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Modeling of Carbonic Acid Pretreatment Process Using ASPEN-Plus®

KEMANTHA JAYAWARDHANA AND G. PETER VAN WALSUM*

Department of Environmental Studies, Baylor University,
PO Box 97266, Waco, TX 76798-7266,
E-mail: gpeter_van_walsum@baylor.edu

Abstract

ASPEN-Plus® process modeling software is used to model carbonic acid pretreatment of biomass. ASPEN-Plus was used because of the thorough treatment of thermodynamic interactions and its status as a widely accepted process simulator. Because most of the physical property data for many of the key components used in the simulation of pretreatment processes are not available in the standard ASPEN-Plus property databases, values from an in-house database (INHSPCD) developed by the National Renewable Energy Laboratory were used. The standard non-random-two-liquid (NRTL) or renon route was used as the main property method because of the need to distill ethanol and to handle dissolved gases. The pretreatment reactor was modeled as a "black box" stoichiometric reactor owing to the unavailability of reaction kinetics. The ASPEN-Plus model was used to calculate the process equipment costs, power requirements, and heating and cooling loads. Equipment costs were derived from published modeling studies. Wall thickness calculations were used to predict construction costs for the high-pressure pretreatment reactor. Published laboratory data were used to determine a suitable severity range for the operation of the carbonic acid reactor. The results indicate that combined capital and operating costs of the carbonic acid system are slightly higher than an H_2SO_4-based system and highly sensitive to reactor pressure and solids concentration.

Index Entries: Acid pretreatment; carbonic acid; ASPEN-Plus model; alcohol fuels; biomass.

Introduction

Computer-aided design and simulation gives the process engineer the ability to evaluate more design alternatives in more detail than was

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*Author to whom all correspondence and reprint requests should be addressed.

possible by hand calculations. Simulation, as used in this article, refers to the creation of a mathematical model or representation of a chemical process. ASPEN-Plus® (Aspen Technologies, Cambridge, MA) software is used to model biomass conversion processes at the Department of Environmental Studies at Baylor University. It is capable of solving steady-state material and energy balances, calculating phase equilibria, and estimating physical properties for thousands of chemical compounds. It can also estimate capital costs of equipment. Originally developed for the Department of Energy (DOE) by the Massachusetts Institute of Technology in 1987, ASPEN-Plus required the user to write an input file containing process specifications. More recent versions of ASPEN-Plus incorporate a graphical user interface, making the simulation software more user friendly.

Although ASPEN-Plus is widely used to simulate petrochemical processes, its uses for modeling biomass processes are limited owing to the limited availability of physical properties that best describe biomass components such as cellulose, xylan, and lignin. For example, Lynd et al. *(1)* used conventional methods to calculate the economic viability of a biomass-to-ethanol process. However, with the development by the National Renewable Energy Laboratory (NREL) of an ASPEN-Plus physical property database for biofuels components, modified versions of ASPEN-Plus software can now be used to model biomass processes *(2)*. Wooley et al. *(3)* used ASPEN-Plus simulation software to calculate equipment and energy costs for an entire biomass-to-ethanol process that made use of dilute-H_2SO_4 acid pretreatment.

Carbonic acid has been proposed as an alternative to dilute sulfuric acid for biomass pretreatment. Proposed advantages of carbonic acid include reduced cost of materials owing to less corrosive conditions and reduced costs associated with the neutralization of H_2SO_4 and consequent disposal of calcium sulfate *(4)*. Recent laboratory studies on carbonic acid have shown that it can enhance hydrolysis of xylan compared to liquid hot water pretreatment, but that hydrolysis falls short of the normal performance range for dilute H_2SO_4 *(4,5)*. Studies on aspen wood have shown little advantage of carbonic acid over liquid hot water pretreatment *(6,7)*, whereas a study on corn stover did show elevated hydrolysis compared to liquid hot water *(8)*. A study conducted by Puri and Mamers *(9)* reported enhanced enzymatic hydrolysis following CO_2-pressurized steam explosion. The central hypothesis of the present study is that reduced metallurgy and waste disposal costs for carbonic acid pretreatment will result in a negative incremental cost for the carbonic acid pretreatment process compared to the H_2SO_4 process. In other words, it is hypothesized that the reduced corrosivity and neutralization requirements for the carbonic acid system will result in cost savings compared to the H_2SO_4 process. Because carbonic acid pretreatment has not been investigated or optimized to the extent achieved with dilute H_2SO_4, conversion effectiveness and final ethanol yield are not factored into this comparison.

