Process and Economic Analysis of Pretreatment Technologies

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Abstract

Five pretreatment processes for the liberation of sugars from corn stover are compared on a consistent basis. Each pretreatment process model was embedded in a full bioethanol facility model so that systematic effects for variations in pretreatment were accounted in the overall process. Economic drivers influenced by pretreatment are yield of both five and six carbon sugars, solids concentration, enzyme loading and hemicellulase activity.

All of the designs considered were projected to be capital intensive. Low cost pretreatment reactors are often counterbalanced by higher costs associated with pretreatment catalyst recovery or higher costs for ethanol product recovery. The result is
little differentiation between the projected economic performances of the pretreatment options.

**Keywords**

Pretreatment, Economics, Bioethanol

**Introduction**

Process engineering and economic analysis for the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) USDA Initiative for Future Agriculture and Food Systems (IFAFS) program were conducted via support from the U.S. Department of Energy’s Office of the Biomass Program. The material balance and technoeconomic models were developed early in the USDA IFAFS project for each pretreatment technology in collaboration with each CAFI researcher. Initially, these models were populated with either assumptions or data generated in previous work, if applicable. The models were updated throughout the course of the IFAFS project as process performance data was generated and thus provided important information for guiding the selection of experimental conditions and the interpretation of experimental results. A series of sensitivity cases were also developed for each pretreatment approach to identify the economic impact of sugar and ethanol yields, enzyme loading and cost, capital costs, and other relevant parameters. The details of the various sensitivity analyses are not covered in this paper, but have been provided to each CAFI researcher.

The data generated in the IFAFS project were primarily focused upon determining glucose and xylose sugar yields upon pretreatment and enzymatic hydrolysis using a standard cellulase loading. Less emphasis was placed on downstream process characterization and optimization, such as identifying improved enzyme preparations for each pretreatment or determination of conditioning requirements on hydrolyzates resulting
from each pretreatment to allow for efficient fermentation at process-relevant sugar concentrations. Therefore, this paper is focused on identifying the process economic impact of the different pretreatment approaches as related to capital and operating cost investment and baseline glucose and xylose sugar yields from each pretreatment.

**Methods**

An ASPEN Plus 10 (Aspen Technology, Inc., Cambridge, MA) simulation model was assembled for each pretreatment process using performance data supplied by each CAFI researcher. Appropriate pretreatment reactor design and materials of construction for each pretreatment technology were developed that are consistent with the pretreatment chemistry, corrosion potential, feedstock solids loading, and residence time. Any necessary pretreatment catalyst recovery and recycle equipment were also included in the process design. The designs are best characterized as conceptual since there is still quite a bit of uncertainty in process performance and optimal pretreatment process flowsheet configuration. This is especially true for any necessary pretreatment catalyst recovery and recycle systems.

Two additional pretreatment cases were considered. The first, called the “No Pretreatment” case, is the simple case in which the only action performed in pretreatment is dilution of the biomass feedstock to 20 wt% solids prior to enzymatic hydrolysis. Pretreatment related capital and operating costs were assumed to be zero. All yield in the no pretreatment case is attributable to enzymatic action on the native biomass (Lee, 2004).

The second additional case is called “Ideal Pretreatment”. Again the biomass feed is diluted to 20 wt% prior to hydrolysis, and zero capital and operating costs were assumed for pretreatment. However, in this case, the yield of glucose and xylose sugars after enzymatic hydrolysis were assumed to be 100% of theoretical.
Each pretreatment model was then inserted into an Aspen simulation of a full bioethanol production facility, shown in Figure 1. The 2001 NREL process engineering design case (Aden et. al., 2001) was used as the template for the full bioethanol facility. The model assumes a 2000 metric ton (dry) per day corn stover feed rate, which corresponds to nominally 50 MMgal/yr of ethanol production for the assumptions used in the models. Some variation from this nominal ethanol production rate is caused by yield differences among the different pretreatment approaches. Simultaneous saccharification and fermentation (SSF) is assumed with an enzyme loading of 15 FPU/g cellulose in untreated corn stover (58 mg protein/ g cellulose in untreated corn stover). Hydrolysis performance was assumed to be the same as the laboratory data using Spezyme CP (Lot 301-00348-257) (Genencor International Inc., Rochester, NY). An unspecified organism that is capable of metabolizing both monomeric xylose and monomeric glucose is assumed for fermentation.

