

MODELING AND OPTIMIZATION OF THE DILUTE-SULFURIC-ACID PRETREATMENT OF CORN STOVER, POPLAR AND SWITCHGRASS

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Abstract

Lignocellulosic biomass may be used as a potential renewable feedstock for biochemical production of ethanol as an alternative transportation fuel. However, cellulose, which is the major source of fermentable sugars in these materials, is protected by a network of lignin and hemicellulose. The dilute-sulfuric-acid pretreatment removes this protecting shield and makes the cellulose more susceptible to enzymatic digestion. In this study, three lignocellulosic feedstocks (i.e. corn stover, poplar and switchgrass) were pretreated with dilute sulfuric acid (0.6, 0.9 and 1.2% w/w) at relatively high temperatures (140, 160 and 180°C) in a Parr batch reactor. The hydrolysis of hemicellulose to its monomeric constituents and possible degradation of these monomers were modeled by a series of first-order reactions. The kinetic parameters of two mathematical models for predicting the percentage of xylan remaining in the substrate after pretreatment and the net xylose yield in the liquid stream were determined using the actual acid concentration in the reactor after accounting for the neutralization effect of the substrates. © 1997 Elsevier Science Ltd.

Key words: Dilute-acid pretreatment, corn stover, poplar, switchgrass, acid hydrolysis, lignocellulosic biomass.

INTRODUCTION

Lignocellulosic biomass, such as municipal solid waste (MSW), agricultural and forest residues and paper waste, is mainly composed of cellulose, hemicelluloses and lignin. Cellulose can be enzymatically hydrolyzed to its monomeric constituents (glucose units) and then fermented to ethanol or other products (Lynd, 1989; Lynd *et al.*, 1991). Cellulose fibers, however, are embedded in a lignin–hemicellulose network. This network retards cellulose

biodegradation by cellulolytic enzymes. In order to remove the protecting shield of lignin–hemicellulose, and make the cellulose more readily available for enzymatic hydrolysis, biomass must be pretreated. Pretreatment can be carried out in different ways, such as physical treatment (e.g. high energy radiation, steam explosion and ball milling), chemical treatment with acid or basic catalysts, and biological treatments (Grohmann *et al.*, 1985).

Pretreatment can affect the structure of biomass by solubilizing or otherwise altering hemicelluloses, altering lignin structure, reducing cellulose crystallinity and increasing the available surface area and pore volume of the substrate. During pretreatment, hemicelluloses may be hydrolyzed to their monomeric constituents and lignin–hemicellulose–cellulose interactions partially disrupted (Ladisich, 1989; Day, 1989).

Pretreatment of biomass with dilute sulfuric acid at high temperatures can effectively dissolve the hemicelluloses (xylan), and increase the enzymatic digestibility of cellulose. High reaction rates (compared with enzymatic processes), low acid consumption, and low cost of sulfuric acid (compared with base-catalyzed pretreatments) are some of the advantages of the dilute-sulfuric-acid pretreatment (Grohmann *et al.*, 1985; Parisi, 1989; Kim & Lee, 1987; Kobayashi, 1956; Singh *et al.*, 1984; Torget *et al.*, 1990; Doran *et al.*, 1994; Grethlein, 1991). A dilute-acid pretreatment plant will not require an acid-recovery system, which seems to be essential for a pretreatment plant using concentrated acid.

In this study, two herbaceous (corn stover and switchgrass) and a woody (poplar) feedstock were pretreated with dilute sulfuric acid (0.6, 0.9 and 1.2% w/w) at relatively high temperatures (140, 160 and 180°C). The change in the amount of xylan remaining in the solids residue with time was modeled by a biphasic equation. The biphasic behavior might be due to mass transfer limitations within the reaction environment, different physical or chemical characteristics of different portions of xylan, or

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structural changes of xylan during hydrolysis (Conner, 1984; Maloney *et al.*, 1985). The rate constants of xylan hydrolysis and xylose degradation reactions were assumed to have an Arrhenius-type temperature dependency.

METHODS

Biomass feedstocks

Herbaceous (corn stover and switchgrass) and woody (hybrid poplar) feedstocks were provided by the National Renewable Energy Laboratory (NREL).