Method

Process Design and Simulation

The process flow diagram (PFD) was developed by selecting all the necessary unit operation blocks from the ASPEN-Plus model library. Once the PFD was sketched out, ASPEN-Plus software was used to build the process model. Figure 1 depicts the carbonic acid pretreatment process flowsheet generated by ASPEN-Plus. The reactor (B1) in this pretreatment process was modeled as a stoichiometric reactor (RSTOIC), since kinetic data for many of the pretreatment reactions were not available. RSTOIC models a reactor when stoichiometry and conversion are known but kinetics are unknown or unimportant. It can also perform product selectivity and heat of reaction calculations. Laboratory investigations carried out at the Department of Environmental Studies at Baylor University showed that a pressure of 2000 psi and reaction severity conditions (as defined by Overend and Chornet *[10]*) on the order of Log(R_o) = 4.2 would produce an effective pretreatment for aspen wood *(7)*. CO_2 compression to 2000 psi is difficult and expensive to implement in commercial scale; therefore, the process was modified to inject the CO_2 into the biomass and water stream (stream no. 4) at a lower temperature (28°C) and pressure (800 psi). The lower temperature increases the solubility of CO_2 in water and requires a pressure of only 800 psi to deliver sufficient CO_2 into the pretreatment reactor. Hence, the compression duty was lowered by a factor of 2.5. To raise the CO_2 pressure from 1 atm (14.7 psi) to 800 psi, a multistage compressor (B13) was used. Stream no. 1, which contains biomass and water, was pressurized to 800 psi using pump B7. The mixing of CO_2 into stream no. 4 (biomass and water at 800 psi) was carried out using an in-line CO_2 mixer (B8). The mixer model in ASPEN-Plus determines the combined outlet stream temperature and phase conditions by performing an adiabatic-phase equilibrium flash calculation on the composite feed streams. A heat exchanger (B11) was employed to preheat the incoming stream using the filtrate (stream no. 16) from a Pneumapress filter (B10) as heat source. Then, the preheated stream no. 5 was pressurized to 2000 psi using pump B12. Heater B9 was employed to further heat stream no. 12 to 220°C. In this manner, high pressure in the pretreatment reactor (B1) was maintained, and the carbonic acid feed was delivered in a liquid state, eliminating the need for compression of gaseous CO_2 to 2000 psi.

The product stream from the reactor (B1) was flash cooled using a flash drum (B3) to separate vapors from the liquid phase. The flash models available in ASPEN-Plus determine the thermal and phase conditions of a mixture with one or more inlet streams. A separator (B6) was employed to separate CO_2 and steam. The resulting recycle streams no. 10 and no. 9 were sent to B13 and B7, respectively. The liquid stream (no. 14) from the flash drum was sent to a Pneumapress filter (B10), where it was separated into filter cake (stream no. 13) and filtrate (stream no. 8). This separation was done to facilitate heat extraction from the product stream for heat exchanger B11.

