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Process and economic analysis of pretreatment technologies

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Abstract

Five pretreatment processes (dilute acid, hot water, ammonia fiber explosion (AFEX), ammonia recycle percolation (ARP), and lime) 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 in some pretreatment processes 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. Additional process performance data, especially involving the identification of optimal enzyme blends for each pretreatment approach and conditioning requirements of hydrolyzates at process-relevant sugar concentrations resulting from each pretreatment may lead to greater differentiation in projected process economics.

Keywords: Pretreatment; Economics; Bioethanol

1. 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 US 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

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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.

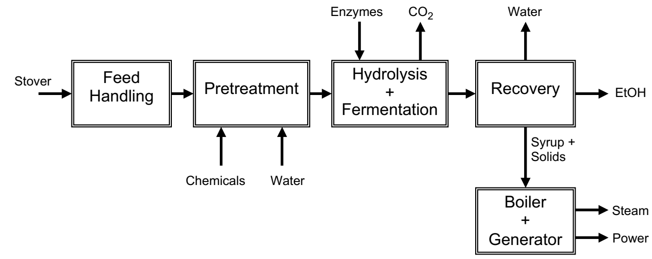


Fig. 1. Block flow diagram for bioethanol facility.

2. 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. Detailed descriptions for each pretreatment process can be found in this volume (Kim and Lee, 2005; Teymouri et al., 2005; Mosier et al., 2005; Lloyd and Wyman, 2005; Kim and Holtzapple, 2005). 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 Fig. 1. The 2001 NREL process engineering design case (Aden and Ruth, 2001), less the pretreatment section, 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). The 15 FPU/g cellulose loading was chosen as a standard loading throughout the experimental work performed by the CAFI group.

Hydrolysis performance was assumed to be the same as the laboratory results 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 burned 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, and 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/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/gal of ethanol with some variation depending upon actual ethanol yields resulting from the particular pretreatment approach. This enzyme price does not reflect current commercial enzyme prices but instead is a reasonable estimate of the contribution of enzymes to the operating costs for future lignocellulosic based biorefineries. 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/kW h.

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. One hundred percent 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.

3. 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 pretreatment 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.

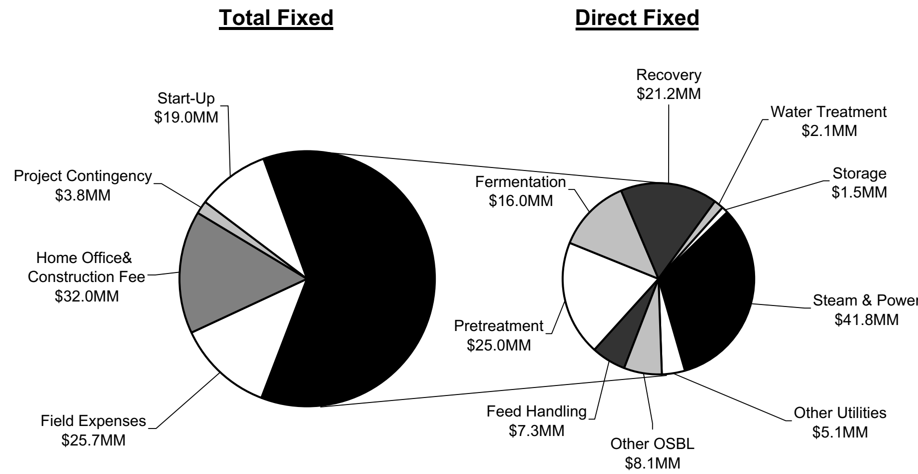
Total capital for the lime case is significantly lower than other cases. The energy balance for this case is significantly different. The fermentation residues are burned to calcine calcium carbonate, converting it to lime for recycle in pretreatment. The calciner also generates steam for the plant, 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/gal 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.

Fig. 2 presents a breakdown of capital investment using the dilute acid case as an example. 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

Table 1
Capital costs

	Pretreatment direct fixed capital, $MM	Pretreatment breakdown, % Reactor/% other	Total fixed capital, $MM	Ethanol production, MMgal/yr	Total fixed capital, $/gal annual capacity
Dilute acid	25.0	64/36	208.6	56.1	3.72
Hot water	4.5	100/0	200.9	44.0	4.57
AFEX	25.7	26/74	211.5	56.8	3.72
ARP	28.3	25/75	210.9	46.3	4.56
Lime	22.3	19/81	163.6	48.9	3.35
No pretreatment	0	–	200.3	9.0	22.26
Ideal pretreatment	0	–	162.5	64.7	2.51



Dilute Acid

	$MM
Direct	128.1
Indirect	57.7
Start-Up & Contingency	22.8
Total Fixed Capital	208.6

Fig. 2. Breakdown of capital costs for dilute acid pretreatment case.

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.

