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TECHNO-ECONOMIC IMPLICATIONS OF FED-BATCH ENZYMATIC
HYDROLYSIS

by

Ellen Emanuel

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Under the Supervision of Professor Deepak R. Keshwani

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TECHNO-ECONOMIC IMPLICATIONS OF FED-BATCH ENZYMATIC HYDROLYSIS

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University of Nebraska, 2017

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As ethanol production continues to increase in the United States, cellulosic ethanol continues to gain traction as a viable option for meeting ethanol demands. In this work, a literature review of techno-economic analyses for cellulosic ethanol was conducted. It was found that pretreatment methods greatly affect the ethanol production costs. There is a lack of techno-economic data comparing a batch enzymatic hydrolysis to a fed-batch enzymatic hydrolysis for a separate hydrolysis and fermentation production process. Consequently, a techno-economic analysis comparing cellulosic ethanol production using batch versus fed-batch enzymatic hydrolysis was conducted. SuperPro Designer software (Intelligen, Scotch Plains, New Jersey), a process simulation tool, was used to simulate ethanol production. The simulation revealed that the biggest difference between batch and fed-batch hydrolysis was facilities costs, which decreased by 41% when using fed-batch enzymatic hydrolysis. A sensitivity analysis revealed that our ethanol production costs were most sensitive to the cost of the corn stover biomass. In general our results support the idea that fed-batch enzymatic hydrolysis does improve the techno-economics of cellulosic ethanol production, even if the improvements came in process steps we did not expect.

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CHAPTER 1: LITERATURE REVIEW

Introduction

Oil and gas still remain the most popular fuels in use throughout the world. However, world-wide energy requirements continue to increase, and these finite resources will eventually be depleted. Ethanol has already emerged as a useful alternative fuel source. Most of the world's ethanol is made from corn or sugarcane. The United States uses corn to produce starch-based ethanol. However, producing only starch-based ethanol will not provide enough ethanol to meet fuel energy needs.

Lignocellulosic ethanol utilizes plant material from dedicated energy crops or post-harvest crop residues, such as corn stover. Crop residue is often left in the field to return nutrients and to protect the soil. However, crop yields are on the rise and therefore, the amount of crop residue produced also increases (Wu et al., 2015). While some crop residue left in the field will benefit the soil, excessive crop residue left in the field may cause problems. Excessive crop residue can slow the drying and warming of soil, negatively affect planting operations and emergence, and complicate tillage (Ertl, 2013). Removing some of this crop residue, therefore, provides benefits to corn production. The removed crop residue becomes an added-value waste product as a relatively cheap and readily-available feedstock for lignocellulosic ethanol.

Ethanol is produced from fermented sugar monomers – usually from glucose monomers, specifically. In most feedstocks, these sugar monomers are stored in chains.

The starch chains found in corn are easily degraded to produce glucose sugar monomers. Lignocellulosic plant material has a much more rigid structure than starch-based feedstocks. The glucose monomers are stored in polymeric chains of cellulose. The cellulose polymers are woven together with two other major components: hemicellulose and lignin. Hemicellulose is a heterogeneous polymer of xylose, arabinose, glucose, mannose, galactose and sugar acids. Xylose is a five-carbon sugar that is not easily fermented. Lignin is not composed of sugar monomers. Its exact composition and structure vary, but it contributes to the rigidity of the overall biomass structure.

Because the lignocellulosic biomass has such a rigid structure, lignocellulosic ethanol production requires an additional pretreatment step. In this pretreatment step, the structure of the lignocellulosic biomass is degraded until the polymers are individually accessible to the enzymes used in enzymatic hydrolysis. Enzymatic hydrolysis breaks down the glucose polymers (starch or cellulose) into glucose monomers. After enzymatic hydrolysis, yeast ferments the sugar monomers to make ethanol. (Yeast prefer six-carbon sugars, such as glucose, which explains why the five-carbon sugar, xylose, is not easily fermented.) After fermentation the ethanol is purified and concentrated by distillation until it reaches fuel-grade ethanol quality.

Pretreatment is often the focus of research to improve the economic feasibility of lignocellulosic ethanol. However, preliminary work in our lab and other studies (Ballesteros, Oliva, Manzanares, Negro, & Ballesteros, 2002; Hodge, Karim, Schell, &

McMillan, 2009; Rudolf, Alkasrawi, Zacchi, & Lidén, 2005) suggest there are benefits to using fed-batch enzymatic hydrolysis that may result in water, chemical and energy savings.

There are multiple ways to hydrolyze cellulose, but hydrolysis with enzymes has many benefits. Enzymes are naturally-occurring compounds, and they run under mild reaction conditions. Mild reaction conditions do not require extreme temperatures, pressures, pH values, corrosive materials, etc. Therefore mild reaction conditions keep utility and disposal costs low and prevent equipment corrosion. Enzymatic hydrolysis also results in high yields without forming by-products (Bansal, Hall, Realf, Lee, & Bommarius, 2009; Van Wyk, 2001).

There are three ways to run enzymatic hydrolysis: batch, fed-batch and continuous. Continuous enzymatic hydrolysis is not common because unwanted microorganisms will feed on the sugars that are being hydrolyzed. Growth of these microorganisms causes issues with contamination. Batch enzymatic hydrolysis is the most common method. In batch enzymatic hydrolysis, all of the reactants (sugar polymers) go into the reactor at one time, and all of the product (sugar monomers) is removed at one time when the reaction is complete. In fed-batch enzymatic hydrolysis, smaller batches of reactants are fed into the reactor at staggered times as the reaction is running. When the reactor is full and the reaction is complete, all of the product is removed at one time.

One major benefit of fed-batch enzymatic hydrolysis over batch hydrolysis is that the enzymatic reaction rate never slows down. As the reaction progresses in batch hydrolysis, the reaction rate slows down. The reason the rate slows is not yet fully understood because the reaction mechanism is complex (Bansal et al., 2009; Gan, Allen, & Taylor, 2003; Laureano-Perez, Teymouri, Alizadeh, & Dale, 2005a; Zhang & Lynd, 2004). However, a smaller amount of biomass is regularly placed into the fed-batch enzymatic hydrolysis system, which stimulates sugar release and keeps the reaction going (Carrard, Koivula, Soderlund, & Beguin, 2000; Zhang & Lynd, 2004).

Fed-batch helps with mass transfer problems. When a lot of substrate is input all at once, the enzymes cannot react with all of it. The internal surface area of the substrate is greater than external surface area of the substrate, and consequently the cellulase enzyme becomes trapped in some pores. Trapped enzymes are unavailable to react at their proper binding sites, thus slowing the rate of hydrolysis (Zhang & Lynd, 2004). As the hydrolysis reaction proceeds and the structure of the substrate changes, internal diffusion becomes more and more difficult (Gan et al., 2003). Also the enzyme accessibility of the substrate continuously decreases over the course of the hydrolysis reaction (Gan et al., 2003). Using a fed-batch process allows for smaller amounts of substrate to be added. When smaller amounts of pretreated biomass are put into the hydrolysis reaction, the enzyme is more available to react with its substrate and break down the sugar polymers.

Fed-batch enzymatic hydrolysis also enables a higher cumulative solids loading in reactors (Ballesteros et al., 2002; Hodge et al., 2009). High ethanol yields are achieved

by pairing low substrate loadings with relatively high enzyme loadings (Ballesteros et al., 2002). However, low solids loading and high enzyme loading is costly. Limiting the substrate input into the reactor also limits the amount of product that can be produced. Reactor design generally prevents initial high solids loadings because the slurry produced is too thick for the stir tank reactors to handle (Hodge et al., 2009). Using a fed-batch method, low concentrations can be entered throughout the reaction in order to compensate for the initial low solids loading (Ballesteros et al., 2002).

The objective of this review study was to examine published literature analyzing production operations used to produce lignocellulosic ethanol with the goal of assessing the contribution of each operation to overall production costs and feasibility. We especially want to compare and evaluate the effect of using a fed-batch hydrolysis operation instead of a batch hydrolysis operation.

Techno-economic Analysis

A techno-economic analysis works to identify and evaluate the process engineering and economic aspects of a production process. For lignocellulosic ethanol production, we will look specifically at water, chemical and energy use throughout the process. We will attempt to identify opportunities for reducing the use, thereby reducing the overall cost of production.

The first step in a techno-economic analysis is to model and simulate each step of the production process. For this study pretreatment, enzymatic hydrolysis, fermentation and distillation will all be modeled using a simulation software. The focus of the study will be to model and simulate the enzymatic hydrolysis process for both batch and fed-batch systems to quantify the difference in water, chemical and energy use for the two methods.

Challenges of Reported Values

Techno-economic analyses of lignocellulosic ethanol production are difficult to compare because these studies require researchers to make many assumptions that render results incomparable. Examples of assumptions made include:

- Reactor capacities
- Product recovery
- Product yield
- Interest rates
- Depreciation periods
- Feedstock price
- Enzyme price
- Scale of operation
- Return on investment period
- Etc.

Note that this list does not include all of the assumptions required to simulate an ethanol production facility. Many of these assumptions are implicit in the simulation software, so they go unreported in published literature. This poses a challenge in comparing research because even small assumptions may have significant impacts on process yields, efficiencies and economics. Therefore, when different research groups make slightly different assumptions, the results of the studies cannot be compared directly. Some published techno-economic papers acknowledge the many inconsistencies in assumptions and how this makes comparing results across studies difficult and complicated: Barta et al. (2010) caution their readers, "Comparisons of the cost obtained in this evaluation with those reported in similar studies applying other assumptions should be performed with great care. Differences in technological...and/or financial parameters...can render such comparisons invalid." Thus they address the complexity of comparing results of different techno-economic analyses.

Another challenge in comparing research results is that data is not reported consistently. There are a variety of units and metrics used to report results, so it is difficult to identify the same kind of information across studies. However, most studies will include one of the following three metrics: minimum ethanol selling price (MESP), product value (PV) or ethanol production cost.

MESP and PV are similar to each other. Both values calculate the selling price of ethanol that would give the project a net present value of zero with a given rate of return and project lifetime. Usually the rate of return is estimated at 10%, and the

project lifetime is 20 or 25 years (Aden et al., 2002; Anex et al., 2010; Eggeman & Elander, 2005; Kazi et al., 2010; Sendich et al., 2008).

The ethanol production cost is the cost required to produce a liter or a gallon of ethanol, given the process design and economic scenario. Sometimes units are given as gallon(s) of gasoline equivalent (GGE). GGE represents the gallons of gasoline that would have an equivalent amount of energy when compared to the quantity of ethanol being represented.