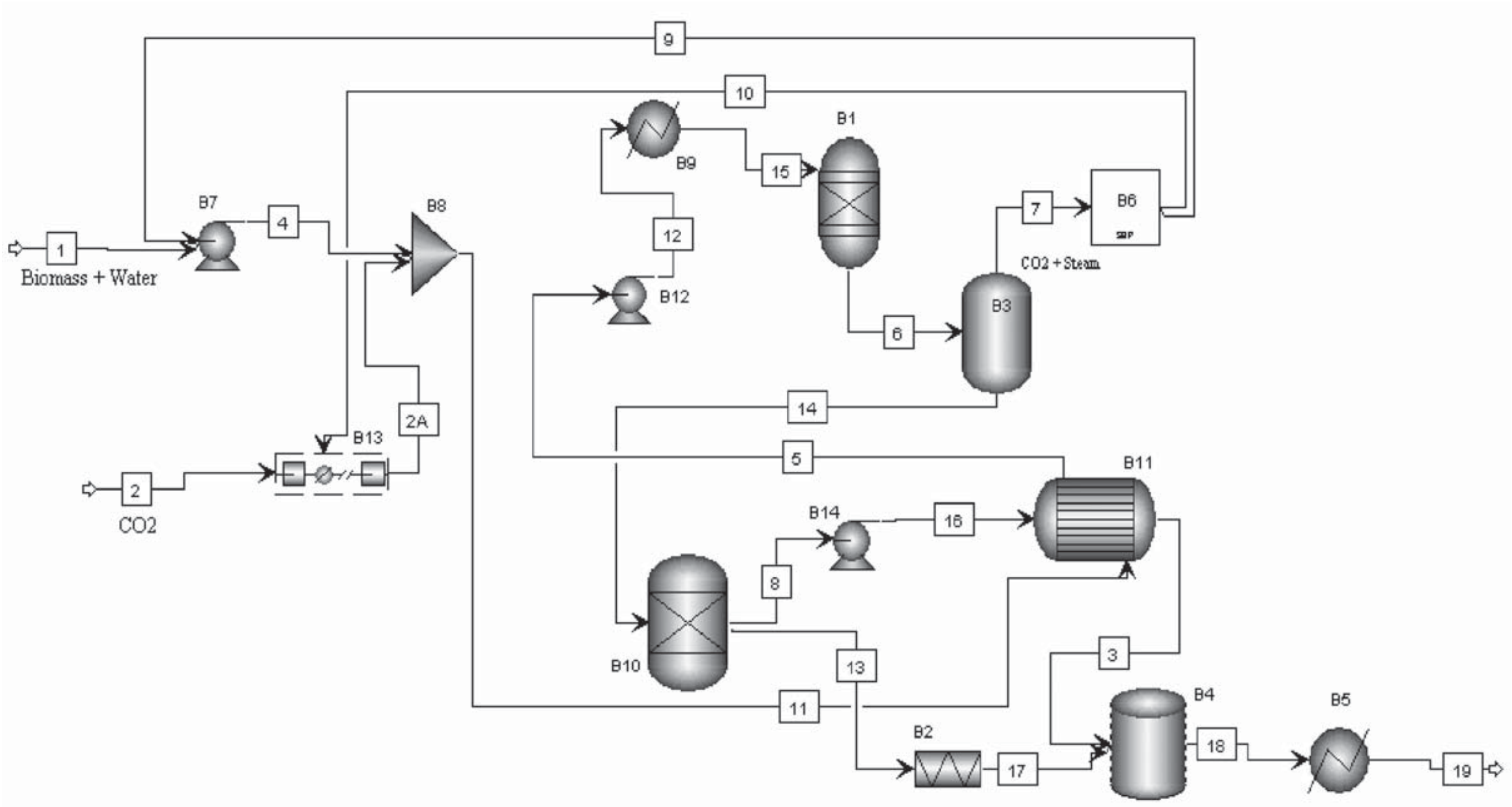

Fig. 1. ASPEN-Plus PFD of carbonic acid pretreatment process as analyzed in this study. B1, pretreatment reactor (Rstoic); B2, screw mixer; B3, blowdown tank and screw conveyor; B4, slurrying tank and tank agitator; B5, cooler; B6, reflux drum and condenser; B7, feed pump; B8, in-line CO_2 mixer; B9, heater; B10, pneumapress filter; B11, heat exchanger; B12, loading pump; B13, CO_2 compressor; B14, primary filtrate pump.

To minimize the pressure differential across the heat exchange surfaces in B11, stream no. 8 was pressurized to 800 psi using pump B14. The filter cake was sent to a mixing tank (B4) through a screw conveyor (B2). At the mixing tank B4, filtrate and cake were thoroughly mixed in order to obtain a slurry. This product slurry was cooled using a cooler (B5) before being sent on to the next stage of the biomass conversion process.

Component Data and Databases

Physical property data for many of the key components used in the simulation for the ethanol-from-lignocellulose process are not available in the standard ASPEN-Plus property databases *(11)*. Indeed, many of the properties necessary to successfully simulate this process are not available in the standard biomass literature. The physical properties required by ASPEN-Plus are calculated from fundamental properties such as liquid, vapor, and solid enthalpies and density. In general, because of the need to distill ethanol and to handle dissolved gases, the standard nonrandom two-liquid (NRTL) or renon route is used. This route, which includes the NRTL liquid activity coefficient model, Henry's law for the dissolved gases, and Redlich-Kwong-Soave equation of state for the vapor phase, is used to calculate properties for components in the liquid and vapor phases. It also uses the ideal gas at 25°C as the standard reference state, thus requiring the heat of formation at these conditions.

Inputs and Basis

After careful investigation of the NREL model, the scale for the carbonic acid model was selected to be 2000 dry metric t/d of biomass. This number represents a scale that would have an economically feasible collection distance for biomass *(3)*.

Biomass: 2000 dry t/d = 2,000,000 dry kg/d = 83,333 dry kg/h.

Moisture content at 52% dry solids = 76,923 kg of water/h.

Total feed = 160,256 kg moist biomass/h.

The composition of poplar wood was used as a model for the feedstock composition; however, as used in this simulation, the poplar is modeled as consisting of only cellulose, xylan, and lignin, with compositions of 49.47, 27.26, and 23.27%, respectively. Laboratory results for carbonic acid pretreatment are relatively scarce, so for the purpose of this comparative study, stoichiometry of pretreatment reactions was assumed to be equal to those used in the comparison model *(3)*: cellulose conversion to glucose; 6.5%; xylan conversion to xylose; 75; and lignins solubilized; 5%. Thus, economic comparisons made with this model assess different equipment and operating costs but not product yields. For the successful convergence of the carbonic acid model, the simulation required initial specification of several variables. These variables included initial estimates for stream variables and inputs for the unit operation blocks.