The coproducts for most corn based ethanol facilities are animal feed ingredients. For example, corn dry mills typically produce DDGS while wet mills produce corn gluten feed, corn gluten meal, corn germ and other related coproducts. In contrast, for corn stover based facilities the recovered syrup and solids has limited feed value, so the model assumes this material is burnt and the heat released is used to raise process steam and electricity via a bottoming cycle.

The economic model consists of four parts: Capital Cost Estimate - The capital cost estimate is a factored estimate. To generate the capital costs, the process model is used to establish the flows for each major piece of equipment, the equipment is then sized using standard engineering methods, purchased costs are estimated using a combination of in-house methods and Questimate (Aspen
Technologies, Inc., Cambridge, MA). The total fixed capital then built by using standard factors for both directs and indirects.

Operating Cost Estimate - Variable operating costs are estimated using material balances from the process model. Corn stover pricing is assumed to be $35 per metric ton (dry) and represents a target price in a future process for which improvements in the costs of corn stover collection over currently available methods have been achieved. Enzyme pricing is assumed such that the total contribution of enzymes to production costs is about $0.15 per gallon of ethanol with some variation depending upon actual ethanol yields resulting from the particular pretreatment approach. Fixed operating costs are estimated from manpower, maintenance, insurance, etc. requirements of ethanol facilities of similar size.

Revenue Summary - Ethanol and electricity sales are the two revenue streams. Power generated in excess of plant needs is sold to the grid at an assumed price of $0.04 per kWh.

Discounted Cash Flow Calculations - The discounted cash flow calculations assume 2.5 years of construction, 0.5 years of start-up and 20 years of operations. 100% equity financing and no subsidy credits are assumed. Ethanol pricing is done on a rational pricing basis rather than a market pricing basis. In other words, this is a cost-plus type of analysis, so rather than comparing net present values we use Minimum Ethanol Selling Price (MESP) as a performance measure. Minimum Ethanol Selling Price is defined as the ethanol sales price required for a zero net present value for the project when the cash flows are discounted at 10% real-after tax.

Results and Discussion

Table 1 compares the capital costs for each case. The pretreatment area direct fixed capital for the dilute acid, AFEX, ARP, and lime cases are roughly the same. The contribution of the pretreatment reactor dominates pretreatment area cost for the dilute acid
case, whereas for AFEX, ARP and lime, other equipment items dominate, with the pretreatment reactor cost being significantly lower than for dilute acid. Much of this other equipment is related to recovery of the pretreatment catalyst, which is necessary in these processes because one-pass use of the catalyst is impractical. As previously mentioned, the design of the various catalyst recovery and recycle systems is very preliminary, which may lead to opportunities for development of more efficient recovery systems.

Pretreatment direct fixed capital for hot water is significantly lower than for the other cases. However, total capital for the hot water case is roughly in line with most of the other cases. This particular version of hot water pretreatment has limitations on the concentration of solids that can be processed during pretreatment. The result is a lower solids concentration in the feed to enzymatic hydrolysis, so all of the downstream equipment is larger for the hot water case to accommodate the increased water load.

Total capital for the lime case is significantly lower than other cases. The energy balance for this case is significantly different. The fermentation residues are burned to calcine calcium carbonate, converting it to lime for recycle in pretreatment. The calciner also generates steam for the plant, however, the amount of excess heat available after meeting the calciner and plant steam requirement is not enough to justify installation of power generation equipment. The lime case does not generate electricity, thus the reduction in total capital.

The last two columns of Table 1 compare yield and capital requirements per annual gallon of capacity. The no pretreatment case has extremely poor yield, giving a very high value for the total fixed capital per annual gallon of capacity. All of the actual pretreatment cases show higher yield and lower capital requirements per annual gallon of capacity as compared to the no pretreatment case. However, all of the cases including the ideal
pretreatment case appear to be capital intensive. As a comparison, today’s new generation of ethanol plant based on corn dry milling technology have capital investment requirements of $1.00-1.50 per gallon of annual capacity (BBI International, 2003). While capital investment for a lignocellulose-to-ethanol plant may not need to be quite as low as for a corn dry mill due to the lower expected feedstock cost for a lignocellulose plant, significant capital investment improvements for processes based upon any of these pretreatment approaches are needed.

Figure 2 presents a breakdown of capital investment for the dilute acid case. Total fixed capital includes both directs and indirects. The indirect costs are factored off the directs, so it is only necessary to examine the direct costs in more detail. The pretreatment, fermentation (including enzymatic hydrolysis), and recovery sections of the plant are responsible for slightly less than half of the total direct fixed capital. The steam and power system is responsible for about one-third of total direct fixed capital.