Throughout this paper we will attempt to assess and compare the contributions of the operations in the ethanol production process to the overall cost of ethanol production. Some data will evaluate the contribution of each operation to the MESP, PV and/or ethanol production cost rather than the overall cost of ethanol production. These values are helpful, but it is important to remember that they are based on *per gallon of ethanol produced* measurements. Therefore, the values reported relative to MESP, e.g., are inherently affected by every operation in the ethanol production process. This is because every operation in the ethanol production process affects the number of gallons of ethanol produced.

The rest of this paper is organized to review the ethanol production process in order of operation. We will first look at feedstock contributions to the techno-economics of lignocellulosic ethanol production. Analysis of feedstock contribution is

followed by analysis of pretreatment, hydrolysis, fermentation and then distillation, as shown in Figure 1.1.

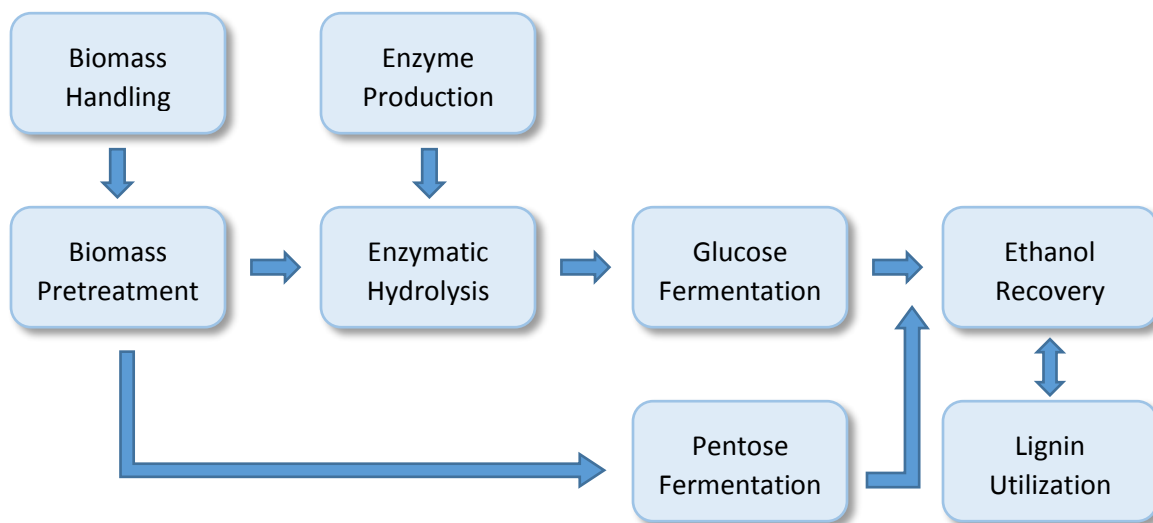


Figure 1.1. Depiction of process overview for ethanol production. Figure adapted from the Renewable Fuels Association.

Feedstock

Cellulosic ethanol is derived from many different kinds of biomass feedstocks: hardwood, softwood, switchgrass, wheat straw, corn stover – just to name a few. Often studies will choose a feedstock that is readily available locally. If the objective of a study does not include investigating the impact of the feedstock used, then a study may choose to use a pure cellulose source, such as filter paper, Avicel or pure glucose.

Most studies report that the type of feedstock used does not greatly impact the overall process economics or efficiency. However, most studies show that biomass

feedstock (regardless of type) and raw materials are the greatest contributors to operating and production costs (Aden & Foust, 2009; Franceschin, Zamboni, Bezzo, & Bertucco, 2008; Juneja, Kumar, & Murthy, 2013; Kazi et al., 2010; Kumar & Murthy, 2011; Piccolo & Bezzo, 2009; Tao et al., 2011). Therefore, the impact of feedstock is not related to the type of feedstock chosen. Rather, the impact of feedstock comes from choosing to use cellulosic biomass feedstock over starch or sugar feedstock.

Kim et al. (2011) found that, the composition of the feedstock among switchgrass varieties did not have much impact on the digestibility of the feedstock. However, the time of harvest (spring vs. fall) did impact the sugar yields from the switchgrass varieties.

Juneja et al. (2013) found that ethanol produced from perennial rye grass and from wheat straw could be competitive to other feedstock alternatives. They did not report that either feedstock studied would be a better option than the other.

Gregg et al. (1998) found that both hardwood and softwood feedstocks had similar responses to their different process scenarios, though they note that the defined process was not optimized for softwood feedstocks.

After comparing the production of ethanol from three types of feedstocks (spruce, *Salix*, and corn stover), Sassner et al. (2008) report that process configuration affects production costs more than choice of feedstock.

Sendich et al. (2008) suggested that high feedstock contribution to overall costs is desirable. A mature process is complete, automated, useful, reliable and always improving. Sendich et al. (2008) measured the process maturity of the ethanol production by the portion of manufacturing costs attributed to feedstock. They indicated that a mature process will have a high feedstock to processing cost ratio. This high ratio would mean that processing costs are relatively low and therefore competitive with petroleum-derived fuels. With this perspective, the ethanol production processes with highest feedstock contributions to overall production costs were the most desirable. Sendich et al. (2008) suggested the ethanol production process will be mature when feedstock contributes 70% of the cost of production. It is important to note that this feedstock contribution affects the overall manufacturing costs of ethanol production – not feedstock contribution to only raw material costs. Often in published literature, feedstock costs are reported as contributions to raw material costs.

Currently feedstocks contribute approximately one-third of ethanol production costs (Juneja et al., 2013; Kazi et al., 2010; Klein-Marcuschamer, Oleskowicz-Popiel, Simmons, & Blanch, 2012; Piccolo & Bezzo, 2009). Therefore there is clearly room for improvement in order to reach the goal of feedstocks contributing 70% of ethanol production costs. Franceschin et al. (2008) used corn as their feedstock, and they found the corn contributed 66-77% of the operating cost. These results would indicate that production of corn ethanol has reached process maturity. With continued research, lignocellulosic ethanol production may also reach that goal.

Pretreatment

Pretreatment is the extra process step that distinguishes the production of lignocellulosic ethanol from production of regular starch ethanol. Pretreatment is the first step in degrading the rigid structure of the biomass feedstock. It requires large amounts of water, chemical and energy as inputs. Therefore, pretreatment is often the focus of research to improve the process economics of lignocellulosic ethanol production. As previously discussed, it is difficult to compare the impact of pretreatment on the overall process economics of lignocellulosic ethanol production. Results in the literature appear inconsistent from one study to another due to different methods for data reporting. Results from different studies are not directly comparable due to different process assumptions made between the studies. The best approach for studying the impact of pretreatment methods on overall process economics is to look at studies that have the same process design and vary only in the pretreatment method. Popular pretreatment methods include dilute acid, dilute alkali, ammonia fiber expansion (AFEX), lime, steam explosion, SO₂-impregnated steam, and hot water.

In a techno-economic analysis comparing six different pretreatment methods, Tao et al. (2011) found that ammonia fiber expansion (AFEX) resulted in the lowest minimum ethanol selling price (MESP). AFEX also had the second lowest capital cost for pretreatment operations (\$31 million). Liquid hot water (LHW) had the lowest capital cost (\$20 million), but the MESP for the LHW pretreatment was relatively high. This is

because a significant portion of the sugars released by the LHW pretreatment are in oligomeric form and therefore, non-fermentable.

Of the six pretreatment methods compared by Tao et al. (2011), lime pretreatment and steam explosion with SO₂ had the highest glucan conversion percentages and good xylan conversion percentages. However, the resulting MESP values fell in the middle of the range (\$2.74/gal - \$4.09/gal) of MESP values for all scenarios in this study because both pretreatment operations were associated with high capital costs.

Kumar and Murthy (2011) compared four pretreatment methods: dilute acid, dilute alkali, hot water and steam explosion. They found that pretreatment by hot water had the lowest ethanol production cost. Dilute alkali pretreatment had the highest ethanol price due to the high purchase cost of alkali chemicals. Dilute acid had the highest capital cost, because it required additional equipment.

Kazi et al. (2010) compared four pretreatment methods: dilute acid (base case), dilute acid with high solids, 2-stage dilute acid, AFEX, and hot water. Comparing product values (PV) resulting from each pretreatment method, the results were (in descending order) hot water, 2-stage dilute acid, AFEX, dilute acid high solids and finally, the dilute acid base case. They noted that, "the PV is most sensitive to pretreatment retention time, xylan conversions, solids loading, and cellulose conversion" (Kazi et al., 2010). Increased residence time resulted in an increased PV because larger reactors were

needed. Decreased xylan conversion increased PV. Increased solids consistency during pretreatment resulted in a lower PV because it could use a smaller reactor volume, which meant a lower process heating requirement.

Using 2-stage dilute acid pretreatment would eliminate the hydrolysis step. Eliminating this step would remove the cost of enzymes and result in lower capital costs for equipment installation. However, Kazi et al. (2010) found that 2-stage dilute acid pretreatment had lower cellulose yields, which led to less ethanol produced using 2 stages vs. normal dilute acid and enzymatic hydrolysis. Therefore, 2-stage dilute acid pretreatment does not improve process economics and is not better than using the normal dilute acid pretreatment with enzymatic hydrolysis.

Hydrolysis

After pretreatment, the biomass structure has been degraded and the polysaccharides have been separated. The polysaccharides are then subjected to hydrolysis to further decompose them into sugar monomers. Monomeric sugar yield has the greatest impact on MESP (Tao et al., 2011). The greater the monomeric sugar yield, the lower the MESP, which makes cellulosic ethanol a better competitor in the fuels market. The goal of hydrolysis is to maximize the production of sugar monomers and thereby maximize ethanol production. Ethanol yield has the greatest impact on overall

process economics. The greater the ethanol yield, the better the process economics will be.

An important step in achieving high ethanol yield is to obtain a high monomeric sugar yield from the biomass through enzymatic hydrolysis. In our review of literature we found a lack of techno-economic studies using fed-batch enzymatic hydrolysis. The studies of batch hydrolysis versus fed-batch hydrolysis compare glucose or sugar yield concentrations and/or cellulose conversion. These studies do not include economic or process energy data. Techno-economic studies that use a fed-batch process also use simultaneous saccharification and fermentation (SSF). In SSF, both the enzymatic hydrolysis and fermentation reactions occur within a single reactor. When considering the results from these studies, it is difficult to determine which results are due to the use of a fed-batch process and which results are due to the use of SSF. Most techno-economic studies suggest or assume that using SSF improves process economics, compared to separate hydrolysis and fermentation (SHF). However, the use of SSF renders the results of such techno-economic studies incomparable to our study, in which we have simulated separate hydrolysis and fermentation processes.