Pretreatment

All pretreatment experiments were carried out in a Parr reactor model #4563. This 600 ml stainless-steel reactor was equipped with a glass liner, a heat exchanger and an impeller-type mixer. Figure 1 shows a schematic diagram of the reactor. The solid concentration in the reaction mixture was 10% (w/w). Aqueous solution of 30.00 g of substrate in the required amount of distilled water was heated to the desired temperature (140, 160, or 180°C), and reaction was initiated by the injection of preheated acid (0.6, 0.9, or 1.2% w/w). The acid injection pressure exceeded the internal reactor pressure by

15 psi. Time zero for all reactions corresponded with acid injection. The reactor temperature was controlled by a Parr controller model #4831. A solenoid valve adjusted the water flow through the internal heat exchanger, and regulated the temperature at $\pm 1^\circ\text{C}$. Each reaction was terminated by running cold water through the internal heat exchanger, while simultaneously removing the heating mantle and spraying the external surface of the reactor with cold water. The chosen method allowed constant stirring while cooling, thereby maintaining a relatively homogeneous environment. This method provided a 20°C temperature decrease within less than 30 s and, therefore, a three-fold decrease in the reaction rate. As a result, reaction was effectively terminated after 30 s. The pretreated materials were then filtered (Whatman No. 5) and washed with distilled water (~ 1500 ml). The total volume of the liquid stream (both filtrate and wash) was recorded, and a 125 ml sample was stored at 4°C until analyzed. The solids residue was dried in an oven at 45°C for 24 h.

Analytical methods

The neutral monosaccharide composition of the constituent polysaccharide in the initial feedstocks was quantified by an HPLC-based assay of the hydrolysate resulting from a two-stage sulfuric acid

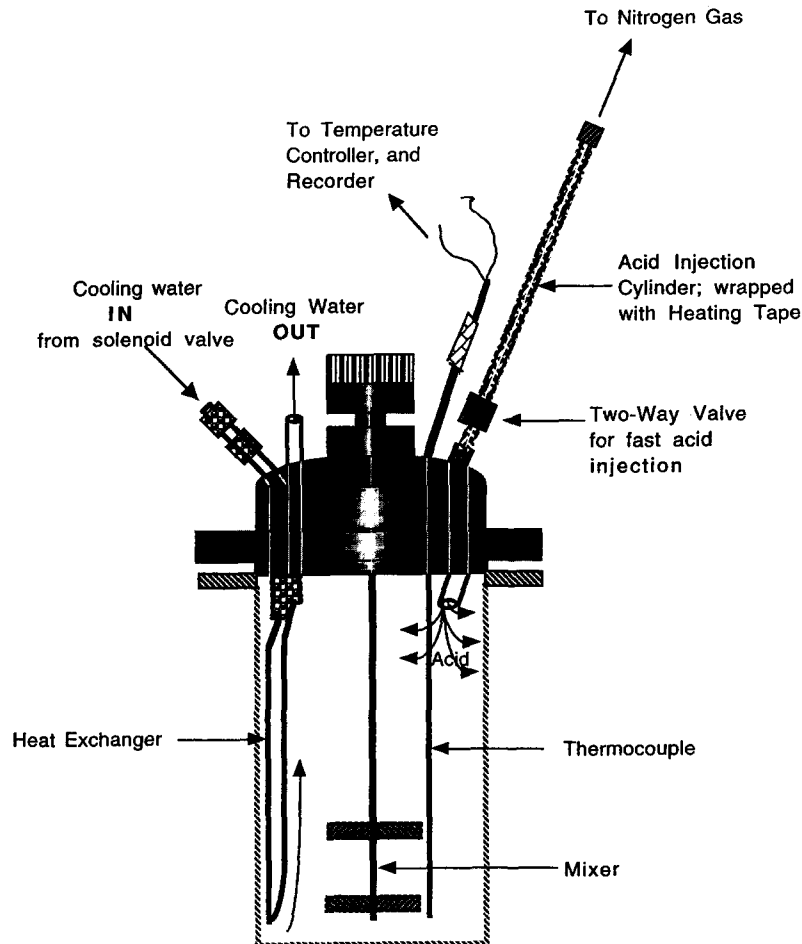


Fig. 1. Stainless-steel reactor (Parr model 4563) with acid-injection system, mixer and cooling coil.

treatment. Sugars were separated using a Bio-rad Aminex HPX-87P column and quantified based on the signal from a Waters 401 refractive index detector using Waters Baseline 810 integration software. The neutral monosaccharide composition of hydrolysates from pretreated residues and the neutral sugar composition of the soluble phase resulting from pretreatments were also determined by this method. Lignin plus other acid-insoluble components were determined as Klason lignin. Moisture and ash contents were determined by standard methods as described in NREL Alternative Fuels Division Chemical Analysis and Testing Standard Procedure No. 005 (Ehrman, 1992). Acetic acid and furfural concentrations of pretreatment filtrates were determined on a Varian 1400 gas chromatograph equipped with a flame-ionization detector.

