

Kinetic Modeling Analysis of Maleic Acid-Catalyzed Hemicellulose Hydrolysis in Corn Stover

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ABSTRACT: Maleic acid-catalyzed hemicellulose hydrolysis reaction in corn stover was analyzed by kinetic modeling. Kinetic constants for Saeman and biphasic hydrolysis models were analyzed by an Arrhenius-type expansion which include activation energy and catalyst concentration factors. The activation energy for hemicellulose hydrolysis by maleic acid was determined to be 83.3 ± 10.3 kJ/mol, which is significantly lower than the reported E_a values for sulfuric acid catalyzed hemicellulose hydrolysis reaction. Model analysis suggest that increasing maleic acid concentrations from 0.05 to 0.2 M facilitate improvement in xylose yields from 40% to 85%, while the extent of improvement flattens to near-quantitative by increasing catalyst loading from 0.2 to 1 M. The model was confirmed for the hydrolysis of corn stover at 1 M maleic acid concentrations at 150°C, resulting in a xylose yield of 96% of theoretical. The refined Saeman model was used to evaluate the optimal condition for monomeric xylose yield in the maleic acid-catalyzed reaction: low temperature reaction conditions were suggested, however, experimental results indicated that bi-phasic behavior dominated at low temperatures, which may be due to the insufficient removal of acetyl groups. A combination of experimental data and model analysis suggests that around 80–90% xylose yields can be achieved at reaction temperatures between 100 and 150°C with 0.2 M maleic acid.

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lignocellulosic materials (e.g., corn stover and fiber, poplar wood chips, switchgrass, etc.) (Himmel et al., 2007; Lynd et al., 1999; Wyman, 2003). In the context of fermentative routes for lignocellulosics utilization, the highly recalcitrant plant cell wall polysaccharides must be depolymerized into their constituting monomeric sugars, mainly glucose and xylose. Among the three main fractions of lignocellulosic biomass (cellulose, hemicellulose, and lignin), hemicellulose is second to cellulose in abundance therefore its effective utilization is important to the overall process economics (Wyman, 2003). Unlike the homopolymeric and crystalline cellulose, hemicellulose is a highly branched, non-crystalline heteropolysaccharide that consists largely of pentoses (xylose and arabinose), with small amount of hexoses (glucose, galactose, mannose, etc.) and uronic acids (glucouronic acid) (Saha, 2003). The sugar residues are partially acetylated thus the breakdown of hemicellulose with water under hydrothermal conditions (e.g., liquid hot water pretreatment) releases acetic acid, which in turn facilitate the hydrolysis (Mosier et al., 2005a,b). The xylose produced from hemicellulose hydrolysis can be utilized for ethanol production through fermentation by recombinant microorganisms (Ho et al., 1998; Ingram et al., 1998; Zhang et al., 1995), or for xylitol production through catalytic hydrogenation (Baudel et al., 2005; Wisniak et al., 1974). Additionally, the removal of hemicellulose makes the remaining cellulose fraction more readily digestible by cellulolytic enzymes due to the removal of the recalcitrant physical shields to cellulose and improving the accessibility of enzymes to the cellulose (Chang and Holtzapple, 2000; Mosier et al., 2005b; Yang and Wyman, 2004).

There have been many studies on the hemicellulose hydrolysis reaction in the presence of different catalysts: compressed liquid hot water (Mok and Antal, 1992; Mosier et al., 2005a; Weil et al., 1997, 1998), strong mineral acids under hydrothermal conditions (Lee and McCaskey, 1983; Schell et al., 2003), and more recently, hemicellulases (Collins et al., 2005; Dien et al., 2006; Polizeli et al., 2005; Shallom and Shoham, 2003). Depending upon the nature

Introduction

Elevating concerns regarding global warming and high crude oil prices over recent years have re-ignited public interest in fuels and chemicals derived from renewable