Tomas-Pejo et al. (2008) compared SSF and SHF using steam exploded wheat straw. They found that SSF improved bioethanol production, but they did not analyze or compare the techno-economics of either process. Alfani et al. (2000) also compared SSF and SHF using steam exploded wheat straw. They found that SHF produced a higher percentage of theoretical ethanol yield. However, SSF required only one bioreactor, and

the process took less than one-third of the total time for SHF. This resulted in lower capital investment and operating costs for SSF.

Ohgren et al. (2006) compared SSF and SHF using steam pretreated corn stover. They also compared washed and non-washed slurries. Results showed higher ethanol yields for the whole slurry using SSF, both with and without additional xylanases. The whole slurries also produced higher ethanol concentrations. For the washed slurry, SHF had a higher ethanol yield and concentration.

All of the previous studies show that SSF increases ethanol yield. These studies did not provide techno-economic information, but we theorize that the increased ethanol yield will improve process economics.

Enzymes

The enzymes used in enzymatic hydrolysis contribute greatly to the total cost of production. When breaking down production costs in techno-economic studies, the purchase cost of enzymes is often grouped into the “raw materials” category with the cost of feedstock. Some studies have recently looked into the techno-economics of producing enzymes on-site. In general, the conclusion is that the increased capital cost for on-site enzyme production outweighs the benefit of not purchasing enzymes. In other words, onsite enzyme production does not improve overall ethanol production economics.

Kazi et al. (2010) found that on-site enzyme production results in lower ethanol yields and a higher PV. However, they found in their uncertainty analysis that variable enzyme costs had the greatest impact on the PV. While on-site enzyme production may give a slightly higher PV, its main benefit could be that it removes the great variable costs from purchasing enzymes produced off-site. Enzymes produced on-site will likely maintain a more stable cost compared to variable purchasing costs.

Gregg, Boussaid and Saddler (1998) estimated the effect of recycling the enzyme when producing ethanol from both hardwood and softwood substrates. Before recycling the enzyme, they found that enzyme production and purchasing costs accounted for 18.55% of the total operating costs for hardwood substrates, and 22.69% total operating costs for softwood substrates. After recycling the enzyme the percent contributions to total operating costs became 4.22% and 12.46% for hardwood and softwood, respectively. Recycling the cellulase enzyme and doubling hydrolysis time together decreased the contributions of enzyme production and purchase to total operating costs by nearly 50%. Gregg et al. do not attempt to determine how much of the reduction can be attributed to recycling the enzymes.

Klein-Marcuschamer et al. (2010) studied the cost of enzyme production and how it affected the economics of biofuel production. They note the general lack of available information detailing the costs of enzymes and their production. This lack of information contributes to the difficulty of studying enzyme production costs. They also note that often in techno-economic studies, enzyme cost contributions to total ethanol

production costs are reported per gallon of fuel produced. The per-gallon metric is inherently dependent upon other parts of the ethanol production process besides enzymes (feedstocks, enzyme loading, overall biofuel yield, etc.).

Literature estimates of enzyme costs vary significantly. In general, studies severely underestimate enzyme cost contribution to biofuel production. Klein-Marcuschamer et al. (2010) conducted a sensitivity analysis enzyme cost contribution to overall ethanol costs. They studied how enzyme cost contribution is sensitive to feedstock (poplar) price and fermentation residence time. Sensitivity analysis of enzyme cost contribution to poplar price showed that “even if the poplar were freely available, enzymes would contribute between \$0.60/gal and \$1.30/gal, [which is] considerably higher than most literature values.” Their sensitivity analysis also showed that a shorter fermentation residence time resulted in less expensive enzymes (\$/gal EtOH). The shorter fermentation residence time led to lower enzyme cost contribution to ethanol production costs. However, Klein-Marcuschamer et al. stated that lowering feedstock costs and fermentation residence times for enzyme production would still not totally alleviate the high enzyme cost contribution to ethanol production. They suggested that lower enzyme loadings used for ethanol production may lead to lower enzyme cost contributions, but this would require further optimization of the cellulase enzymes and ethanol production processes.

Klein-Marcuschamer et al. (2010) noted that current research for cellulase enzymes works to improve enzyme activity. They speculated that improved enzyme

activity could lessen time required for saccharification and reduce total capital costs for a biorefinery. However, further techno-economic analysis of enzyme production could lead to improved technology that would lower enzyme production costs. Lower enzyme production costs would lead to lower operating costs for a biorefinery. The cost savings from lower operating costs have potential to be greater than the cost savings from reduced capital costs. Therefore Klein-Marcuschamer et al. (2010) suggest further techno-economic analysis may be more beneficial than research solely focused on improved enzyme activity.

Overall, there is still a lot of room for further research to examine the techno-economics of hydrolysis. Multiple studies have shown improved ethanol yield with SSF, which we hypothesize would improve process economics. This hypothesis has yet to be proven. There is also a need for further research examining production of enzymes. Reducing the production costs of enzymes offsite would hopefully lower purchasing costs, thus lowering the contribution of enzymes to the production costs of ethanol.

Fermentation

After hydrolysis, the sugar monomers are fermented into ethanol. As previously mentioned, it has been well established that ethanol yield has the greatest effect on process economics and ethanol selling price – the greater the ethanol yield, the better the process economics will be. However, there has been little analysis of how the

fermentation process affects the techno-economics of ethanol production. If a study did include fermentation in the analysis, likely the study examined only its contribution to total project investment cost. These analyses account for capital cost of the fermentation reactor and its installation but not for operating costs of fermentation.

Eggeman and Elander (2005) determined that fermentation contributes about 12% of total direct fixed costs for their dilute acid pretreatment case. Piccolo and Bezzo (2009) conducted a techno-economic study of ethanol production comparing an enzymatic hydrolysis and fermentation (EHF) process to a gasification and fermentation (GF) process. They indicated that for the EHF process the equipment cost for the fermentation section are \$12.86 million – the second highest number on the list. Only the pretreatment section had higher equipment installation costs. In the Piccolo and Bezzo (2009) study, equipment installation costs for the fermentation section comprise about 11% of total on-site installation costs. For the GF process fermentation equipment installation costs are about the same (\$12.87 million), but there are other areas of the GF process that have much higher equipment installation costs. The installation cost of fermentation equipment represents only about 6% of the total on-site installation cost for the GF process.

Often fermentation is combined with saccharification in an SSF process. This combination results in use of a single bioreactor for both processes, so contribution to total project investment cost is attributed to both processes.

Barta et al. (2010b) found that yeast cultivation and SSF contributed 9.3% to the total capital investment cost in their reference case. Aden and Foust (2009) found that saccharification/fermentation contributed about 5% of the total project investment costs. Aden et al. (2002) determined that saccharification/fermentation contributed 8.3% of the total installed equipment costs. Kazi et al. (2010) determined that saccharification and fermentation contributed about 13% of the capital cost for their dilute acid scenario.

Only two studies examined the contribution of fermentation to the price of selling ethanol. Aden and Foust (2009) used a hybrid hydrolysis and fermentation process that contributed 8% to the overall MESP. Aden et al. (2002) determined that saccharification/fermentation contributed 8% of the ethanol selling price.

Sassner et al. (2008) found that as yeast concentration increases, production costs of ethanol also increase. Therefore, increasing yeast concentration to reduce residence time is not a good idea. They state that “the aim must be to keep the yeast concentration as low as possible.”

Some studies have investigated the effect of pentose fermentation. Kumar and Murthy (2011) determined that “cost of ethanol production was observed to be sensitive to the pentose fermentation efficiency.” Pentose fermentation improves ethanol yield, which generally improves process economics per unit of ethanol produced.

Juneja, Kumar and Murthy (2013) found that fermentation of pentose sugars decreased ethanol production costs from both perennial ryegrass (about 9%) and wheat straw (about 7%).

Sassner et al. (2008) studied the techno-economics of producing ethanol from three different feedstocks: *Salix*, corn stover and spruce. They used SSF in their simulations. To investigate the effect of fermentation of pentose sugars, they simulated a scenario in which 90% of the xylose and arabinose in SSF were converted to ethanol. This increased ethanol yields by 32% for *Salix*, 42% for corn stover and 8% for spruce, relative to the base cases. The pentose fermentation process required higher heat duties for two reasons. First, the higher ethanol concentration in the rectification column requires a higher reboiler duty. Second, there is a greater steam requirement for evaporation. However, the pentose fermentation heat duties per liter of ethanol produced are actually lower than the corresponding base cases by 16% (*Salix*), 22% (corn stover) and 5% (spruce).

Total energy efficiency of ethanol production is defined as energy output divided by energy input. Energy input occurs as raw material. Energy output occurs as both ethanol and solid fuel. Fermentation of pentose sugars causes a greater portion of the energy output to be ethanol, but it has essentially no effect on the total energy efficiency of ethanol production.

Kazi et al. (2010) found that separate fermentation of C5 and C6 sugars resulted in a higher overall ethanol yield. However, a separate fermentation increased the PV, because of the need for additional fermentation tanks and operating expenses, as well as the lower concentration of ethanol in the beer.

Recall that Gregg and Saddler (1998) studied the effect of enzyme recycling and increased hydrolysis time on the techno-economics of ethanol production using generic hardwood and generic softwood. Table 1.1 shows the contributions of C5 and C6 fermentation and ethanol production to the total cost of ethanol production. Note that total cost combines capital cost and operational costs. For each case, nearly all of the contribution from ethanol recovery is contributed to operating costs, and very little contribution is toward capital costs. In this study, total contribution of fermentation of both types of sugar (C5 and C6) are close to the contribution of ethanol recovery.

Table 1.1 Contribution of subprocesses to total costs (operation costs + capital costs) of ethanol production before and after enzyme recycle and doubled hydrolysis residence time.