Since the basic cations of lignocellulosics can partially neutralize the sulfuric acid (Grohmann *et al.*, 1985; Malester *et al.*, 1992; Springer & Harris, 1985), the acidity of the reaction mixture is lowered by the neutralizing capacity of the substrate. The neutralizing ability (NA) of each feedstock was determined by measuring the pH of sulfuric acid (0.6, 0.9 and 1.2%)/distilled water solutions before (pH_{DW}) and after (pH_{S}) mixing with the feedstock. The proportions of substrate, acid and water were the same as in the pretreatment experiments. The following eqn (1) was used to correlate the change of pH of acid

solution to the neutralizing ability (g H_2SO_4 /g dry substrate) of a feedstock:

$$\text{NA} = \text{MW}_{\text{H}_2\text{SO}_4} \times [10^{-\text{pH}_{\text{DW}}} - 10^{-\text{pH}_{\text{S}}}] / \text{solid concentration} \quad (1)$$

The solid concentration in the reactor is expressed as g dry substrate/l liquid (acid+water).

KINETIC MODEL DEVELOPMENT

Results of dilute-acid pretreatment of lignocellulosic feedstocks (hardwoods, softwoods, grasses and wastepaper) indicate that the amount of xylose remaining in biomass changes in a biphasic fashion with time (Grohmann *et al.*, 1985; Kim & Lee, 1987; Kobayashi, 1956; Maloney *et al.*, 1985; 1986; Nee & Wen, 1976; Conner, 1984). It is assumed that there are two types of xylan in biomass, i.e. fast- and slow-reacting, and the overall hemicellulose hydrolysis reaction is presented as

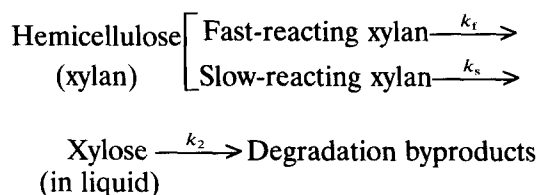


Table 1. Compositional analysis of raw biomass samples (percent by weight)

Component	Switchgrass		Poplar		Corn stover	
	Mean	SEM ^a	Mean	SEM ^a	Mean	SEM ^a
Total glycans	56.6	—	58.2	—	59.9	—
glucan	32.2	0.29	39.8	0.01	36.0	0.4
xylan	20.3	0.26	14.8	0.03	19.8	0.25
galactan	—	—	—	—	1.3	0.05
arabinan	3.7	0.04	1.2	0.02	2.8	0.06
mannan	0.4	0.02	2.4	0.04	—	—
Klason lignin	19.5	0.3	26.9	0.26	17.8	0.08
Acid-soluble lignin	3.7	0.03	2.2	0.06	1.9	0.03
Ash	7.1	0.06	1.3	0.02	7.2	0.01
Uronic acid	1.1	0.01	2.4	0.13	nd ^b	—
Other	12.0	—	9.0	—	13.2	—

^aStandard error of the mean.

^bNot determined.

Table 2. Kinetic parameters of the biphasic model: $X = X_f \cdot e^{-k_f t} + X_s \cdot e^{-k_s t}$ for switchgrass, poplar and corn stover

		Switchgrass	Poplar	Corn stover
X_f (average):		76.8%	83.8%	64.4%
	A_o	1.9×10^{21}	3.3×10^{21}	6.7×10^{16}
k_f :	E (kJ/mol)	169.0	176.7	129.8
	n	0.4	0.4	1.5
X_s (average):		23.2%	16.2%	35.6%
	A_o	4.2×10^{23}	3.3×10^{22}	6.9×10^{19}
k_s :	E (kJ/mol)	201.7	192.0	167.6
	n	2.0	1.5	1.6

All three reactions (k_f , k_s , k_2) are assumed to be of first order:

$$d[\text{xylan}]_{\text{fast}}/dt = -k_f[\text{xylan}]_{\text{fast}} \quad (2)$$

$$d[\text{xylan}]_{\text{slow}}/dt = -k_s[\text{xylan}]_{\text{slow}} \quad (3)$$

$$d[\text{xylose}]/dt = k_f[\text{xylan}]_{\text{fast}} + k_s[\text{xylan}]_{\text{slow}} - k_2[\text{xylose}]_{\text{in liquid}} \quad (4)$$

$$d[\text{byproducts}]/dt = k_2[\text{xylose}]_{\text{in liquid}} \quad (5)$$

By integrating eqns (2) and (3):

$$X_f = X_{f0} \cdot e^{-k_f \cdot t} \quad (6)$$

$$X_s = X_{s0} \cdot e^{-k_s \cdot t} \quad (7)$$

The total amount of xylan remaining in the solids residue can be obtained by adding these two portions, i.e. X_f and X_s :