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of the catalysts and the relative severity of the reaction conditions, hemicellulose is depolymerized primarily into either xylan oligomers or monomeric xylose or a mixture of both. We previously reported a new catalytic route for corn stover hemicellulose hydrolysis which employs maleic acid as the catalyst, where the difference in xylose degradation kinetics made maleic acid a superior catalyst to sulfuric acid at high solid-loading reaction conditions (Lu and Mosier, 2007). The preliminary study experimentally identified an optimal reaction condition for the maleic acid-catalyzed hemicellulose hydrolysis: over 90% xylose yield could be achieved with a maleic acid concentration of 0.2 M for 12 min at 170°C (Lu and Mosier, 2007). However, the additive effects of catalyst concentration, reaction temperature and time on the kinetics of this process had not yet been studied systematically. In this study, to obtain an in-depth mechanistic understanding to the catalytic reaction and an optimum reaction condition for the process, the reaction kinetics at a complete set of reaction conditions were investigated. Classic kinetic models (Saeman, and biphasic hydrolysis models) were applied to fit the experimental data, and used to illustrate the detailed kinetics of the reactions. The estimated kinetic constants were evaluated against experimental data and expanded with an empirical Arrhenius-type expression. The refined model was employed to predict the reaction over a wide range of reaction conditions to determine optimal hydrolysis conditions.

Theory

The kinetics of hemicellulose hydrolysis catalyzed by dilute mineral acids or water at hydrothermal conditions has been studied comprehensively, and the development of kinetic models has improved the understanding of the complex reaction (Lee et al., 1999; Wyman et al., 2005b). Due to the compositional complexity of hemicellulose, the hydrolysis reaction is constituted of parallel paths that lead to a complex mixture of sugars and organic acids (Fig. 1a). The published models, however, were primarily focused on xylan solubilization, xylose release, and acetyl fraction hydrolysis. In analogy to Saeman's early work on dilute sulfuric acid catalyzed cellulose hydrolysis (Saeman, 1945), the hemicellulose hydrolysis reaction was modeled as consecutive homogeneous pseudo-first-order steps: xylan is first hydrolyzed to xylose, and the xylose is degraded to furfural once it is liberated from the solid matrix and exposed to the acidic solution. An improved model proposed by Kobayashi and Sakai (1956) was based upon the observation that a biphasic pattern existed during hemicellulose hydrolysis: one part (easy-to-hydrolyze hemicellulose) of the total hemicellulose fraction tends to hydrolyze faster than the other part (hard-to-hydrolyze hemicellulose). Varying slightly among different substrates, the hard-to-hydrolyze fraction typically accounts for about 35% of the total hemicellulose (Wyman et al., 2005b). Figure 1b shows the portion of the hemicellulose hydrolysis reaction often

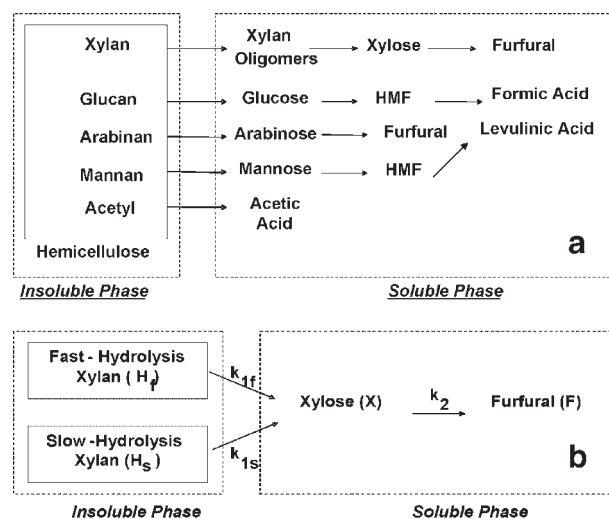


Figure 1. Schematic diagram of (a) complete reaction pathway of the hemicellulose hydrolysis process; (b) the biphasic hydrolysis model for xylan hydrolysis.

modeled assuming biphasic hydrolysis behavior. In order to maximize xylose yield while avoiding the degradation reaction, the kinetic models based on dilute sulfuric acid suggested that high temperatures with short reaction times are required to push the reaction path towards the direction that favors xylose accumulation (Esteghlalian et al., 1997).