With the exception of the lime case discussed earlier, the models assume a circulating fluidized bed boiler is used to combust insoluble lignin-rich residues to generate high pressure steam (8.62 kPa = 1250 psig, 510 °C = 950 °F), which is let down across a condensing turbine system to produce electricity. These systems are quite expensive. By comparison, today’s dry mills often install low-cost natural gas boilers that only produce low pressure steam and purchase all electricity needs from the grid.

There are at least three reasons why bioethanol facilities are projected to be capital intensive when compared to dry mills. First, bioethanol facilities have to spend a significant amount of capital on pretreatment, which is not required in dry mills. Second, bioethanol facilities have to find an acceptable home for the lignin and other fermentation residues. Usually it is assumed that these are burned to produce steam and electricity,
which is a capital intensive option. By comparison, the fermentation residues for dry mills are usually processed into animal feeds and much simpler steam and power systems are installed. Third, the concentration of ethanol in the fermentation broth is projected to be low (4-5 wt% vs. 10-12 wt% for a corn dry mill), so larger equipment is needed for the same production rate.

Figure 3 compares the plant level cash costs and MESP across the pretreatment cases using the fourth year of operation as the proof year. The no pretreatment case is not displayed since the cash costs ($2.43 per gal) and MESP ($6.45 per gal) would distort the graph.

The plant level cash cost is also the same as the lowest ethanol price at which the plant will stay operational, even though the plant would be losing money at these market conditions. As such, it defines the competitive position of the proposed facility within the existing ethanol market. In this analysis, cash cost is comprised by three components: net stover, other variable costs, and fixed costs without depreciation. Net stover, by analogy with the net corn concept used in corn processing, is defined as the cost of stover feedstock less the value of the electricity coproduct. Other variable costs accounts for the cost of enzymes, chemicals, etc. in which the quantities required are tied to the plant production rate. Fixed costs include labor, maintenance, insurance, and other costs not tied to production rate. Projected cash costs range from $0.54 per gallon for the ideal pretreatment case to $1.05 for lime pretreatment. The projected cost for the lime case is higher than the others because this case imports electricity, giving a large net stover contribution.

The MESP includes additional charges related to depreciation, income taxes and return on capital. The ideal pretreatment case has an MESP of $0.99 per gallon, while the other cases range from $1.34 to $1.67 per gallon. The gap between the ideal pretreatment
and the other cases is measure of how much improvement could ideally be obtained by future R&D efforts focused just on pretreatment.

A closer look at the models shows that MESP is sensitive to yield of ethanol from both five and six carbon sugars present in the starting biomass. Table 2 compares of both oligomeric and monomer xylose and glucose for the pretreatment. It is important underscore that the values shown previously in Figure 3 assumed only conversion of monomer sugars to ethanol.

Looking at the glucose data in Table 2, we see that after hydrolysis almost all of the soluble sugars are present in the monomeric form. However, the xylose data in Table 2 shows that as pH of the pretreatment increases, the amount of soluble xylose in the form of oligomers becomes significant. It is possible that an increase in the xylanase activity of the enzyme preparation used for hydrolysis could be done at little additional enzyme cost. Figure 4 shows the changes in the resulting MESP’s under the assumption that all soluble xylose and glucose sugars, both monomeric and oligomeric, contribute to ethanol production at no additional cost than for the baseline cellulase loading. The result is that there is very little economic differentiation between the pretreatment options after customizing the enzyme formulations to the needs of the process in this manner.

**Conclusions**

The pretreatment processes were compared on a consistent basis. Each pretreatment process model was embedded in a full facility model so that systematic effects for variations in pretreatment were accounted in the overall process. Economic drivers influenced by pretreatment are yield of both five and six carbon sugars, solids concentration, enzyme loading and hemicellulase activity.
All of the designs considered were projected to be capital intensive. Low cost pretreatment reactors are often counterbalanced by higher costs associated with pretreatment catalyst recovery or higher costs for ethanol product recovery. The result is little differentiation between the projected economic performances of the pretreatment options. This is especially true when credit is taken for availability of the oligomer sugars generated in the non-acidic pretreatment processes.

The designs generated during this study are best characterized as conceptual. Their accuracy is sufficient to guide research but should not be taken as a basis for an actual construction project. Improved rigor is needed in pretreatment catalyst recovery system design and costing. Low cost methods for conversion of xylose oligomers need to be implemented, and additional fermentability testing of the hydrolyzates at reasonable sugar concentrations is needed.