Table 3. Percentage of fast-reacting xylan (X_{f0}) in different types of lignocellulosic feedstocks

Reference	Feedstock	X_{f0} (%)
Conner (1984)	Southern red oak	73.9
	Paper birch	71.6
	Red maple	80.3
	Quacking aspen	76.0
	American elm	84.3
Grohmann <i>et al.</i> (1985)	Aspen	76.0
	Wheat straw	67.0
Maloney <i>et al.</i> (1985)	Paper birch	68.4
Kim & Lee (1987)	Southern red oak	69.7
This study	Corn stover	64.4
	Switchgrass	76.8
	Poplar	83.8

$$X_R = X_f + X_s = X_{f0} \cdot e^{-k_f \cdot t} + X_{s0} \cdot e^{-k_s \cdot t} \quad (8)$$

where X_R : percentage of total xylose equivalents remaining in the solids residue relative to the initial weight of xylose in the substrate; X_f , X_s : percentage of fast- and slow-reacting xylan at any time; X_{f0} , X_{s0} : percentage of fast- and slow-reacting xylan at $t = 0$; $X_{s0} = 100 - X_{f0}$; k_f and k_s : rate constants of fast- and slow-reacting xylan hydrolysis (min^{-1}); t : time (min).

The reaction rate constants (k_f , k_s , k_2) are assumed to have an Arrhenius-type temperature dependence (Maloney *et al.*, 1985; Ranganathan *et al.*, 1985; Nee & Wen, 1976):

$$k = A \cdot e^{-E/R \cdot T}$$

A : pre-exponential factor; E : activation energy (kJ/mol); R : 8.3143×10^{-3} (kJ/mol.K). The pre-exponential factor, A , is assumed to be dependent upon acid concentration (C_a):

$$A = A_0 \cdot C_a^n$$

therefore

$$k = A_0 \cdot C_a^n \cdot e^{-E/R \cdot T} \quad (9)$$

The actual acid concentration, C_a , can be calculated from the nominal acid concentration (C) using eqn (10), in which the coefficient 0.1 represents the solid ratio in the reactor (g dry substrate/g total mass of reaction mixture) for all pretreatments:

$$C_a = C - (0.1 \times \text{neutralizing ability of the substrate})$$

Table 4. Kinetic parameters of xylan hydrolysis rate constant: $K = A_0 C_a^n \cdot e^{-E/RT}$

Reference	Feedstock	Parameter		
		A_0	n	E (kJ/mol)
Grohmann <i>et al.</i> (1985)	Wheat straw			
	k_f	nd ^a	nd	50.2
	k_s	nd	nd	104.6
	Aspen wood			
	k_f	nd	nd	117.2
	k_s	nd	nd	154.8
Kim & Lee (1987)	Southern red oak			
	k_f	1.04×10^{14}	1.54	120.1
	k_s	6.00×10^{12}	1.19	118.0
Maloney <i>et al.</i> (1985)	Paper birch			
	k_f	2.67×10^{16}	1	126.6
	k_s	16×10^{19}	1	156.5
This study	Switchgrass			
	k_f	1.9×10^{21}	0.4	169.0
	k_s			
	Poplar			
	k_f	4.2×10^{23}	2.0	210.7
	k_f	3.3×10^{21}	0.4	176.7
	k_s	3.3×10^{22}	1.5	192.0
	Corn stover			
k_f	6.7×10^{16}	1.5	129.8	
	k_s	6.9×10^{19}	1.6	167.6

^aNot determined.

Table 5. Parameters of xylose degradation rate constant: $K_2 = A_{o2} \cdot C^{n_2} \cdot e^{-E_2/RT}$ in acid hydrolysis of switchgrass, poplar and corn stover

	Switchgrass	Poplar	Corn stover
A_{o2}	3.8×10^{10}	8.5×10^{10}	3.7×10^{10}
E_2 (kJ/mol)	99.5	102.0	98.4
n_2	1.45	0.55	0.50

(10)

The neutralizing abilities (g H₂SO₄/g dry substrate) of the three feedstocks are reported in the Results and Discussion section.