Results and Discussion

An ASPEN-Plus model was used to calculate the heat and energy demands of the process units. Simulation results were generated for 15 different pretreatment conditions, consisting of a full factorial design comprising three temperatures (180, 200, and 220°C) and five pressures (800, 1000, 1200, 1600, and 2000 psi). Then, equipment and energy costs were calculated in 2001 US $. For each set of parameters, a corresponding material and energy balance sheet was generated by the ASPEN-Plus software.

Calculation of Reactor Wall Thickness

The use of carbonic acid for pretreatment results in mild acidity inside the pretreatment reactor, with pH in the range of 3.5–4.0 *(4,8)*. Owing to this only moderately corrosive environment, fabrication of pretreatment reactors could be carried out using commonly used metal alloys. In the present study, it is assumed that pretreatment reactors are fabricated using stainless steel 316 L (SS316), which has been found to stand up well in laboratory experiments on carbonic acid.

Pretreatment reactor residence time was varied from 2 to 10 min, and the corresponding reactor sizes and wall thicknesses were calculated for all the pretreatment conditions (i.e., from 800 psi, 180°C to 2000 psi, 220°C).

The thickness of the reactor walls can be calculated using Eq. 1 *(12)*:

$$t = P \times R/(S \times E - 0.6 \times P) \tag{1}$$

in which t is the reactor wall thickness (in.); R is the radius of the reactor (in.); P is the pressure of the reactor (psi); S is the maximum allowable stress (psi); and E is the joint efficiency, set to 0.85 *(12)*.

As can be seen from Eq. 1, increasing the radius will proportionately increase the required thickness of the reactor walls. To accommodate the large quantity of biomass flowing through the system, the use of a single reactor would necessitate a very large reactor, with a correspondingly large diameter. This increases the thickness of the reactor walls, making it difficult and expensive to build the reactor. The use of several smaller reactors in parallel can be a more economically feasible method, because it diminishes the wall thickness and total amount of metal needed. However, the use of multiple reactors will multiply the requirements for auxiliary equipment and process control instrumentation. By optimizing between the cost of a single large, expensive reactor and multiple parallel units, the optimum number of reactors for the pretreatment process was determined to be three. For 12-m-long reactors with 10% headspace and a pretreatment residence time of 4 min, the required reactor radius is 0.376 m. Wall thickness and cost for these reactors were calculated for different conditions of temperature and pressure and are presented in Table 1; for comparison, the conditions of the single NREL model reactor, at the pressure of saturated water at 190°C (representative of dilute H_2SO_4 pretreatment), is included.

NREL reported that the pretreatment reactor built using Hastelloy C would cost $2,505,084, which is 50% more expensive than to build with

Table 1
Reactor Wall Thickness and Cost Calculation
at Different Pretreatment Conditions (Residence Time: 4 min)

Parameter	R_D (m)	S	Wall thickness (m)	Material volume (m^3)	Original price (2000 US$)
CO2 model (3 needed)					
2000 psi, 220°C	0.376	13,080	0.07587	2.153	4,846,878
2000 psi, 200°C	0.376	13,342	0.07421	2.105	4,740,436
2000 psi, 180°C	0.376	13,846	0.07120	2.020	4,548,291
1600 psi, 220°C	0.376	13,080	0.05927	1.681	3,785,890
1600 psi, 200°C	0.376	13,342	0.05799	1.645	3,704,670
1600 psi, 180°C	0.376	13,846	0.05570	1.580	3,557,842
1200 psi, 220°C	0.376	13,080	0.04342	1.232	2,773,880
1200 psi, 200°C	0.376	13,342	0.04251	1.206	2,715,716
1200 psi, 180°C	0.376	13,846	0.04086	1.159	2,610,421
NREL reactor (1 needed)					
179 psi, 190°C	0.7933	13,594	0.0124	0.742	1,670,056

SS316 *(3)*. The same reactor design built of SS316 would cost only $1,670,056 (2000 US$). Reactor costs for carbonic acid pretreatment were calculated by using the reactor wall thickness to determine the volume of metal required to meet the demands of various temperature and pressure conditions. The material volume for fabrication of the reactor was calculated using Eq. 2:

$$V = 2 \times \pi \times R \times h \times t \tag{2}$$

in which V is the volume of metal in the reactor (m^3), R the radius (m), h the reactor height (m), and t is the wall thickness (m). With these data, reactor cost can be calculated for different pretreatment conditions as given in Table 1.

