	27	28	29	30
Capital Investment	\$0	\$0	\$0	\$0	\$0
Ethanol Sales	\$86,892,596	\$86,901,010	\$86,909,423	\$86,917,836	\$86,943,076
By-product Credit	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000	\$2,700,000
Total Sales	\$89,592,596	\$89,601,010	\$89,609,423	\$89,617,836	\$89,643,076
Feedstock Costs	\$17,435,428	\$17,445,907	\$17,456,392	\$17,466,883	\$17,477,381
Operating Costs	\$22,634,055	\$22,989,867	\$23,365,286	\$23,761,085	\$24,178,090
Total Costs	\$40,069,484	\$40,435,775	\$40,821,678	\$41,227,969	\$41,655,471
Depreciation	\$0	\$0	\$0	\$0	\$0
Taxable Income	\$49,523,113	\$49,165,235	\$48,787,745	\$48,389,868	\$47,987,605
Income Tax	\$16,342,627	\$16,224,528	\$16,099,956	\$15,968,656	\$15,835,910
Discount Factor	0.092	0.084	0.076	0.069	0.063
Cash Flow	\$33,180,485	\$32,940,708	\$32,687,789	\$32,421,211	\$32,151,695
Year Net Present Value	\$3,062,559	\$2,763,725	\$2,494,078	\$2,246,790	\$2,025,557

Cumulative Net Present Value \$59,720,230

Appendix H - Enlarged Process Flow Diagram from HYSYS



Appendix I - Industry Codes Applied to Design

FEDERAL, STATE, AND COUNTY CODES, STANDARDS AND REGULATIONS:

- California Air Pollution Control Board (APCD)
- California Environmental Protection Agency (Cal/EPA) Regulations
- Dept of Toxic Substances Control
- National Electrical Code (ANSI/NFPA 70).
- OSHA Regulations.
- Regional Water Quality Control Board
- State Water Resources Control Board
- US Environmental Protection Agency (EPA) Regulations

INDUSTRY STANDARDS

ASME, ISA, ASCE, ACI, AISC Standards

- ASME Boiler & Pressure Vessel Code VIII Pressure Vessels Division I
- Instrument Society of America (ISA) Recommended Practices.
- ASCE 7-05, Minimum Design Loads for Buildings and Other Structures.

ASME/ANSI Standards

- B16.5 Pipe Flanges and Flanged Fittings
- B31.3 Process Piping – Code for Pressure Piping
- B31.4 Pipeline Transportation Systems for Liquid Hydrocarbons

API Standards

- 11P Specification for Packaged Reciprocating Compressors for Oil and Gas Production Services

- Spec 12F Specification for Shop Welded Tanks for Storage of Production Liquids
- API RP 5L7 Recommended Practice for Unprimed Internal Fusion Bonded Epoxy Coating of Line Pipe
- API RP 5L9 Recommended Practice for External Fusion Bonded Epoxy Coating of Line Pipe
- API 610 Centrifugal Pumps for General Refinery Service
- API 619 Rotary Type Positive Displacement Compressors for Petroleum, Chemical and Gas Industry Services
- API 650 Welded Steel Tanks for Oil Storage, 11th Edition.
- API Std 674 Positive Displacement Pumps – Reciprocating
- API Std 676 Positive Displacement Pumps – Rotary
- API 939 D SCC-CS in Fuel Grade Ethanol-Study