At each set of reaction conditions (temperature and acid concentration), pretreatments were carried out at different reaction times. After each pretreatment, the amounts of xylose remaining in the solids residue (X_R), and in the liquid stream were measured. There was no indication of xylan hydrolysis at elevated temperatures (140, 160 and 180 °C) during the preheat time prior to initiating the reaction with acid. The kinetic parameters of the biphasic model [eqn (8)] were calculated by non-linear regression analyses (Microsoft Excel) on eqn (8) using measured values of X_R and corresponding times (t). Thus, nine k_f , k_s and X_{fo} values were calculated (one per each set of T and C). There was no apparent relationship between the percentage of fast-reacting xylan (X_{fo}) and pretreatment conditions. Therefore, the average value of X_{fo} was used to calculate X_R . The calculated values of k_f and k_s were used to determine the kinetic parameters (A_o , n and E) of

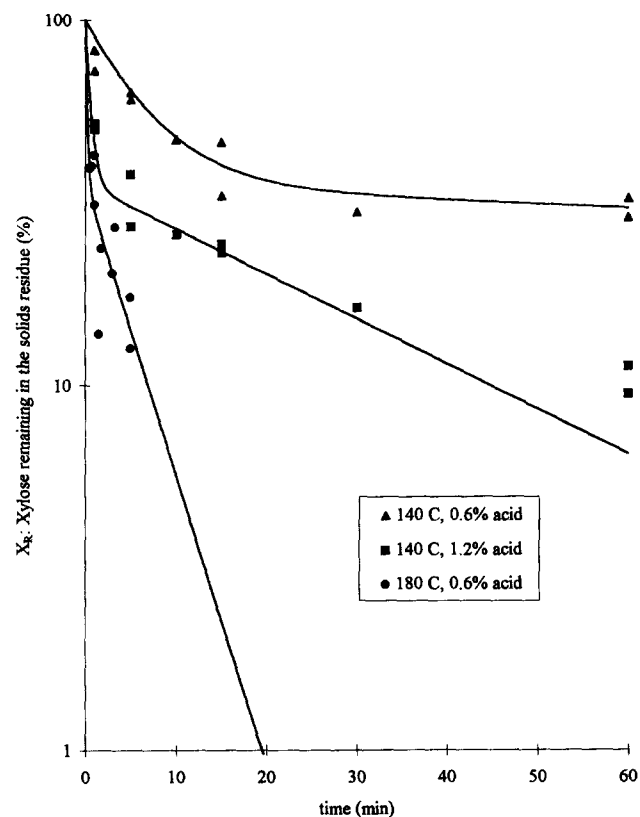


Fig. 2. Xylan hydrolysis of corn stover.

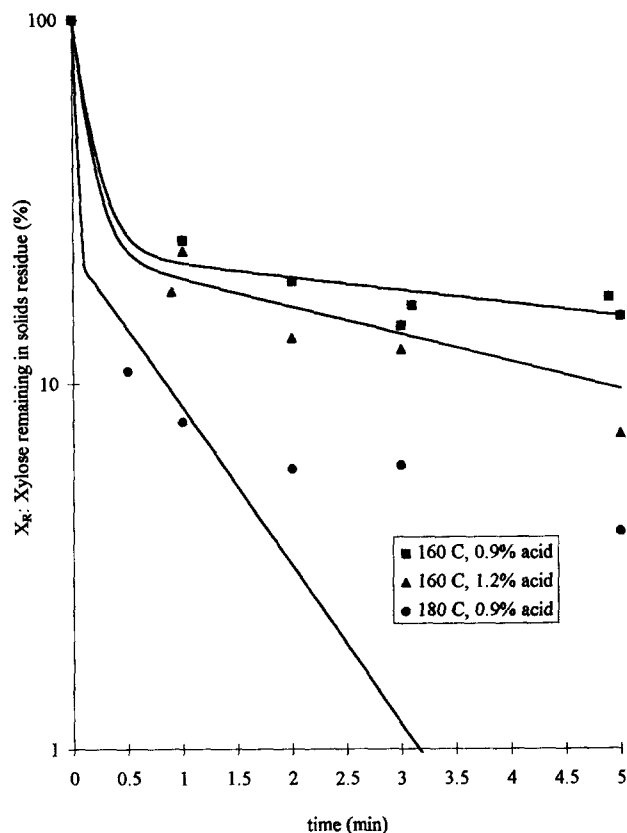


Fig. 3. Xylan hydrolysis of switchgrass.