Ethanol Subprocess	Hardwood		Softwood	
	Before recycle (%)	After recycle (%)	Before recycle (%)	After recycle (%)
C6 fermentation	5.25	5.50	7.82	7.97
C5 fermentation	4.23	4.80	0.00	0.00
Ethanol recovery	7.26	9.18	6.93	8.49

Tao et al. (2011) studied six pretreatment methods. They found that between 2% and 22% of sugars yielded from pretreatment are in oligomeric form. These results gave MESP values ranging from \$2.74/gal to \$4.07/gal. This study examines the effect of fermenting the oligomeric sugars by assuming they are either further hydrolyzed to monomer sugars or they are fermentable in oligomeric form. If the oligomeric sugars are fermented, the MESP drops below \$3.00/gal for all pretreatment methods. This study suggests that the fermentation of oligomeric sugars improves yield and reduces the variation of the economic performance for each of the different pretreatment methods.

Fermentation has been found to contribute 5% to 13% of the total installation costs. Aden and Foust (2009) and Aden et al. (2002) both found that fermentation contributed 8% of the MESP. Fermentation of pentose sugars and/or oligomer sugars improved ethanol yields in all cases, which generally improved process economics. It appears that fermentation has its greatest effect on the techno-economics of ethanol production in the installation capital costs because almost no studies included information about its contribution to operating costs.

Distillation

After fermentation, the ethanol is distilled until it reaches fuel-grade quality. Distillation is known to be an energy intensive process. However, there is little data

showing its effect on the techno-economics of ethanol production. Similar to fermentation, if a study includes distillation in its analysis, the study likely examines only its contribution to total project investment cost.

Eggeman and Elander (2005) determined that ethanol recovery contributed 16.5% of total direct fixed capital costs. Barta et al. (2010a) found that distillation contributed 3.7% to the total capital investment cost in their reference case. Kazi et al. (2010) found that distillation and solids recovery contributed about 15.9% of capital cost.

Two studies also examined the impact of distillation on ethanol selling price. Aden and Foust (2009) found that distillation contributed about 12% of the total project investment costs. Distillation and solids recovery together contributed 11% to the overall MESP. Aden et al. (2002) determined that distillation and solids recovery contributed 19.2% to the total installed equipment costs and 12% of the ethanol selling price.

Sassner et al. (2008) examined heat duty requirements. They found that distillation accounted for just over half of the overall heat duty for the ethanol production process. Preheating the mash accounted for one-third of the overall heat duty. Pretreatment and drying made only small contributions to the overall heat duty because these process steps generate steam that can be used elsewhere in the process.

Kazi et al. (2010) investigated the effects of using pervaporation instead of distillation. Pervaporation is less energy-intensive than distillation, so they thought pervaporation would reduce operating costs compared to distillation. Pervaporation successfully reduced energy consumption and allowed for more exported energy. The increased exported energy resulted in greater profit from exported energy compared to the base case. However, using pervaporation increased the PV of the ethanol because pervaporation requires use of an expensive membrane. Installation of the membrane cost \$46.5 million, compared to only \$1.5 million for the normal distillation beer column.

Conclusions

After examining the techno-economic literature for cellulosic ethanol production, we find that feedstock type does not affect process techno-economics. The pretreatment procedure greatly affects capital and operating costs. However, it is difficult to compare results across studies because of the great variety in pretreatment methods and assumptions. We did not find any techno-economic analysis comparing SHF to SSF, so we cannot compare efficiencies or costs between these processes. The published literature does show SSF increases ethanol yields, so we would expect it to improve process economics. Klein-Marcuschamer et al. (2012) show that most literature underestimates enzyme contribution to biofuel production costs. The lack of public

information detailing enzyme cost and production procedures obfuscate data needed to better determine the enzyme cost contributions to production costs. Fermentation contributes primarily to capital costs – not operating costs. Improved pentose fermentation would increase ethanol yields, but it may not prove to be beneficial. The ethanol yield increase may come with trade-offs in increased capital and operation expenses. Distillation is mostly analyzed for its contribution to capital costs. There was little information regarding the distillation process energy requirements in the techno-economic analyses we studied.

We find there is significant information analyzing the techno-economics of pretreatment. However, there are many techno-economic analyses yet to be completed in order to fully optimize the cellulosic ethanol production process.

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CHAPTER 2: SIMULATION AND COMPARISON OF BATCH AND FED-BATCH ENZYMATIC HYDROLYSIS OPERATIONS IN CELLULOSIC ETHANOL PRODUCTION

Introduction

At the beginning of the commercial fuel industry ethanol and gasoline were equal competitors. Early cars and engines were built to run on ethanol. Henry Ford even built a flex-fuel Model T in 1908. This car could be adjusted to run on ethanol, gasoline or a blend of the two (Solomon, Barnes, & Halvorsen, 2007). Cellulosic ethanol was first produced by a French chemist, Henri Braconnot, in 1898 (Kovarik, 2013). A couple small commercial cellulosic ethanol production plants were built and operated in the United States in the early 1900s, but they closed for economic reasons after World War I (Kovarik, 2013; Solomon et al., 2007). Nearly 100 years later in September 2014, the first modern commercial cellulosic ethanol plant in the United States began operation in Iowa. There are now seven operating cellulosic ethanol plants in the United States (U.S. ethanol plants.2017) and ethanol production continues to grow, as shown in Figure 2.2.

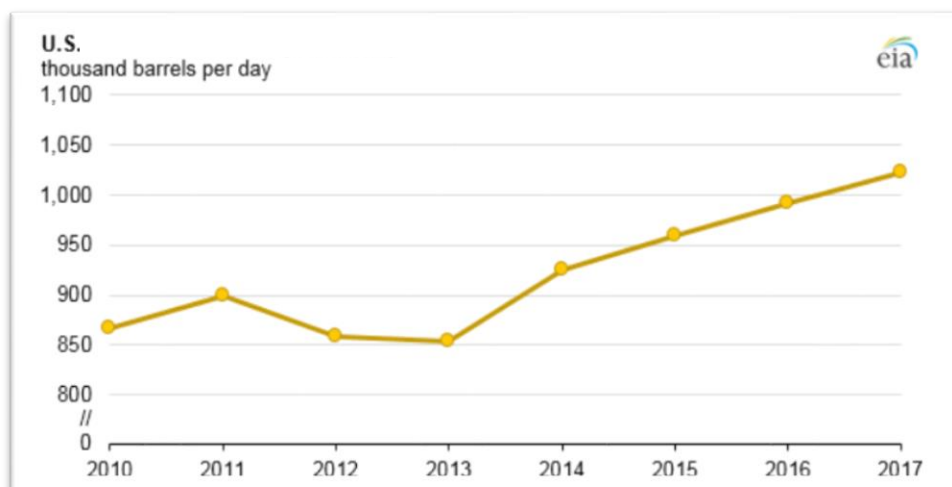


Figure 2.2. U.S. ethanol production (2010-2017) (Hill & Hanson, 2017)

As the demand for ethanol continues to increase, there are many opportunities for optimizing the cellulosic ethanol production process. For example, most cellulosic ethanol production uses a batch method for the hydrolysis step. Previous work in this lab and other studies (Ballesteros et al., 2002; Hodge et al., 2009; Rudolf et al., 2005; Tai, Arellano, & Keshwani, 2014) have investigated the potential benefits of utilizing fed-batch enzymatic hydrolysis in cellulosic ethanol production. Research suggests that using a fed-batch method will maintain a higher reaction rate (Bansal et al., 2009; Gan et al., 2003; Laureano-Perez, Teymouri, Alizadeh, & Dale, 2005b; Zhang & Lynd, 2004), relieve mass transfer problems, and allow for higher total cumulative solids in the hydrolysis reactor (Ballesteros et al., 2002; Hodge et al., 2009).

We suspect that using a fed-batch process could also lead to improvements (reductions) in water, chemical and energy use in cellulosic ethanol production. Kazi et

al. (2010) found that increasing solids consistency during pretreatment improved the product value because it could use a smaller reactor volume, which meant a lower process heating requirement. We would expect similar findings for fed-batch enzymatic hydrolysis.

In this chapter, we identify and quantify techno-economic differences between cellulosic ethanol production using batch enzymatic hydrolysis versus production using fed-batch enzymatic hydrolysis. We will also conduct a sensitivity analysis for both the batch and fed-batch scenarios to study the magnitude of effects caused by changing parameters. We will compare these effects between the batch and fed-batch scenarios and with their respective base case scenarios.

Methodology

Process description (base cases)

We built two separate simulations: one using batch enzymatic hydrolysis and one using fed-batch enzymatic hydrolysis. The simulations were exactly the same for every other process operation. These two simulations became our base cases. We compared simulation results from the base cases to identify techno-economic effects of using a fed-batch operation instead of a batch operation.

Simulation software

We used the SuperPro Designer (SPD) simulation software (Intelligen, Scotch Plains, New Jersey) because it was designed specifically to model bioprocesses. SPD also has built-in economics calculations, which was a key component of this study. It is important to note that there are three levels of complexity in a SPD simulation. “The simplest physico-chemical transformation step that can be modeled by SuperPro Designer [is a unit operation]. Operations are strung together to form a unit procedure and unit procedures are put together to make up a process (or a recipe)” (Intelligen Inc., 1991). An operation may be as simple as ‘Charge’ or ‘Mix,’ or it may be more complex, e.g. ‘Distill’ or ‘React.’ A procedure is “a sequence of actions representing the most elementary physico-chemical transformations supported by the software all assumed to take place within the same equipment resource” (Intelligen Inc., 1991). Throughout this thesis we will use the same naming convention for these steps.

SPD comes with an example process flow sheet for converting corn stover to ethanol. We started with this process flow sheet and modified it to fit our needs (see Appendix A). The operating parameters for the simulation can be found in Table 2.2.

Table 2.2. Operating parameters for SuperPro Designer base case simulations.

	Batch Base Case	Fed-batch Base Case
Process type	Continuous	Continuous
Hours of operation per year	7920	7920
Plant capacity	2000 metric tons/day	2000 metric tons/day
Depreciation	10 years, straight-line method	10 years, straight-line method
% equity financed	100%	100%
Project life	20 years	20 years
IRR (after tax)	3.52%	6.33%
Startup period	4 months	4 months
Construction period	30 months	30 months
Year of analysis	2013	2013
Inflation	4.00%	4.00%

Feedstock

We chose corn stover as our biomass because it has shown promise as a lignocellulosic ethanol feedstock, and it is readily available in Nebraska. We assumed the composition of the corn stover was as follows (mass percentages given): 5.2% ash, 37.4% cellulose, 21.1% hemicellulose, 18% lignin and 18.3% other solids (Aden et al., 2002). This corn stover was mixed with water before being used in the ethanol production process. The feedstock mixture for the ethanol production process consisted of 50% corn stover, 50% water (mass percentages given). We assumed the corn stover biomass would be transported 50 km, where each shipment contained 20 metric tons. Our overall operation would require nearly 66,000 shipments/year.