Fig. 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/gal) and MESP ($6.45/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

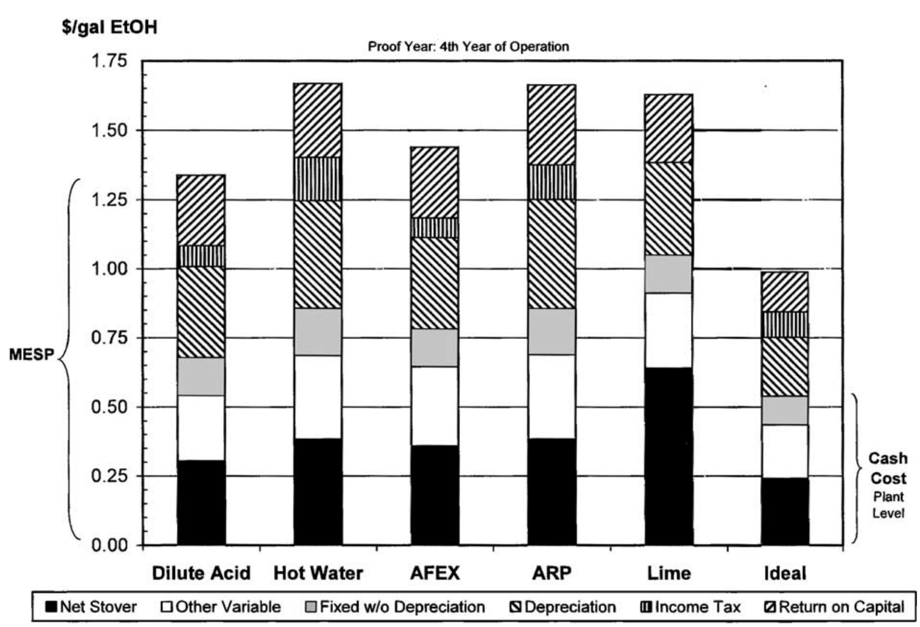


Fig. 3. Cash costs and MESP comparison.

Table 2
Yields

Pretreatment	Xylose yields, % of theoretical[a]		Glucose yields, % of theoretical[a]	
	After pretreatment	After enzymatic hydrolysis	After pretreatment	After enzymatic hydrolysis
Dilute acid	90.2/89.7	95.6/95.1	8.0/7.5	85.1/84.6
Hot water	50.8/7.3	81.8/38.3	4.5/2.0	90.5/88.0
AFEX	0/0	92.7/77.6	0/0	95.9
ARP	47.2/0	88.3/41.1	1.4	90.1
Lime	24.3/0.8	75.3/51.8	1.6/0.5	92.4/91.3
No pretreatment	0	8.5	0	15.7
Ideal pretreatment	–	100	–	100

[a] Cumulative soluble sugars as (oligomers + monomers)/monomers. Single number = just monomers.

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/gal 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/gal, while the other cases range from \$1.34 to \$1.67/gal. 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.

The lime pretreatment case has zero income tax in the chosen proof year. The main reason for this is that the lime kiln, which also produces steam for the facility, was classified as a piece of process equipment rather than a power generation system for depreciation purposes. The economic model assumes general process equipment is depreciated using the Modified Accelerated Cost Recovery System (MACRS) method with a seven year class life, while power systems are depreciated using the MACRS method with a 20 year class life. Classifying the lime kiln as a piece of process equipment gives a faster rate of depreciation, which in turn delays the start of income taxes in the cash flow calculations.

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 Fig. 3 assumed only conversion of monomer sugars to ethanol.

Looking at the glucose data in Table 2 we see that after enzymatic 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

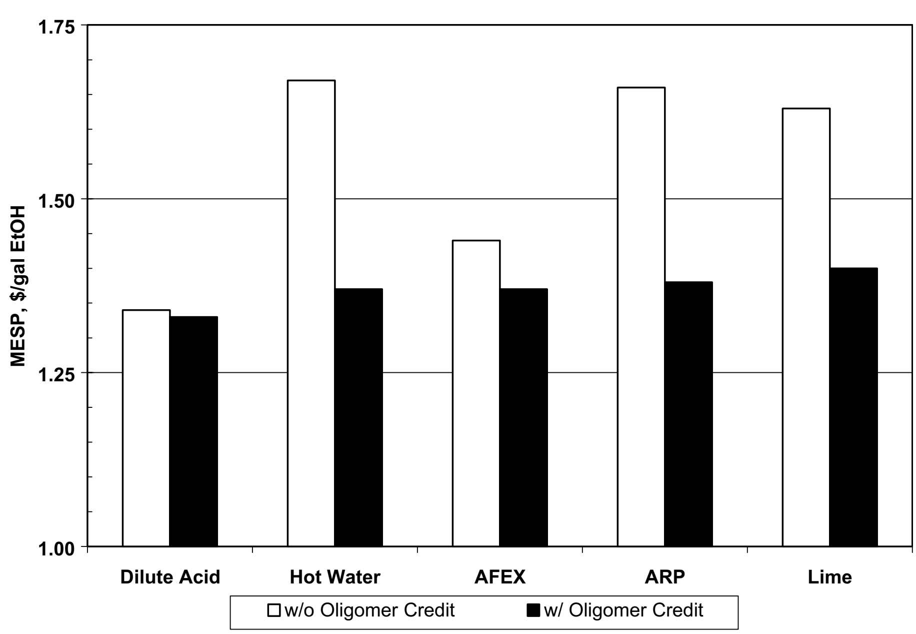


Fig. 4. Effect of oligomer credit.