each reaction rate constant (k_f and k_s) using linear regression analyses (Microsoft Excel) on a transformed Arrhenius equation:

$$\ln(k) = \ln(A_o) + n \cdot \ln(C_a) - E/RT \quad (11)$$

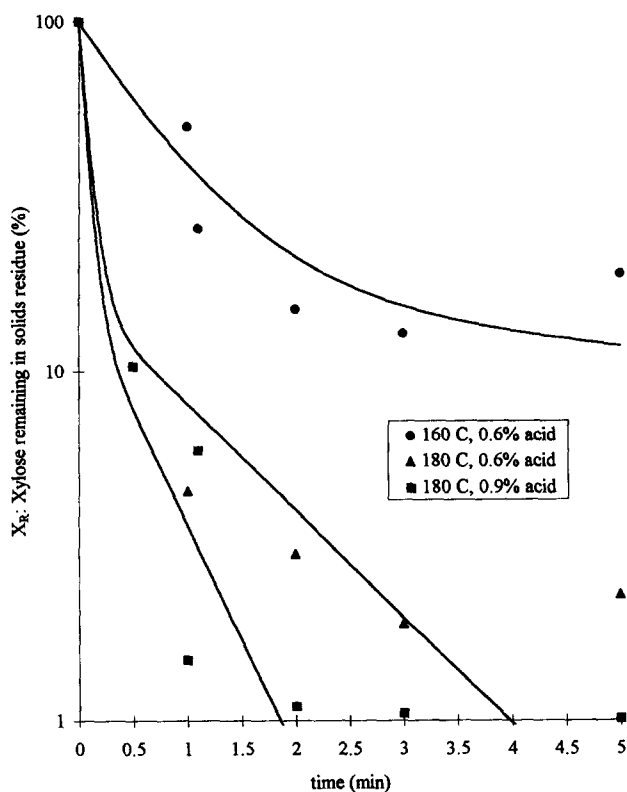


Fig. 4. Xylan hydrolysis of poplar.

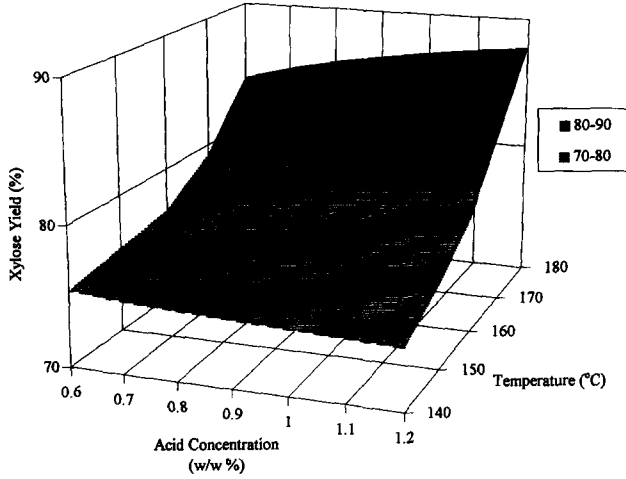


Fig. 5. Percentage of sugar (xylose) recovery from pre-treatment of switchgrass.

Net xylose yield in liquid prehydrolysate

The xylose monomers, produced from xylan hydrolysis, may be converted to other byproducts, such as furfural. Although oligomers of xylose have been reported using other reactor configurations, in a batch mode under the conditions of time, temperature and acid concentration employed in this study no oligomers were observed. The net amount of xylose in the liquid stream (X_L) is determined by the following differential equation accounting for both formation and possible degradation of xylose:

$$dX_L/dt = k_f \cdot X_f + k_s \cdot X_s - k_2 \cdot X_L \quad (12)$$

Using eqns (8) and (12):

$$dX_L/dt + k_2 \cdot X_L = k_f \cdot X_{f0} \cdot e^{-k_f \cdot t} + k_s \cdot X_{s0} \cdot e^{-k_s \cdot t} \quad (13)$$

By solving eqn (13), X_L can be expressed as

$$X_L = [(k_f \cdot X_{f0}) / (k_2 - k_f)] \cdot [e^{-k_f \cdot t} - e^{-k_2 \cdot t}] + [(k_s \cdot X_{s0}) / (k_2 - k_s)] \cdot [e^{-k_s \cdot t} - e^{-k_2 \cdot t}] \quad (14)$$

where X_L : net sugar yield – percentage of xylose in liquid (relative to initial weight of xylose in starting material); X_{f0} : percentage of fast-reacting xylose at $t = 0$; X_{s0} : percentage of slow-reacting xylose at $t = 0$; $X_{s0} = 100 - X_{f0}$; t : time (min); k_f and k_s : rate constants of fast- and slow-reacting xylan hydrolysis (min^{-1}); k_2 : xylose conversion rate constant (min^{-1}) given by

$$k_2 = A_{o2} \cdot C_a^{n_2} \cdot e^{-E_2/RT} \quad (15)$$

where $R = 8.3143 \times 10^{-3}$ kJ/mol.K; T : temperature (K); C_a : actual acid concentration (wt%); see eqn (10). The best estimates of k_2 [eqn (14)] at each set of reaction conditions (T and C) were determined by using the best estimates of k_f , k_s and X_{f0} [see eqn (8)] and X_L values measured analytically. These values (k_2) were then used to calculate the kinetic constants of eqn (15) by non-linear regression analysis (Microsoft Excel).