Calculation of Equipment Cost

The equipment requirements were determined from the ASPEN-Plus model. The quantity and size of each piece of equipment was determined on the basis of the mass flow rate through the equipment. From the thickness calculations, it was found that three reactors were optimal to accommodate a mass flow rate of 83,333 dry kg/h. It was also found that the solids concentration of the pretreated material made it necessary to use more than one Pneumapress filter.

The installation and scaling factors were taken from the NREL modeling report *(3)*. For the reactor, the installation factor was taken as 1.7, which is appropriate when SS316 is used as the material of construction *(3)*. Table 2 lists equipment costs for this scenario at 2000 psi, 220°C, and 4-min residence time. Equipment costs were obtained from vendor quotations when possible; however, the majority of the equipment costs were derived from NREL's economic model *(3)*.

Table 2
Equipment Cost for Carbonic Acid Pretreatment Process (2000 psi, 220°C, 4 min)

Equip no.	Qty. required (spare)	Equipment name	Scaling stream	Stream flow (kg/h)	Scale exp.	Inst'n factor	Installed cost (2001 US$)
B8	1	In-line CO_2 mixer	11	208,280	0.48	1	2951
B7	1 (1)	Feed pump	4	203,879	0.7	2.8	235,516
B12	1 (1)	Loading pump	5	208,280	0.7	2.8	239,064
B3	1	Blowdown tank	6	208,280	0.93	1.2	61,924
B3	1	Screw conveyor	14	160,401	0.78	1.3	60,810
B10	3	Pneumapress filter	SLD 14	62,647	0.6	1.05	5,694,196
B14	1 (1)	Primary filtrate pump	8	97,012	0.79	3.56	178,184
B11	1 (1)	Heat exchanger	Area/ft^2	6805	0.68	2.1	377,755
B13	1 (1)	CO_2 compressor	2A	4401	0.34	1.3	253,336
B9	1 (1)	Heater	Duty (cal/s)	3,890,560	0.68	2.1	428,191
B2	1	Screw conveyor	17	63,390	0.78	1.3	29,477
B4	1	Tank agitator	18	160,401	0.51	1.2	29,394
B4	1	Slurrying tank	18	160,401	0.71	1.2	31,138
B5	1 (1)	Cooler	Duty (cal/s)	2,185,707	0.68	2.1	524,086
B1	3	Reactor	15		1	1.7	24,869,613
B6	1	Separator (condenser)	Duty (cal/s)	5,556,935	0.68	2.1	494,241
B6	1	Separator (reflex drum)	Duty (cal/s)	5,556,935	0.93	2.1	415,773
						Total	33,925,650
		Additional equipment					
A205	1	Hydrolysate mix tank agitator					35,068
C202	1	Hydrolysate washed solid belt conveyor					116,103
H200	1	Hydrolysate cooler					127,051
P205	2 (1)	Pneumapress feed pump					154,290
P225	1 (1)	ISEP elution pump					43,462
P226	1 (1)	ISEP reload pump					74,798
S221	1	ISEP					2,739,939
T205	1	Hydrolysate mixing tank					39,812
						Total	3,330,522
						Grand total	37,256,172

Table 3
Electricity Cost

Equipment	Number (NREL no.)	Power (kW)	Cost ($/h)	Cost (2001 $/yr)
Feed pump	B7	268	10.72	84,902
Loading pump	B12	451	18.04	142,877
Primary filtrate pump	B14	162	6.48	51,322
Compressor	B13	235	9.4	74,448
Reactor screw (3 nos.)	B1 (WM 202)	863.08	34.5	273,424
Screw conveyor	B3 (WC 201)	36.96	1.5	11,709
Screw conveyor	B2 (WC 202)	44.59	1.8	14,126
Tank agitator	B4 (WT 232)	25.55	1.0	8094
Press filter (3 nos.)	B10 (WS 202)	133.8	5.4	42,388
Total		2219.98		703,290
Total for H_2SO_4 system *(3)*		1754.17		555,721

Scaling of process equipment was done using the following exponential scaling expression *(13)*:

$$\text{New cost} = \text{Original cost} \times \left(\frac{\text{New size}}{\text{Original size}} \right)^{s} \tag{3}$$

in which S is the scaling exponent, determined separately for each type of equipment. Instead of size, a characteristic that is linearly related to size, such as mass throughput, can be used in Eq.3. Another characteristic that can be used in Eq.3 is heat duty for a heat exchanger when the temperature differentials are held constant. For equipment that is not listed in a standard reference such as *Handbook of Chemical Engineering (12)*, the scaling exponents were obtained from the NREL dilute-acid report *(3)*. To maintain consistency between models, the installation costs were also taken from the NREL economic model. Since original equipment costs were calculated in different cost years, the chemical engineering cost indices *(14)* were used to calculate their cost in 2001 US$.