Below are the detailed equations for the two classic kinetic models that will be used to analyze this work's experimental data:

Model I (Saeman model)

$$\frac{d[H]}{dt} = -k_1[H] \quad (1)$$

$$\frac{d[X]}{dt} = k_1[H] - k_2[X] \quad (2)$$

$$\frac{d[F]}{dt} = k_2[X] \quad (3)$$

$$[X] \frac{k_1[H_0]}{k_2 - k_1} [\exp(-k_1t) - \exp(-k_2t)] \quad (4)$$

(i.e. $[X]_0 = 0$).

Model II (biphasic hydrolysis model)

$$\frac{d[H_f]}{dt} = k_{1f}[H_f] \quad (5)$$

$$\frac{d[H_s]}{dt} = k_{1s}[H_s] \quad (6)$$

$$\frac{d[X]}{dt} = k_{1f}[H_f] + k_{1s}[H_s] - k_2[X] \quad (7)$$

$$\frac{d[F]}{dt} = k_2[X] \quad (8)$$

$$[X] = \frac{k_{1f}[H_f]_0}{k_2 - k_{1f}} [\exp(-k_{1f}t) - \exp(-k_2t)] + \frac{k_{1s}[H_s]_0}{k_2 - k_{1s}} [\exp(-k_{1s}t) - \exp(-k_2t)] \quad (9)$$

(i.e. $[X]_0 = 0$, $[H_f]_0 + [H_s]_0 = [H]_0$).

Later models were essentially built upon these two classic models with more in depth considerations of the reaction intermediates (e.g., sugar oligomers formation) (Abatzoglou et al., 1986, 1992), or by including mass transfer (Brennan and Wyman, 2004) and heat transfer (Abasaheed et al., 1991) effects. Observations of deviation from first-order kinetics had been reported repeatedly, especially in situations where xylan oligomers are the main products of the hydrolysis reaction (Wyman et al., 2005b; Yang et al., 2004). Indicators of such deviations were reported as solid-loading levels effect (Jacobsen and Wyman, 2002), and the influence of flow rate in flow-through reactor configurations (Liu and Wyman, 2003). The deviations suggested that the over-simplified assumptions did not match the true complexity of the reactions occurring at the solid-liquid interphase. Moreover, a few critics have questioned the comparability of the results of published modeling work: the use of weight-percent of acid concentration (exclusively used in papers reported before 1990) does not match the nonlinearity of H_3O^+ molar concentration (Malester et al., 1992); and the “matrix” effects of the heterogeneous substrate resulting from the interaction of cellulose-hemicellulose-lignin components were often ignored (Abatzoglou et al., 1992), while the effects of mass transfer limitation at solid surface become obvious at different reactor configurations (percolation vs. flow-through vs. batch) (Abatzoglou et al., 1992; Liu and Wyman, 2003). However, numerous studies use the first-order kinetic models for analysis and optimization purposes, and most claim high fitness was achieved between the model and experimental data. Since in this study our focus was to analyze the kinetics of the hemicellulose hydrolysis reaction catalyzed by maleic acid, the classic models (Saeman and biphasic) were applied to our data to obtain insights on the reaction kinetics, though deviations were observed and possible remedies are discussed.

Materials and Methods

Materials

All chemicals used in this study were purchased from Sigma-Aldrich (St. Louis, MO). General lab supplies were purchased from Fisher Scientific (Pittsburgh, PA) and VWR Scientific Products (Batavia, IL), unless otherwise stated

below. Crimp top clear vials (12 mm × 32 mm, 1.5 mL working volume) with TFE/Silicone/TFE liner seals were purchased from Alltech Associates, Inc. (Deerfield, IL). Corn stover was obtained from the National Renewable Energy Laboratory (NREL) as part of the CAFI 2 (the Biomass Refining Consortium for Applied Fundamentals and Innovation) project. NREL washed, dried, and knife-milled the stover to pass a 1/4 in. (6.4 mm) screen (Wyman et al., 2005a). The corn stover was further ground in a Wiley[®] mill with a 1-mm screen to collect 40-mesh sized particles. The ground particles were then air-dried at room temperature to 7.8% moisture content, and the composition of the structural carbohydrates of the corn stover was analyzed with LAP 002 of NREL procedures (Ruiz and Ehrman, 1996).