In order to determine the maximum amount of X_L at a given set of temperature and acid concentration:

$$dX_L/dt = 0 \quad (16)$$

Applying this condition to eqn (14) gives

$$\begin{aligned} & [(k_f \cdot X_{f0}) / (k_2 - k_s)] / [(k_s \cdot X_{s0}) / (k_2 - k_f)] \\ &= [(k_s / k_2) \cdot e^{(k_2 - k_s) \cdot t_{\max}} - 1] / [1 - (k_f / k_2) \cdot e^{(k_2 - k_f) \cdot t_{\max}}] \end{aligned} \quad (17)$$

where t_{\max} is the reaction time (min) at which the net sugar yield in the liquid phase (at given temperature and acid concentration) is maximum. At a given set of temperature and acid concentration, the left-hand side of eqn (17) is a constant ($K_{T,C}$), and the equation has a unique solution (t_{\max}) which may be determined by iteration. The following equation derived from eqns (13) and (16) gives the maximum sugar yield (X_L) in the liquid phase:

$$\begin{aligned} X_L @ t_{\max} &= (k_f \cdot X_{f0} / k_2) \cdot e^{-k_f \cdot t_{\max}} \\ &+ (k_s \cdot X_{s0} / k_2) \cdot e^{-k_s \cdot t_{\max}} \end{aligned} \quad (18)$$

Finally, the amount of xylose converted to byproducts (L) is determined by combining eqns (8) and (14):

$$\begin{aligned} L &= 100 - [X_R + X_L] = 100 \\ &- X_{f0} [(k_f \cdot e^{-k_f \cdot t} - k_2 \cdot e^{-k_f \cdot t}) / (k_f - k_2)] \\ &- X_{s0} [(k_s \cdot e^{-k_s \cdot t} - k_2 \cdot e^{-k_s \cdot t}) / (k_s - k_2)] \end{aligned} \quad (19)$$

where L : percentage of xylose loss by degradation reaction (relative to initial weight of xylose in starting material); X_L : percentage of xylose in liquid (relative to initial weight of xylose in starting material).

RESULTS AND DISCUSSION

The chemical composition of the three feedstocks, corn stover, poplar and switchgrass, is shown in Table 1. The major components of these substrates were glucan, lignin and xylan. Corn stover and switchgrass (herbaceous substrates) had higher ash contents than poplar.

The neutralizing abilities of corn stover, switchgrass and poplar were determined as 43.7, 25.8 and 16.7 mg $\text{H}_2\text{SO}_4/\text{g}$ dry substrate, respectively. The higher neutralizing ability of corn stover and switchgrass was in agreement with their higher ash content. Poplar had a considerably higher neutralizing ability (16.7 mg $\text{H}_2\text{SO}_4/\text{g}$ dry wood) than other hardwoods, e.g. paper birch (3.5 mg $\text{H}_2\text{SO}_4/\text{g}$ dry wood) and red oak (8–9 mg $\text{H}_2\text{SO}_4/\text{g}$ dry wood) reported by Maloney *et al.* (1985). This difference can be attributed to the relatively high ash content (1.3%) of poplar used in this study. Lower ash con-

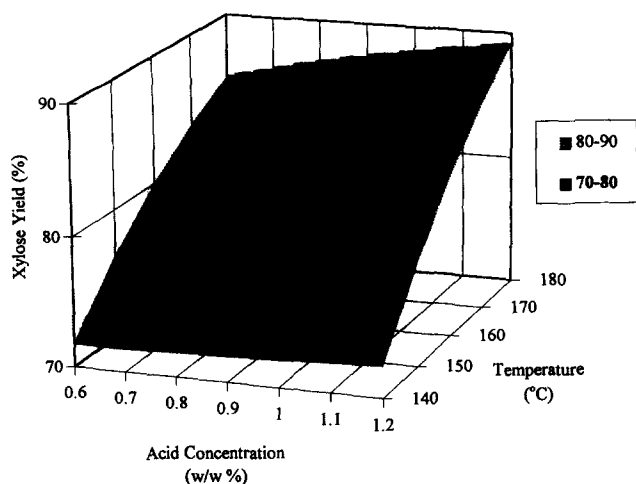


Fig. 6. Percentage of sugar (xylose) recovery from pretreatment of poplar.

tents have been reported for poplar and other hardwoods: 0.7 and 0.6% for two types of poplar (Torget *et al.*, 1990); 0.8% for aspen wood; 0.4% for sweetgum (Grohmann *et al.*, 1985); and 0.3% for red oak wood (Conner, 1984).