Calculation of Energy Cost

Energy cost of the pretreatment section was determined using energy demand values generated by the ASPEN-Plus model. Assumptions made for the economic analysis included 7920 operating hours per year and utilities valued at 4 ¢/kwh for electricity, 5.5¢ 1000 lb of 15°C cooling water, and 2000 psi steam at $4.50/1000 lb. For pumps and compressors such as B7, B12, B14, and B13, the power requirements were determined by the ASPEN-Plus model. However, some internal components of major process units such as reactor screws and tank agitators were not explicitly modeled in this process. Because these are standard types of process equipment, power requirements for these devices were assumed to be the same as those provided in the NREL economic model *(3)*. For example, the power requirement for reactor screw (B1) was taken to be the same as WM202 given in the NREL model. The total electricity cost was calculated as given in the Table 3.

Table 4
Cooling and Heating Duty and Costs

Equipment name	Number	Duty (kW)	Flow rate (kg/h)	Cost ($/yr)
Cooler	B5	9151	461,395	442,164
Separator/condenser	B6	23,266	284,890	273,016
Compressor cooler	B13	689	59,057	56,596
Total cooling			80,5342	771,775
Heater	B9	16,289	23,422	1,836,506
Total heating				1,836,506

Table 5
Annual Total Energy Cost

Energy type	Energy cost ($/yr)	Energy cost ($/gal)
Electricity	703,290	0.0137
Cooling duty	771,775	0.0150
Heating duty	1,836,506	0.0358
Total energy cost (2001 US$)	3,311,571	0.0645

Table 3 also includes the total power requirements for the pretreatment section of the NREL model *(3)*. The cooling duty and the heating duty of different process units were also determined by the ASPEN-Plus model. These data were used to calculate the total cooling and heating duties for the carbonic acid pretreatment and finally the total energy cost of the pretreatment process. These results are summarized in Tables 4 and 5.

Sensitivity Analyses

Sensitivity analyses were conducted to address the question of whether there is an optimum pretreatment condition that could be used for carbonic acid pretreatment. Laboratory results from Yourchisin and van Walsum *(7)* and McWilliams and van Walsum *(6)* indicate that optimal reaction severity would be in the range of Log(R_o) = 4.2, where the severity R_o is as defined by Overend and Chornet *(10)*. Relatively high temperature (220°C) and short retention time (4 min) were chosen to achieve this severity, since reactor costs dominate the economics and longer retention times would increase capital costs significantly. Pretreatment temperatures and pressures were varied for this study to determine the sensitivity of the cost to adjustments in these parameters.

In its economic model *(3)*, NREL used the discounted cash flow method to calculate the yearly total equipment cost for different process sections. To simplify economic comparisons between the two pretreatment designs,