Overview of production process

Pretreatment

After the feedstock arrives at the plant facility it is first washed and ground to reduce particle size. Then pretreatment begins. Our design uses a thermal hydrolysis (hot steam) pretreatment. The thermal hydrolysis pretreatment will degrade the structure of the biomass and leave the cellulose more accessible to the enzyme in the upcoming enzymatic hydrolysis operation. Hot, high-pressure steam is fed into the reactor at a rate of 30 MT/h, temperature of 200°C and pressure of 10 bar. The feedstock slurry enters the reactor at 215 MT/h, 88°C and 10 bar. Within the reactor, the contents sit at 180°C and 10 bar. The residence time is 30 minutes. During this time some cellulose is broken down into glucose, and a majority of the hemicellulose is broken down into xylose. The conversion of cellulose to glucose is set to 10%. The conversion of hemicellulose to xylose is set to 70%. The pretreatment reaction is assumed to be adiabatic.

Entering the pretreatment reactor, the feedstock slurry has the following composition (approximate mass percentages given): 15% cellulose, 9% hemicellulose, 48% water, 13% lignin, 3% glucose, 1% xylose, 11% other. Leaving the pretreatment reactor, the slurry composition changes as follows (approximate mass percentages given): 12% cellulose, 2% hemicellulose, 53% water, 11% lignin, 4% glucose, 7% xylose, 11% other.

After the thermal hydrolysis the slurry is flash cooled. Some excess water is removed and some of the xylose is filtered out of the slurry. After cooling and filtration the slurry has the following composition (mass percentages given): 16% cellulose, 3% hemicellulose, 45% water, 15% lignin, 3% glucose, 6% xylose, 12% other. The hydrolase enzyme is next mixed into the slurry for the enzymatic hydrolysis operation at a rate of 13 MT/h, 25°C and 1 bar. After mixing the enzyme into the slurry stream, the hydrolase comprises just 0.2% mass composition of the stream.

Hydrolysis

We assume the hydrolase is purchased from an external source at \$11.40/kg protein. This price factors out to about \$0.50/gallon of ethanol produced.

For both simulations (batch and fed-batch) the hydrolase enzyme is mixed into the stream before the slurry enters the hydrolysis reactor. The batch enzymatic hydrolysis reaction uses only 2,123 metric tons of hydrolase enzyme per year, which comes to 0.268 metric tons per hour. The batch enzymatic hydrolysis reaction is assumed to be adiabatic. The contents of the reactor were recorded at about 45°C and a pressure of about 10 bar. We assume the cellulose to glucose reaction was run to 90% completion and the hemicellulose to xylose reaction was run to 70% completion. After batch enzymatic hydrolysis, the slurry stream composition is as follows (approximate mass composition percentages given): 2% cellulose, 1% hemicellulose, 48% water, 14% lignin, 18% glucose, 7% xylose, 10% other.

The simulated fed-batch enzymatic hydrolysis reaction uses only 2,091 metric tons of hydrolase enzyme per year, which comes to 0.264 metric tons per hour. The fed-batch enzymatic hydrolysis is also assumed to be adiabatic. The contents of the reactor were recorded at about 45°C and a pressure of about 10 bar. We assume the reaction is run to full completion due to the nature of a fed-batch operation within a continuous process. After fed-batch enzymatic hydrolysis, the slurry stream composition is as follows (approximate mass composition percentages given): 0% cellulose, 3% hemicellulose, 47% water, 14% lignin, 19% glucose, 6% xylose and 11% other.

After hydrolysis the hydrolysate slurry is filtered. The stream containing mostly glucose and water is sent on to fermentation. The stream containing mostly lignin, ash and water was further processed. Most of the lignin is sent to be burned in the utilities section of the plant to generate power.

Fermentation

In the fermentation section of the plant, some of the slurry is used in seed fermentation tanks to grow the yeast cells. The whole slurry is fermented into ethanol. Our process used four 2,220 m³ fermentation tanks with a temperature of 37°C and a cycle time of 48 hours. The slurry stream then enters a storage holding tank until it can be distilled to a higher percentage of ethanol.

Distillation and adsorption

The simulated slurry stream leaves the storage holding tank and enters a heat exchanger to facilitate the distillation process. Leaving the heat exchanger, the stream has a temperature of 47°C. The stream is now 9% ethanol and 80% water (approximate mass percentages given) when it begins the distillation process. The distillation columns operate at a temperature of 106°C. Leaving distillation the stream is 90% ethanol, 9% water (approximate mass percentages given). Next an adsorption operation further dehydrates the stream, removing the little water remaining, such that the ethanol product reaches 99.9% purity.

Utilities

The utilities section of the plant burns lignin to generate power. The generated power is sold back to the grid; it is not used within the plant. Selling the power generates additional profit for the production plant facility. The utilities section also recycles water for continued use within the plant.

Sensitivity analysis

We used our simulation to investigate the sensitivity of the ethanol production cost to different process parameters. We found differing values for parameters in the literature, so we varied the parameter values one at a time and monitored the change in ethanol production cost. The base case parameters from the SPD example process

design are close to the base case parameters from the NREL studies. We set parameter values to better match those of the NREL base case studies (Aden et al., 2002; Davis et al., 2015) in order to compare results of the NREL base case to the SPD base case.

General process design and data

Plant specifications

We assume the plant in this study is located in Ravenna, Nebraska. Currently, there is no cellulosic ethanol plant in Ravenna; however, there has been recent discussion about building a cellulosic ethanol plant there.

The plant capacity is set at 2,000 metric tons of dry biomass per day. This matches the processing capacity of plant designs in other techno-economic analyses, such as the NREL standard (Aden et al., 2002; Davis et al., 2015) and others (Aden & Foust, 2009; Anex et al., 2010; Eggeman & Elander, 2005; Kazi et al., 2010; Klein-Marcuschamer et al., 2010). This means 660,000 metric tons of biomass are processed per year.

The plant is set to operate for 7,920 hours per year. All equipment is sized by the software and assumed to be constructed of either CS or SS316. Only the fermenter is assumed to be made of SS304.

Economics

Table 2.3 gives an economic summary of some basic economic parameters for our simulated SPD base cases. We chose to report all economic values for this study in US 2013 dollars.

We took information for utility costs from the website for the Nebraska Energy Office. The average industrial rate for electricity cost in the Dawson Public Power District (service provider for Ravenna, NE) in November 2016 was 12 ¢/kW-h (2015 utility bundled retail sales- industrial.2016).

We assume all labor workers in the plant were standard operators receiving the same wages of \$25 per hour. We took information for operator salaries from the NREL studies (Aden et al., 2002; Davis et al., 2015) and from the website for the United States Bureau of Labor and Statistics (Occupational employment and wages, may 2016: 51-9011 chemical equipment operators and tenders.2016). We looked at information for chemical plant and systems operators. This data was most recently updated in May 2016.

It is important to note that the given ethanol production cost accounts for all operations within the production process. Pretreatment, fermentation, distillation and the utilities operations of the simulation all impact the ethanol production cost; it is not only affected by the enzymatic hydrolysis operation even though we are studying the impact of the enzymatic hydrolysis operation.

Table 2.3. Economic summary of SuperPro Designer base cases

	Batch	Fed-batch
Total capital investment (\$)	196,487,072	167,194,736
Annual operating cost (\$/yr)	117,650,740	111,650,689
Annual ethanol revenue (\$/yr)	116,565,239	115,657,243
Ethanol unit production cost (\$/gal)	2.4537	2.3469
Ethanol unit production revenue (\$/gal)	2.4848	2.4855
ROI (%)	9.27	11.29
IRR (after tax) (%)	3.52	6.33
Input target ethanol sell price (\$/gal)	2.50	2.50

Results and discussion

Batch Case

The plant design using batch enzymatic hydrolysis had a capital cost of \$196,487,072. It produced 47.9 million gallons of ethanol per year. This plant required 50,386,181 kW-h of power for operation throughout the course of the year, which resulted in a power cost of \$2,519,309 per year. Total utilities cost \$7,254,020 per year. The labor requirement was 189,541 hours/year, which cost \$4,957,604 per year. The batch enzymatic hydrolysis operation used 2,123 MT/year of hydrolase enzyme for a total enzyme cost of \$24,202,200 per year. Figure 2.3 shows the breakdown of annual operating costs for the batch SPD base case.

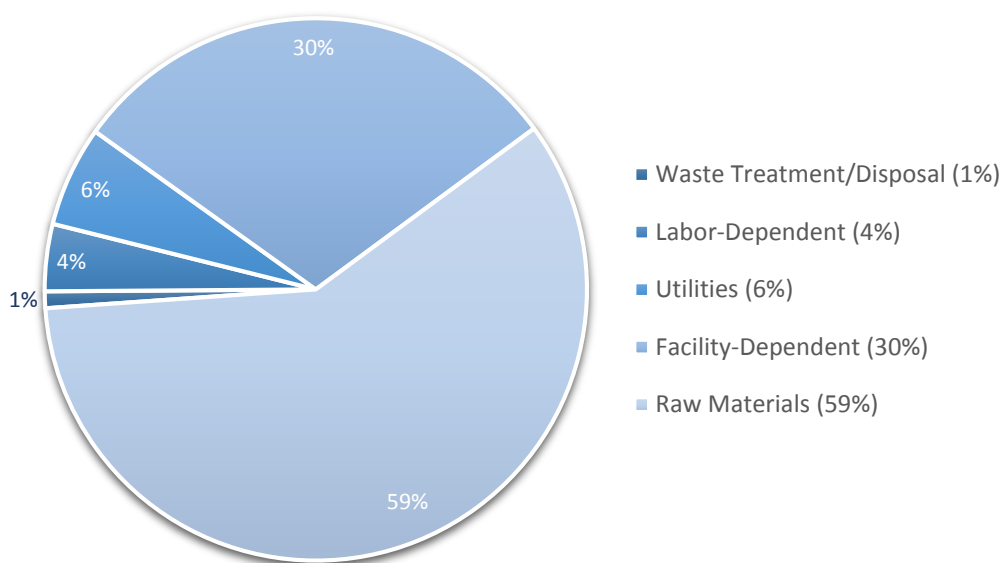


Figure 2.3. Annual operating cost breakdown for batch SPD base case

Fed-batch Case

The plant design using fed-batch enzymatic hydrolysis had a capital cost of \$167,194,736. It produced 47.6 million gallons of ethanol per year. This plant required 50,151,126 kW-h of power for operation throughout the course of the year, which resulted in a power cost of \$2,507,556 per year. Total utilities cost \$7,323,292 per year. The labor requirement was 182,941 hours/year, which cost \$4,578,098 per year. The fed-batch enzymatic hydrolysis operation used 2,091 MT/year of hydrolase enzyme, for a total enzyme cost of \$23,837,400 per year. Figure 2.4 shows the breakdown of annual operating costs for the fed-batch SPD base case. Table 2.4 gives a side-by-side comparison of these values for the batch and fed-batch SPD base case models.