The kinetic parameters of the biphasic model [eqn (8)] and reaction rate constants (k_f , k_s) are presented in Table 2. The percentage of fast-reacting xylan (X_{f0}) is the average of values determined at different reaction conditions. Table 3 shows that X_f values of corn stover, switchgrass and poplar determined in this study are comparable to those reported for other lignocellulosic substrates. The woody feedstock (poplar) had a higher percentage of fast-reacting xylan (X_{f0}) than herbaceous substrates (switchgrass and corn stover). Such a difference between woody (aspen) and herbaceous (wheat straw) feedstocks was also reported by Grohmann *et al.* (1985) (see Table 3).

The activation energy of fast-reacting xylan in poplar was found to be higher than those of switchgrass and corn stover. This can be attributed to the difference in chemical composition of hemicelluloses in woody and herbaceous materials. Hardwood hemicelluloses are mainly composed of 4-O-methyl-

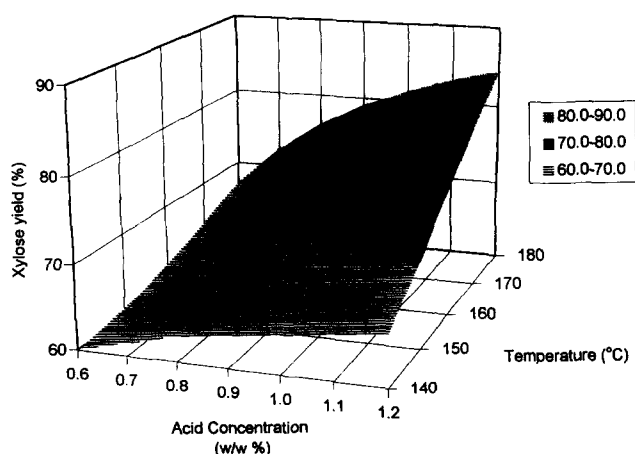


Fig. 7. Percentage of sugar (xylose) recovery from pretreatment of corn stover.

glucuronoxylan, whereas in herbaceous materials arabinoxylans are the principal hemicelluloses (Grohmann *et al.*, 1985; Sjoström, 1993). Table 4 summarizes some of the kinetic parameters of acid pretreatment of other feedstocks. These data are comparable with those found in this study. A direct comparison, however, cannot be made because of the difference in reaction conditions.

The kinetic parameters of xylose degradation rate constant (k_2) are presented in Table 5. The rate of xylose conversion is thought to be substrate independent. The results of this study also indicate some similarities between the degradation rates of xylose resulting from the three feedstocks. Activation energies are essentially equal and preexponential factors (A_0) and acid-dependency exponents (n) are very close. However, k_2 values calculated by using these constants are slightly different. This discrepancy might be due to the difference in products of xylan hydrolysis from different feedstocks and their consequent effect on degradation of xylose. However, this cannot be verified at this level of resolution.

Figures 2–4 show the experimental and model-predicted values of xylose remaining in the solids residue (X_R) for corn stover, switchgrass and poplar, respectively. The results indicate that by using concentrated sulfuric acid ($\sim 0.9\%$) at higher temperatures ($\sim 180^\circ\text{C}$) about 90% of the xylan could be dissolved within the first minute of the reaction period.

The maximum net sugar yields resulting from pretreatment of switchgrass, poplar and corn stover at different reaction conditions with optimum reaction time [X_L at t_{\max} , eqn (18)] are shown in Figs 5, 6 and 7, respectively. An interesting fact revealed by Figs 5 and 6 is that temperature (not the acid concentration) is the major factor affecting the extent of sugar recovery from pretreatment of poplar and switchgrass. It is only at high temperatures (e.g. 180°C) that increasing the acid concentration can affect the sugar recovery. In comparison, the xylose yield from corn stover is more sensitive to a change in acid concentration level, especially at higher temperatures. Likewise, the effect of temperature is more pronounced at higher levels of acid concentration.

Figures 5–7 also indicate that pretreatment of the feedstocks at harsher conditions produces higher net sugar yields. At temperatures between 170 – 180°C and with acid concentrations greater than 0.9% , sugar yields from poplar and switchgrass are reasonably high (80%). The reaction times for obtaining the maximum sugar yield under these conditions are between 0.5 and 1 min. In case of corn stover, however, an 80% sugar recovery requires higher acid concentrations (1.0%) at the same temperature range (170 – 180°C). The net sugar yield from corn stover is lower compared to those resulting from poplar and switchgrass using similar reaction condi-

tions. This might be in part due to the higher neutralizing ability of corn stover, which substantially lowers the acid concentration in the reaction mixture.

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