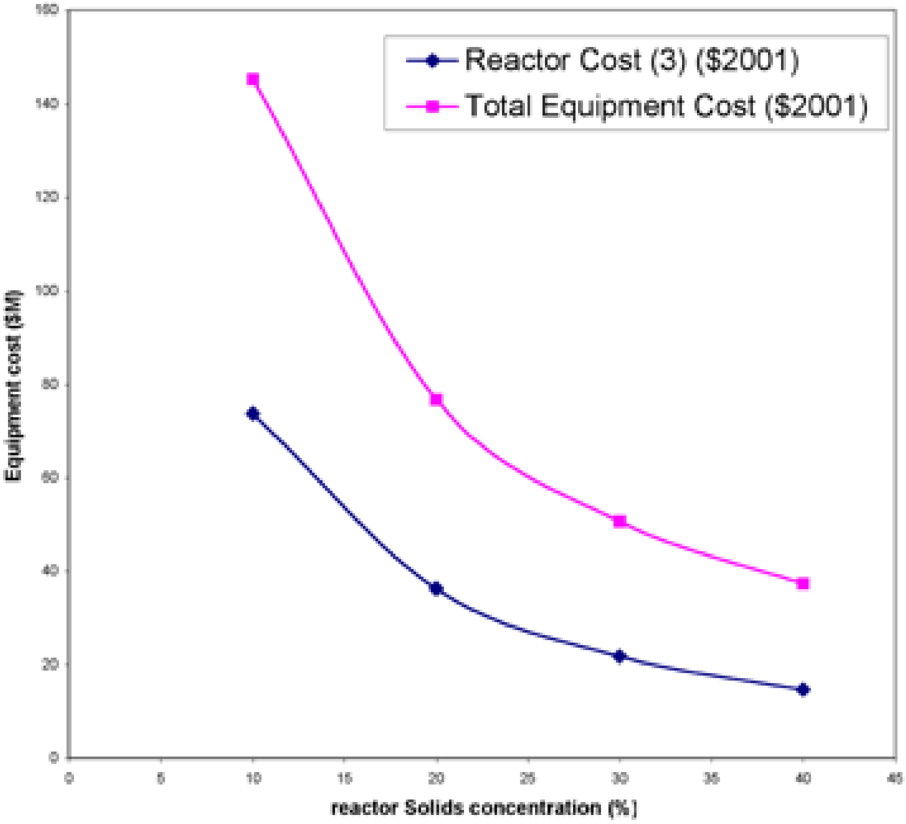

Fig. 2. Sensitivity of carbonic acid equipment costs to reactor solids concentration.

we assumed for both cases a 20% per year capital recovery factor to give the contribution of capital. This value was chosen to be consistent with investment returns for mature, low-risk technology *(1)*. With this assumption, it was possible to calculate total cost of pretreatment per year for different pretreatment conditions as given in Table 6. All values are in 2001 US$.

Variation of Equipment Cost with Reactor Solids Concentration

Experimental results for carbonic acid pretreatment have been generated at low solids concentration *(6,8,9)*, but no data are available for pretreatment conversions at higher solids concentrations, as are available for dilute H_2SO_4. The equipment costs for carbonic acid pretreatment were calculated for different solids concentrations (Fig. 2), and it can be seen that equipment costs are highly sensitive to solids concentration. For comparison to the dilute-acid system, a high reactor solids concentration of 40% was chosen to enable direct comparison with the NREL model.

Table 6
Variation of Total Cost at Constant Pressure

Parameters		Total equipment cost ($)	Equipment cost (per yr)($)	Operating cost (per yr) ($)	Total cost ($/yr)	Total cost ($/gal)
Pressure (psi)	Temp (°C)					
2000	220	37,256,172	7,451,234	3,311,571	10,762,805	0.210
2000	200	36,642,711	7,328,542	2,742,546	10,071,088	0.190
2000	180	35,659,532	7,131,906	2,208,698	9,340,604	0.180
1600	220	31,758,432	6,351,686	3,280,963	9,632,649	0.187
1600	200	31,342,841	6,268,568	2,712,051	8,980,619	0.175
1600	180	30,591,542	6,118,308	2,178,089	8,296,397	0.162
1200	220	26,580,118	5,316,024	3,250,150	8,566,174	0.167
1200	200	26,282,500	5,256,500	2,681,126	7,937,626	0.155
1200	180	25,743,721	5,148,744	2,147,277	7,296,021	0.142
1000	220	24,080,135	4,816,027	3,234,846	8,050,873	0.157
1000	200	23,834,986	4,766,997	2,665,821	7,432,818	0.145
1000	180	23,401,891	4,680,378	2,131,973	6,812,351	0.133
800	220	21,636,822	4,327,364	3,219,542	7,546,906	0.147
800	200	21,448,875	4,289,775	2,650,517	6,940,292	0.135
800	180	21,105,669	4,221,134	2,116,669	6,337,803	0.123

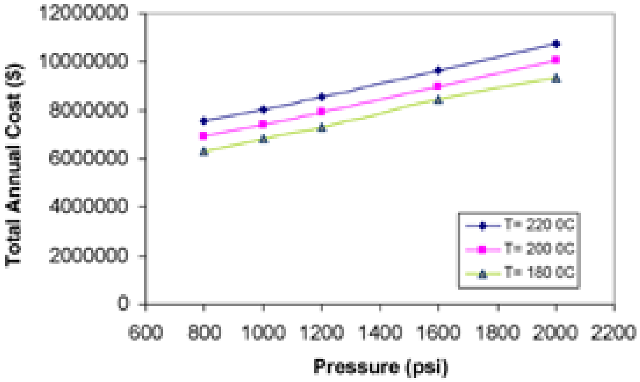

Fig. 3. Sensitivity of total (capital and operating) cost with variation in pretreatment pressure and temperature.

Variation of Total Cost with Temperature and Pressure

As explained in previous sections, equipment and operating costs were calculated for different pretreatment conditions. Reactor solids concentration and residence time remained constant at 40% and 4 min, respectively, throughout these calculations. Figure 3 depicts the variation of the total cost with pressure at different reaction temperatures. It is evident that the pressure of the system strongly affects the overall cost and is a dominant concern for cost reduction. Likewise, temperature also affects cost, with higher temperatures costing more. Increased temperature and pressure both increase reaction severity, although for some substrates such as aspen wood, only increased temperature results in clearly enhanced pretreatment effectiveness *(6,7)*. As a result, reducing pressures is more likely to improve overall economics than reducing temperatures.