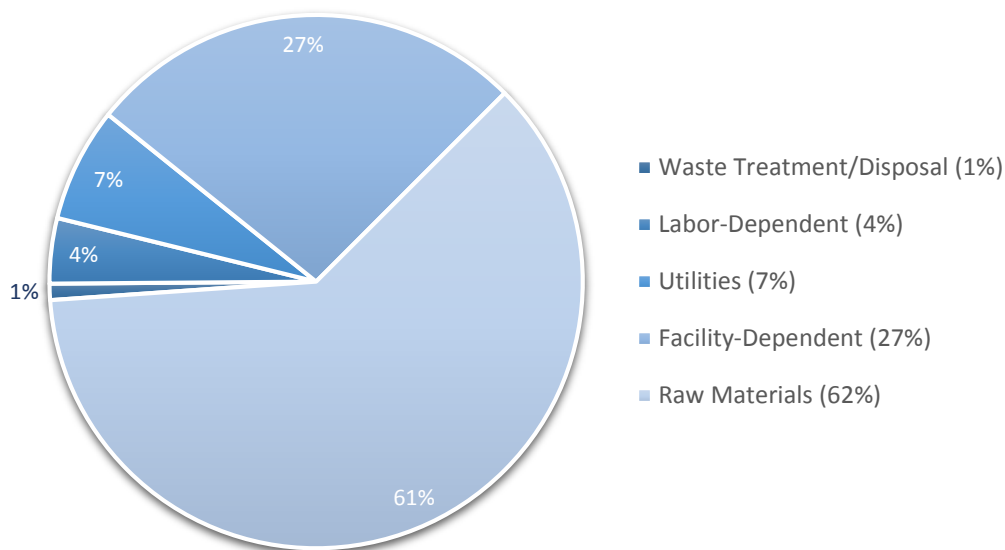


Figure 2.4. Annual operating cost breakdown for fed-batch SPD base case

Table 2.4. Side-by-side comparison of batch and fed-batch SuperPro Designer base case results

	Batch	Fed-batch	Comparison
Capital cost (\$)	196,487,072	167,194,736	- 29,292,336
Ethanol produced (gal/year)	47,900,000	47,600,000	- 300,000
Power required (kW-h/year)	50,386,181	50,151,126	- 235,055
Total utilities cost (\$/year)	7,254,020	7,323,292	+ 69,272
Total labor cost (\$/year)	4,957,604	4,578,098	- 379,506
Facilities costs (\$/year)	34,888,000	29,634,000	- 5,254,000
Amount of enzyme used (MT/yr)	2,123	2,091	- 32
Cost of enzyme (\$/year)	24,202,200	23,837,400	- 364,800
Ethanol unit production cost (\$/gal)	2.4537	2.3469	- 0.1068

For both the batch and the fed-batch SPD base cases, the utilities section used the greatest percentage of bulk materials (e.g. water, air, corn stover biomass, etc.). The

steam turbine used to generate steam in the utilities section is by far the most power-intensive step of the whole production process in both batch and fed-batch simulations. However between the batch and fed-batch processes the utilities costs and utilities use remained about the same. The fed-batch process decreased both utilities cost and use by only 0.5%.

Enzyme cost and use was also essentially the same between the batch and fed-batch processes. The fed-batch process decreased both labor costs and facilities costs by 21% and 41%, respectively. The fed-batch process also decreased total capital costs by 15%. Likely the lower capital cost is due to the fact that the fed-batch process requires one fewer GAC column, and 4 fewer stirred tank reactors.

Palmqvist, Wiman and Liden (2011) found that increased enzyme load lowered the required amount of mixing energy for the hydrolysis reactor. Since our enzyme use was the same for the batch and fed-batch processes, it makes sense that our utilities use was also the same for these processes.

Sendich et al. (2008) suggested that examining the contribution of raw materials cost to the overall manufacturing costs may indicate process maturity. They suggested raw materials – and especially biomass feedstock – will contribute 70% of overall manufacturing costs for a mature process. As seen in Figure 2.3 and Figure 2.4 our simulated process is nearing maturity, as raw materials contributed about 60% of annual operating costs for both the batch and fed-batch processes. This value was higher than

we expected. Other studies showed feedstocks contributing only about 30% of ethanol production costs. We propose two reasons for our study showing a higher contribution from raw materials: first, we looked at contribution of all raw materials – not only feedstock costs. Second, our hydrolase enzyme cost was higher than most studies, and the hydrolase enzyme contributes to raw materials costs.

Sensitivity analysis

Sugar conversion

We wanted to observe the effect of sugar conversion on the ethanol production cost. In the base case scenarios, we assumed the glucan to glucose conversion reaction would reach 90% completion and the xylan to xylose conversion reaction would reach 50% completion. Unfortunately the fed-batch operation in SPD is rigid, and we could not alter the extent completion for the fed-batch process base case. In the batch process base case scenario, we first adjusted the glucan to glucose conversion from 90% up to 100% and then down to 75%. Then we adjusted the xylan to xylose conversion from 50% up to 75%. For both reactions, when extent of conversion increased, the ethanol production cost decreased relative to the base case. When the extent of conversion decreased for the glucan to glucose reaction, ethanol production cost increased relative to the base case. Figure 2.5 shows the change in ethanol production cost for each of the adjusted conversions.

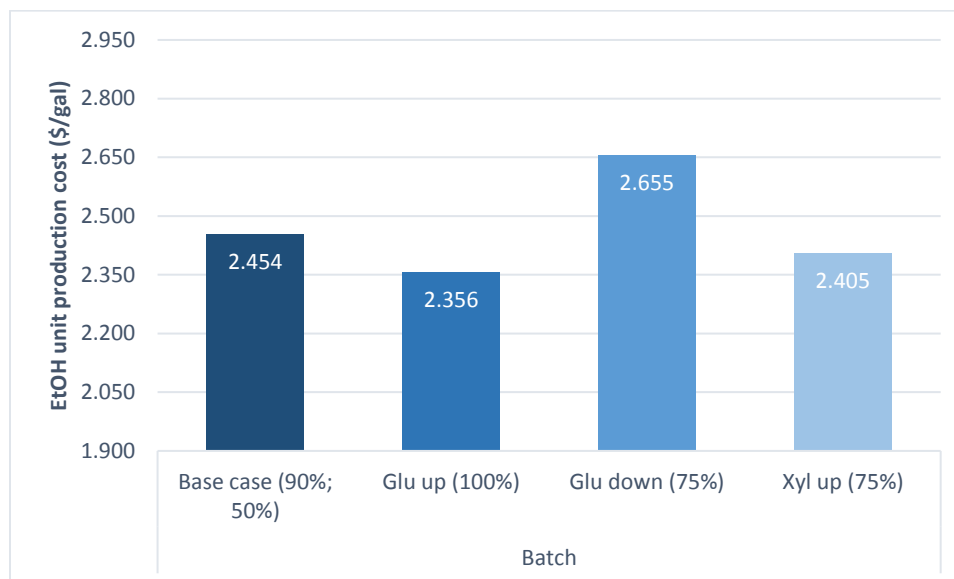


Figure 2.5. Comparison of ethanol production cost for the batch SuperPro Designer base case and adjusted sugar conversion extensions

Plant capacity

We wanted to see how increasing the plant capacity affected the ethanol production cost. We assumed we could still get this amount of biomass from the same land area, so transportation distance and cost did not change. This is likely an oversimplification and would not actually be true in real life. Likely the required land area for biomass collection would increase, which would increase travel and transport costs for the biomass. SPD automatically resized the equipment within the process design as necessary. By increasing the plant capacity to 2500 metric tons per day we decreased the ethanol production cost by approximately \$0.05/gal for the batch case and by \$0.06/gal for the fed-batch case. Figure 2.6 illustrates the change in ethanol production costs as a result of increasing plant capacity.

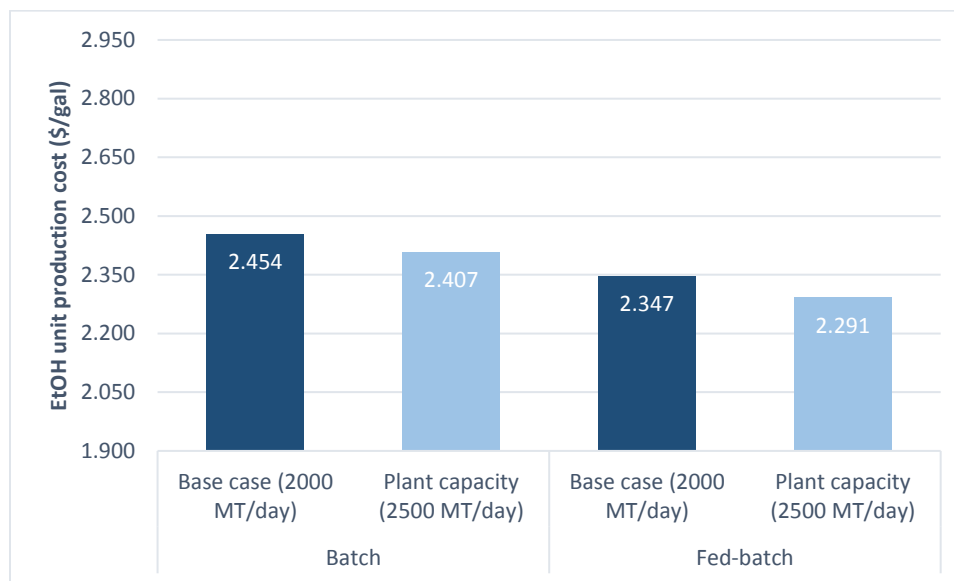


Figure 2.6. Comparison of ethanol production cost for the SuperPro Designer base case and adjusted plant capacity

Feedstock cost

Feedstock is a large contributor to raw materials costs in cellulosic ethanol production. Other studies show raw materials comprise approximately 30% or more of total operating costs (Aden et al., 2002; Aden & Foust, 2009; Eggeman & Elander, 2005; Juneja et al., 2013; Kazi et al., 2010; Klein-Marcuschamer et al., 2010; Kumar & Murthy, 2011; Tao et al., 2011). We were interested to see how changing the feedstock costs would affect the ethanol production cost. In the SPD base cases we assumed that the stover feedstock cost \$50 per metric ton. To test the sensitivity of the ethanol production cost to the cost of the feedstock, we increased the price to \$80 per metric ton. For the batch process, the ethanol production cost increased by \$0.47/gal. For the fed-batch process, the ethanol production cost again increased by \$0.47/gal. Figure 2.7

illustrates the change in ethanol production cost as a result of changing the biomass cost.