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References


Total Fixed

Direct Fixed

- Enzymes
- CO₂
- Water

Hydrolysis + Fermentation

- Pretreatment
- Fermentation
- Recovery

Recovery

- Water Treatment
- EtOH

Stover

- Syrup + Solids
- Chemicals
- Water
- CO₂
- Water

Dilute Acid

|$MM|

Direct
Indirect
Start-Up & Contingency
Total Fixed Capital

128.1
57.7
22.8
208.6
Figure Captions

Figure 1 – Block Flow Diagram for Bioethanol Facility

Figure 2 – Breakdown of Capital Costs for Dilute Acid Pretreatment Case

Figure 3 – Cash Costs and MESP Comparison

Figure 4 – Effect of Oligomer Credit
<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Pretreatment Direct Fixed Capital, $MM</th>
<th>Pretreatment Breakdown, % Reactor / % Other</th>
<th>Total Fixed Capital, $MM</th>
<th>Ethanol Production, MMgal/yr</th>
<th>Total Fixed Capital, $/gal Annual Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute Acid</td>
<td>25.0</td>
<td>64 / 36</td>
<td>208.6</td>
<td>56.1</td>
<td>3.72</td>
</tr>
<tr>
<td>Hot Water</td>
<td>4.5</td>
<td>100 / 0</td>
<td>200.9</td>
<td>44.0</td>
<td>4.57</td>
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<tr>
<td>AFEX</td>
<td>25.7</td>
<td>26 / 74</td>
<td>211.5</td>
<td>56.8</td>
<td>3.72</td>
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<tr>
<td>ARP</td>
<td>28.3</td>
<td>25 / 75</td>
<td>210.9</td>
<td>46.3</td>
<td>4.56</td>
</tr>
<tr>
<td>Lime</td>
<td>22.3</td>
<td>19 / 81</td>
<td>163.6</td>
<td>48.9</td>
<td>3.35</td>
</tr>
<tr>
<td>No Pretreatment</td>
<td>0</td>
<td>-</td>
<td>200.3</td>
<td>9.0</td>
<td>22.26</td>
</tr>
<tr>
<td>Ideal Pretreatment</td>
<td>0</td>
<td>-</td>
<td>162.5</td>
<td>64.7</td>
<td>2.51</td>
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</tbody>
</table>
Table 2 – Yield Comparison

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Conditions</th>
<th>Xylose Yields, % of Theoretical* After Pretreatment</th>
<th>Glucose Yields, % of Theoretical* After Pretreatment</th>
<th>Xylose Yields, % of Theoretical* After Enzymatic Hydrolysis</th>
<th>Glucose Yields, % of Theoretical* After Enzymatic Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute Acid</td>
<td>1 wt% Acid, 140 °C</td>
<td>90.2 / 89.7</td>
<td>8.0 / 7.5</td>
<td>95.6 / 95.1</td>
<td>85.1 / 84.6</td>
</tr>
<tr>
<td>Hot Water</td>
<td>13.9 wt% Solids, 180 °C</td>
<td>50.8 / 7.3</td>
<td>4.5 / 2.0</td>
<td>81.8 / 38.3</td>
<td>90.5 / 88.0</td>
</tr>
<tr>
<td>AFEX</td>
<td>Stover:NH₃:H₂O = 1:1:0.6 (weight), 90 °C</td>
<td>0 / 0</td>
<td>0 / 0</td>
<td>92.7 / 77.6</td>
<td>95.9</td>
</tr>
<tr>
<td>ARP</td>
<td>Liquid Loading = 3.185 g/g Stover, 170 °C</td>
<td>47.2 / 0</td>
<td>1.4</td>
<td>88.3 / 41.1</td>
<td>90.1</td>
</tr>
<tr>
<td>Lime</td>
<td>Lime = 0.08 g as CaO/g Stover, 55 °C</td>
<td>24.3 / 0.8</td>
<td>1.6 / 0.5</td>
<td>75.3 / 51.8</td>
<td>92.4 / 91.3</td>
</tr>
<tr>
<td>No Pretreatment</td>
<td>-</td>
<td>0</td>
<td>8.5</td>
<td>0</td>
<td>15.7</td>
</tr>
<tr>
<td>Ideal Pretreatment</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

*Cumulative soluble sugars as (oligomers+monomers) / monomers. Single number = just monomers.