Comparison of Carbonic Acid Pretreatment and H_2SO_4 Pretreatment

The central hypothesis of this research is that there will be negative incremental cost for the carbonic acid pretreatment process compared with the H_2SO_4 process. However, the equipment and energy costs for the carbonic acid system as calculated in this study are higher than those for the H_2SO_4 system. Although the cost of materials was reduced by making use of SS316, these savings were lost to provide the extra wall thickness needed for the higher pressures. The energy cost associated with CO_2 compression is not highly significant; for example, the power requirement for the reactor screw, which is common to both the carbonic and H_2SO_4 systems, is four times as great as that of the CO_2 compressor. Cost results are as follows:

Total equipment cost (2001 US$) = $37,256,172
Annual energy cost (2001 US$) = $3,311,571

A comparison of sulfuric and carbonic acid pretreatment flowsheets shows that some operations associated with processing requirements of

Table 7
Cost of Reagents and Waste Disposal in Dilute H_2SO_4 Pretreatment Process *(3)*

Component	Stream no.	kg/h	t/yr	Price ($/t)	Year	Total cost ($/yr)
H_2SO_4	STRM0710	2128	16,854	25	2001	421,344
Lime	STRM0745	913	7231	70	2001	506,167
Gypsum disposal		2433	19,269	22	2001	423,926
Total						1,351,437

Table 8
Comparison of Costs of Carbonic Acid and Sulfuric Acid Processes

Pretreatment method	Pretreatment equipment cost ($)	Pretreatment capital cost ($/yr)	Variable operating cost (2001 US$) at 2000 t/d	Total annual cost ($/yr)	EtOH (gal/yr)	EtOH ($/gal)
Carbonic acid	37,256,172	7,451,235	3,311,571	10,762,805	51,300,000	0.210
H_2SO_4	29,235,023	5,847,005	4,515,439 (approx)	10,435,565	51,300,000	0.202

the H_2SO_4 process that are absent from the carbonic acid system. These include the use of acid-neutralizing reagents and the resulting disposal of the waste calcium sulfate precipitate. Results compiled from the NREL report *(3)* are used to quantify these additional costs (Table 7). For the purpose of comparison, these costs are rolled into the operating cost of the H_2SO_4 pretreatment. Because the pretreatment section of the NREL model is embedded in a much larger model of the entire biomass-to-ethanol process, it was not possible to accurately determine steam and cooling water costs associated with only the pretreatment section. For the purpose of this comparison, energy costs for steam and cooling in the H_2SO_4 system were approximated as being equal to those calculated for the carbonic acid pretreatment. With this assumption, the total variable operating cost for the H_2SO_4 system is given in Table 8 as approx 4.5 million US$. Cost contributions to final ethanol selling price for the two pretreatment systems (assuming equal ethanol yields) are comparable, with dilute H_2SO_4 being slightly more economical.

Dilute H_2SO_4 is a well-studied pretreatment system that has been shown to be effective but expensive. Limited studies on carbonic acid have shown that this mild acid offers some benefit compared to liquid hot water *(4,5)*, but that performance is generally less effective than optimized dilute H_2SO_4. Laboratory investigations of carbonic acid pretreatment have shown that pretreatment effectiveness is primarily a function of time and temperature, and that high CO_2 pressure enhances hydrolysis on some substrates such as corn stover *(8)* but offers little benefit on aspen wood *(6,7)*. Thus, for certain substrates such as aspen wood, lower pressure values are likely to offer performance similar to higher pressures. To date, no study integrating carbonic acid pretreatment, enzymatic hydrolysis, and fermentation has been carried out to determine the overall ethanol yield compared to similar.

Conclusion

Although at the beginning of the design process it was hypothesized that reactor cost could be lowered owing to the use of stainless steel instead of Hastelloy C, the pretreatment reactor turned out to be the most expensive piece of equipment in the carbonic acid pretreatment, costing about twice as much as the NREL reactor constructed of Hastelloy C. High pressures associated with carbonic acid pretreatment made it extremely expensive to build reactors out of SS316 L. One option that can be used to minimize this cost is to clad the reactor with polymeric material such as Teflon and to reinforce it with stainless steel; this approach would likely offer similar benefits to the dilute H_2SO_4 system as well. Energy requirements for compression of CO_2 were relatively minor and did not greatly affect overall process economics. This was partly owing to the ambient temperature (high solubility) conditions at which CO_2 was dissolved into solution. About 50% of the total operating cost is owing to the heat demand of the process. This appears to be unavoidable because of difficulties in process heat recovery.

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