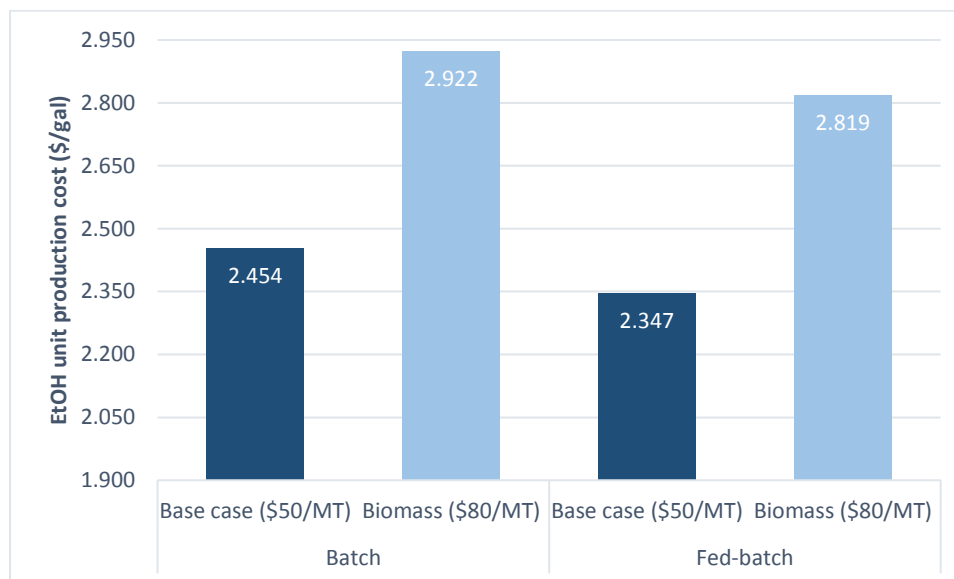


Figure 2.7. Comparison of ethanol production cost for the SuperPro Designer base case and adjusted biomass cost

Power cost

Power costs vary widely by location, and they are subject to change. We wanted to see the effect of power cost on ethanol production cost after noticing the high energy requirements of cellulosic ethanol production. The SPD base case assumed a power cost of \$0.05, which was close to the NREL base case assumption of \$0.06. We checked the Nebraska Energy Office and found that Ravenna, NE is in the Dawson Public Power district (DPPD). The data on the NEO website showed the average industrial energy cost for DPPD was \$0.12/kW-h. We adjusted the power cost up to \$0.12 to match this data

(2015 utility bundled retail sales- industrial.2016). The increase in power cost caused the ethanol production cost in the batch process to increase by \$0.08/gal. The ethanol production cost in the fed-batch process increased \$0.07/gal. Figure 2.8 illustrates the change in ethanol production cost as a result of changing the power cost.

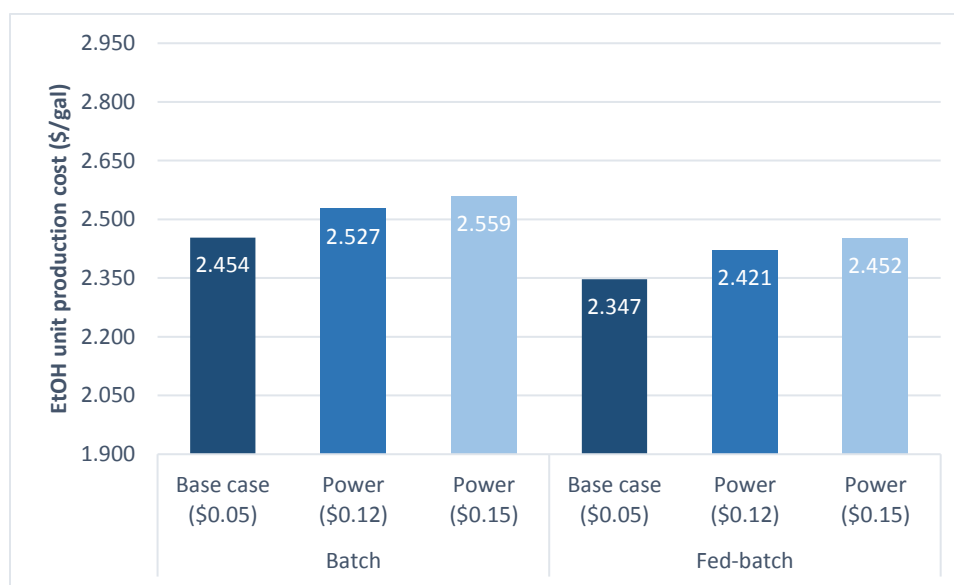


Figure 2.8. Comparison of ethanol production cost for the SuperPro Designer base case and adjusted power costs

Labor cost

We wanted to test the sensitivity of the ethanol production cost to the labor cost after noticing the high labor requirements for cellulosic ethanol production and how it changed greatly by using either batch or fed-batch enzymatic hydrolysis. We used data from the US Bureau of Labor and statistics to adjust the salary costs for operators that would be working in the plant. The data showed that a \$40 hourly wage

represented the 90th percentile of all chemical plant operators, so we chose this as our high estimate. We chose an \$18 hourly wage as a low estimate for the sake of observing sensitivity. When we increased the hourly wage for operators, the ethanol production cost for the batch process design increased only \$0.08/gal. The ethanol production cost for the fed-batch process design increased only \$0.01/gal. When we decreased the hourly wage for operators, the ethanol production cost for both the batch process design and the fed-batch process design decreased by \$0.01/gal. Note that during this simulation we still assumed the same hourly wage for all workers in the plant, even though this would not be the case. In reality there would be supervisors and managers that would receive different wages than the operators. Figure 2.9 illustrates the change in ethanol production cost as a result of changing labor costs.

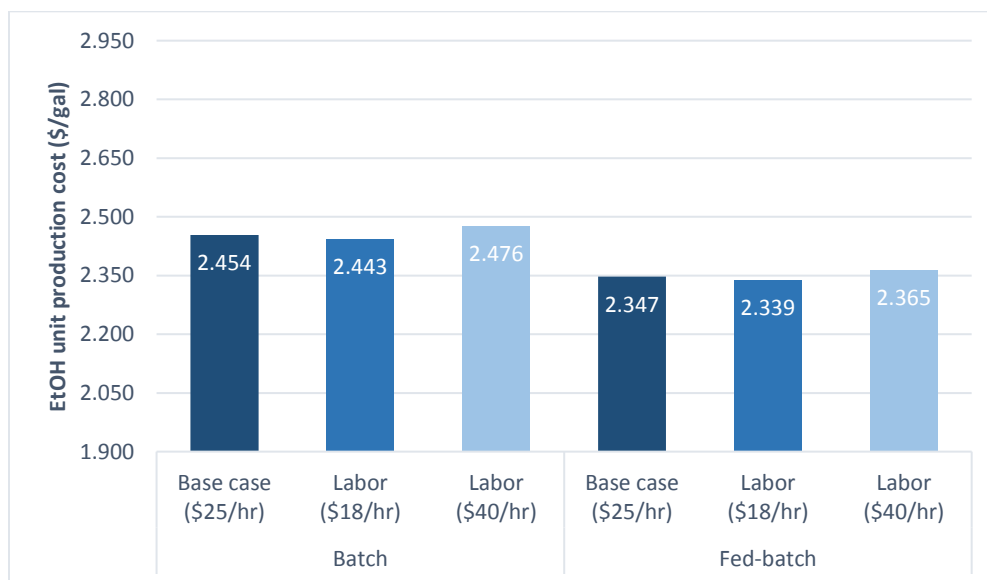


Figure 2.9. Comparison of ethanol production cost for the SuperPro Designer base case and adjusted labor costs

Enzyme cost

Enzyme costs are tricky to estimate. Often the data needed to calculate enzyme cost and cost contributions is difficult to find and/or determine due to confidentiality surrounding commercial enzyme production. Since the cost of the enzymes are subject to change we wanted to test the effect of enzyme price on the ethanol production cost. The SPD base case assumes an enzyme cost of \$11.40/kg protein, which translated to a cost of \$0.50 per gallon of ethanol produced. The NREL base case (Aden et al., 2002; Davis et al., 2015) suggested an enzyme cost of \$0.17 per gallon of ethanol produced would be more ideal. We estimated that to lower the cost per gallon to \$0.17, the cost of enzyme per kilogram of protein would decrease to only about \$3.50, so we ran a simulation at this lower cost. Because of the difficulties estimating enzyme cost, we also wanted to see the effect of nearly doubling the cost of enzyme. So we also simulated an enzyme cost of \$20/kg protein. At the lower enzyme cost, the ethanol production cost for both the batch and fed-batch process designs decreased by \$0.35/gal. At the higher enzyme cost, the ethanol production cost increased by \$0.38/gal and by \$0.37/gal for the batch and fed-batch process designs, respectively. Figure 2.10 illustrates the change in ethanol production cost as a result of changing the enzyme cost.