Table 3
Energy usage

Pretreatment	Pretreatment conditions	Pretreatment effluent, wt% liquid	Fermentation beer, wt% of ethanol in liquid	Process steam usage			Electrical power	
				HP steam, kg/h	LP steam, kg/h	VLP steam, kg/h	Total generated, MWe	Process needs, MWe
Dilute acid	1 wt% acid, 140 °C	66.8	5.07	14,663	83,377	16,426	42.1	14.0
Hot water	13.9 wt% insolubles, 180 °C	83.7	3.09	34,281	146,580	48,374	42.2	13.5
AFEX	Stover:NH_3:H_2O = 1:1:0.6 (weight), 90 °C	61.2	4.62	0	154,980	31,932	35.6	17.4
ARP	Liquid loading = 3.185 g/g stover, 170 °C	74.5	5.06	112,330	56,972	11,469	38.0	11.9
Lime	Lime = 0.08 g as CaO/g stover, 55 °C	80.0	3.16	0	160,540	42,265	0	14.4
No pretreatment	–	80.0	0.92	0	59,697	51,477	88.8	13.9
Ideal pretreatment	–	80.0	5.86	0	71,230	20,160	45.2	32.4

an increase in the xylanase activity of the enzyme preparation used for hydrolysis could be done at little additional enzyme cost, but this has not been fully demonstrated. Fig. 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.

Solvent loading in pretreatment, whether the solvent is water or some other chemical, is an important model parameter since it affects the overall plant energy balance and capital costs for fermentation and downstream recovery equipment. Table 3 shows the solvent loadings assumed for each pretreatment, the concentration of ethanol in the beer, the plant steam usage, and the plant power balance. HP steam is supplied at 1317 kPa and 268.2 °C; LP steam is supplied at 448 kPa and 163.5 °C; VLP steam is supplied at 170 kPa and 115.2 °C. Fig. 5 shows the total process steam usage is proportional to the solvent concentration in the pretreatment reactor effluent, not counting the special cases (i.e. no pretreatment and ideal pretreatment).

4. 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

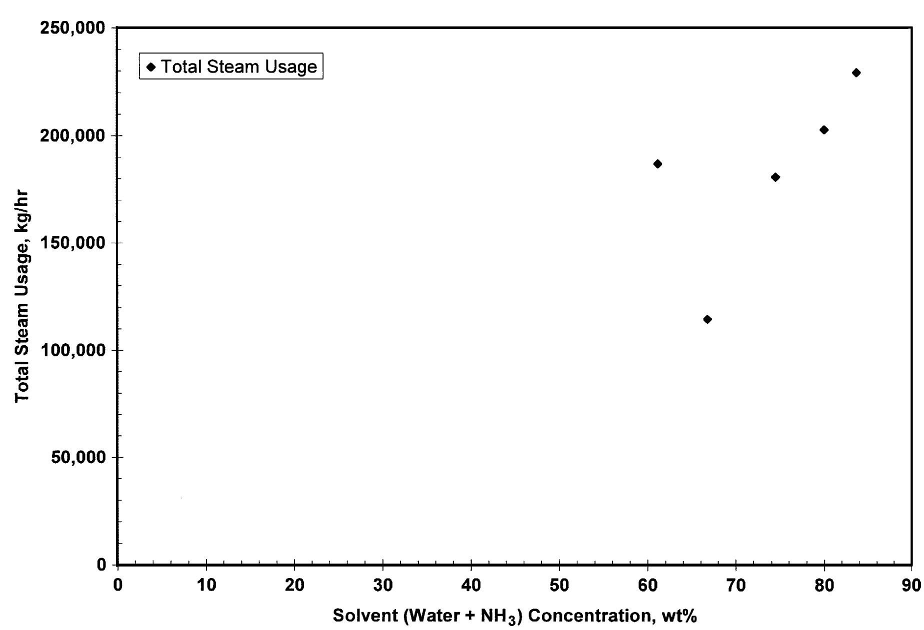


Fig. 5. Effect of solvent loading in pretreatment on process steam usage.

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. No differentiation was made for variations in the state of development between the pretreatments. It is not completely fair to made economic comparisons between the pretreatment options without additional financial modeling since there is a wide range in the current state of development. A real options analysis (Glantz, 2000) that uses the discounted cash flow results of this work as one of the inputs is one way to formally adjust for the differences in state of development. Real option analyses could also be formulated to formally handle other less tangible issues such as differences in process complexity and reliability, differing potential for creating environmental and safety issues, etc.

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