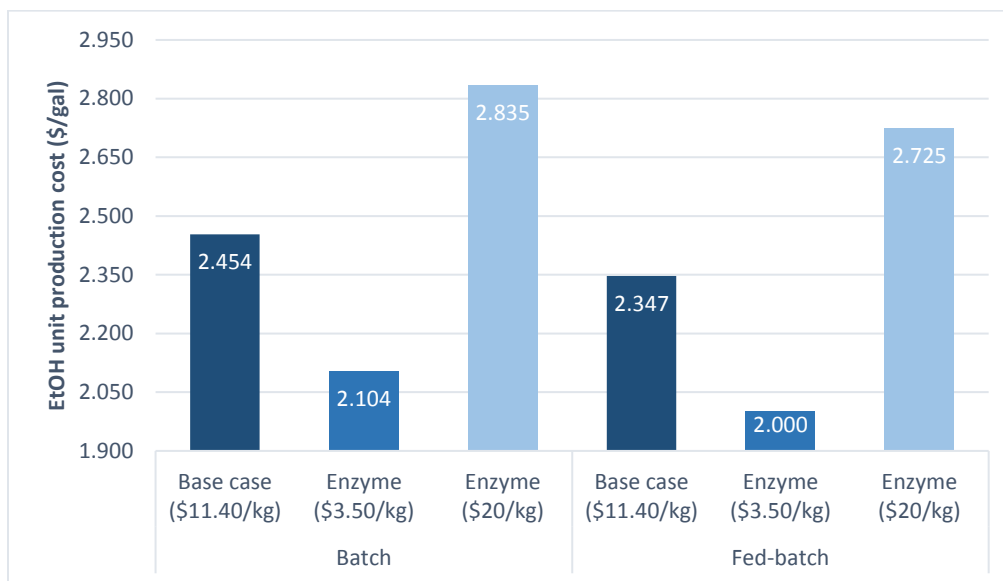


Figure 2.10. Comparison of ethanol production cost for the SuperPro Designer base case and adjusted enzyme costs

SPD parameters vs. NREL parameters

The base case parameters within SPD are similar to the base case parameters in NREL studies (Aden et al., 2002; Davis et al., 2015). In order to be sure the slight differences did not have a great effect on ethanol production cost, we changed the cost of labor, power, enzyme, corn stover and the annual operating hours to better reflect the NREL studies. Table 2.5 shows the comparison between the SPD base case values and the NREL base case values. The NREL parameters resulted in a higher ethanol production cost for the batch and fed-batch processes. Figure 2.11 illustrates the changes in ethanol production.

Of all the parameters changed, the feedstock cost had the greatest effect. The NREL base case values had a lower cost for the corn stover feedstock (see Table 2.5).

This resulted in a lower cost for raw materials, lower operating costs and therefore, higher profits.

The percent change in ethanol production cost from SPD base case values to NREL base case values was roughly equivalent between the batch and fed-batch operations. In the batch operation the ethanol production cost increased by 6.20% from SPD base case values to NREL base case values. In the fed-batch operation the ethanol production cost increased by 6.75% from SPD base case values to NREL base case values. The response to the change in values for both batch and fed-batch operations had about the same magnitude. We saw this in the other sensitivity analysis scenarios, too. We saw the percent change from the base case to the adjusted parameter scenarios was roughly equivalent between the batch and the fed-batch processes. Since the changes were so uniform, we conclude that SPD evaluates the batch and fed-batch processes in a similar manner.

Table 2.5. Comparison of parameter values for the SuperPro Designer base case and the NREL base case.

Values for the batch enzymatic hydrolysis process are given first. Values for the fed-batch enzymatic hydrolysis process are given in parenthesis.

	SuperPro Designer Base Values	NREL Base Values
Labor (\$/hr)	25	23
Standard power (\$/kW-h)	0.05	0.06
Enzyme cost (\$/kg)	11.40	4.00
Corn stover cost (\$/MT)	50	80
Annual operating hours (hr/yr)	7920	7880
Ethanol production cost (\$/gal)	2.4537 (2.3469)	2.6059 (2.5053)

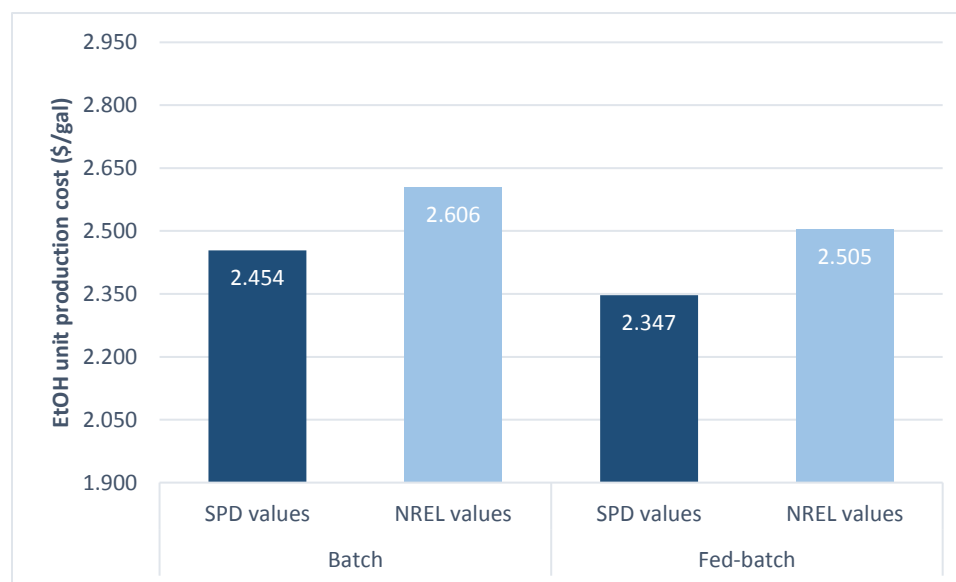


Figure 2.11. Comparison of ethanol production cost for the SuperPro Designer base case values and NREL base case values

Conclusions

In this paper we examined the techno-economic differences between cellulosic ethanol production using batch enzymatic hydrolysis and production using fed-batch enzymatic hydrolysis. We expected to see differences in water, chemical and energy use, but these values were roughly the same for the batch and fed-batch processes. We identified the greatest differences in facilities costs, labor costs and capital costs. Using a fed-batch operation decreased facilities costs by 41%, labor costs by 21% and capital costs by 15%. In our sensitivity analysis we found that cost of biomass cost had the greatest effect on ethanol production cost, which caused a 20% increase in ethanol production costs. Enzyme cost had the second greatest effect, decreasing ethanol production costs by 15% when we decreased enzyme cost by 70%. Ethanol production cost increased 16% when we increased the enzyme cost by 75%.

Our results support the proposition that fed-batch enzymatic hydrolysis does improve the techno-economics of cellulosic ethanol production, even if not in all the ways we expected. In the future we hope to implement a custom feeding profile for the fed-batch enzymatic hydrolysis operation. This feeding profile would be based on previous work in our lab group. The feeding profile for a fed-batch operation in SPD is unchangeable, so we were unable to implement our profile for this study. We would like to know whether our optimized feeding profile could further improve enzymatic hydrolysis and the techno-economics of cellulosic ethanol production overall.

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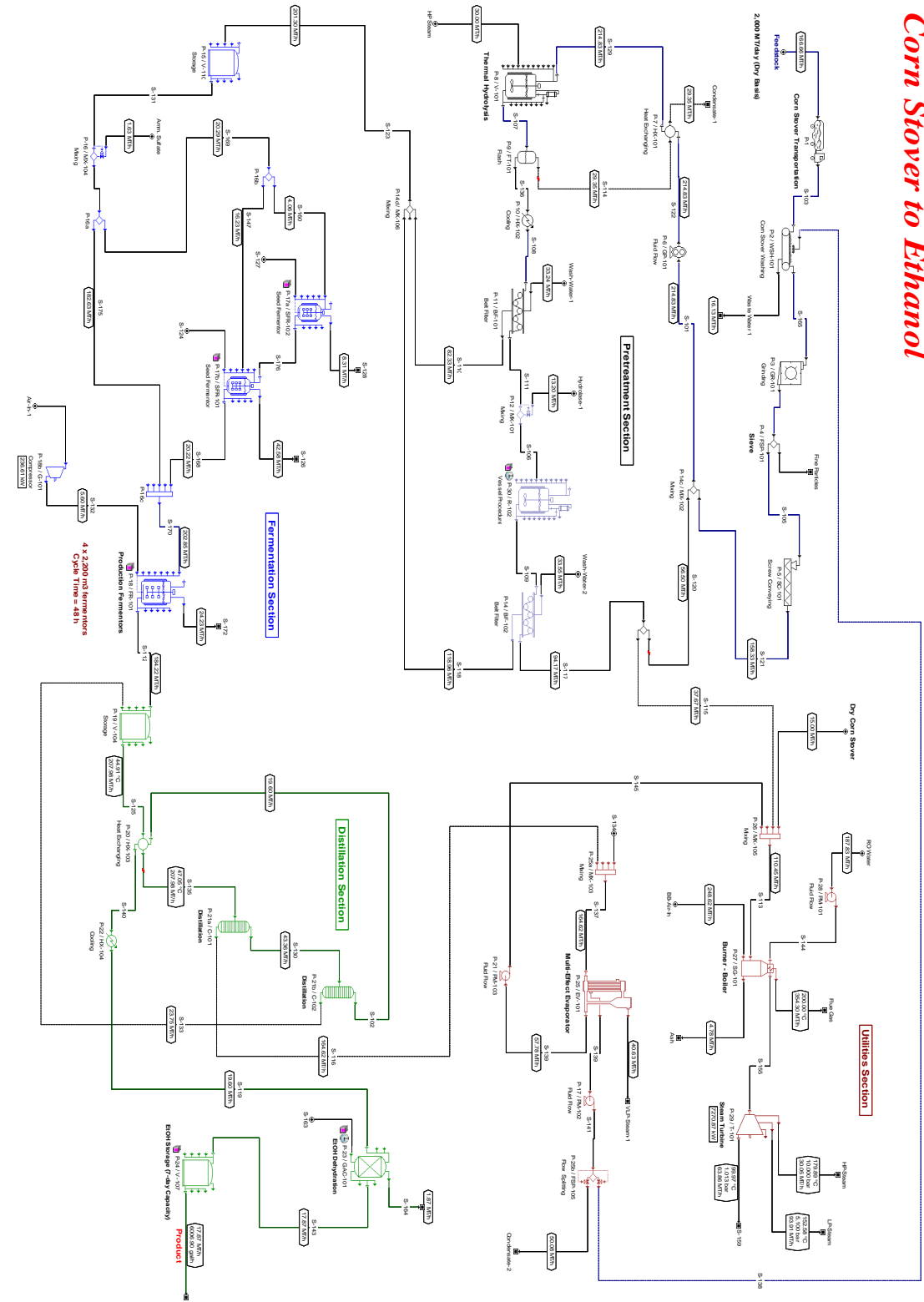
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APPENDIX A: SAMPLE SUPERPRO DESINGER PROCESS FLOWSHEET

Corn Stover to Ethanol



APPENDIX B: ELECTRONIC FILES

All electronic SuperPro Designer files are available upon request.