Methods

Glass vials were used as miniature batch reactors (1.5 mL total volume) for the hemicellulose hydrolysis kinetics study. A modification was made to the vials by the insertion of a 0.003-in. thick brass circle fitted between the cap and liner, in order to allow the seal to withstand the high vapor pressure generated at high reaction temperatures (150–170°C). One hundred grams per liter of solid corn stover (with a moisture content of 7.8%) and 1.2 mL acid solution was loaded into the reactor vials. A total of 135 reactions for corn stover hemicellulose hydrolysis were carried out in the modified miniature glass reactors. The reaction temperatures were set at 150, 160, and 170°C. Maleic acid concentrations were at 0.05, 0.1, and 0.2 M, and the reactions were stopped by immersing the reactor vials into icy water after 5, 10, 15, 30, and 60 min of reaction. Triplicates were run for each of the above-mentioned reaction conditions. Based on the triplicate experiments, standard errors on each data point were computed to indicate 95% confidence intervals (CIs) for each point. The reaction temperature control was achieved with a Techne SBS-4 fluidized sand bath equipped with a TC-8D temperature controller (Cole-Parmer, Vernon Hills, IL). The heat-up profile within the miniature reactors was considered instantaneous (due to the size of the reactor) and was not subtracted while calculating the reaction time. The hemicellulose hydrolysate was diluted 10-times with addition of DI H₂O, and the liquor was filtered through 0.2 μm filter and analyzed for glucose, xylose, arabinose, acetic acid, furfural, and hydroxymethyl furfural (HMF) concentrations by HPLC. The HPLC system employed a Bio-Rad HPX-87H organic acid column (Bio-Rad Laboratories Inc., Hercules, CA) with refractive index detection and Empower software for HPLC operation control and data analysis. The mobile phase was 5 mM sulfuric acid in distilled, deionized water filtered through 0.2 μm nylon filters. Operating conditions for the HPLC column were 60°C with a mobile phase flow rate of 0.6 mL/min. For sample analysis, 50 μL of sample was injected and complete sample elution could be accomplished within 55 min per injection. A standard solution was prepared by dissolving

pure (>99% purity) compounds (glucose, xylose, glycerol, xylitol, furfural, acetic acid, and ethanol) in the HPLC mobile phase. Fractional dilutions of the standard solution ranging from 0.5–4 g/L were prepared to provide standards for HPLC calibration. The linear regression for the curves between computed elution peak area and concentration was computed to give $>0.9999R^2$ -value for all compounds.

Xylose degradation experiments were carried out under the same reaction conditions as described for the corn stover hemicellulose hydrolysis reactions (150–170°C, 0.05–0.2 M maleic acid concentration, 0–60 min reaction time). Under reaction conditions where solid-loading was at 150 g/L, the maximal final xylose concentration (after hemicellulose hydrolysis reaction) would be around 35 g/L. However, if the xylose degradation reaction follows first-order kinetics, the initial xylose concentration should not affect estimated the kinetic parameters. In order to examine the validity of the first-order kinetics assumption, initial xylose concentrations were set at 10 (in the lower concentration vicinity) and 50 g/L (in the higher concentration vicinity).

Parameter estimation for fitting the non-linear kinetic models (Saeman and biphasic) of hemicellulose hydrolysis was computed with SAS 9.1 (SAS Institute Inc., Cary, NC). The Newton–Raphson method was the optimization algorithm used for the SAS “proc model” syntax, which minimized sum of squares of deviation between numerical and experimental values. The iteration for the program was allowed for 100 times and the convergence criteria was set at converge = 0.001. The accountability of the estimated parameters was evaluated with statistical analysis, with which the R^2 and P -values were obtained.

Results and Discussion

Hemicellulose Hydrolysis Experimental Results

The main products from the maleic acid-catalyzed hemicellulose hydrolysis reaction were monomeric xylose and acetic acid, with the degradation product (furfural) concentration at minimal levels (only detectable at the 30 and 60 min data points at 170°C). Therefore, only xylose and acetic acid yields were plotted (Fig. 2). The xylose profile suggests that catalyst concentration weighed more than reaction temperature in improving the xylose yield. Over 85% of xylose yields were obtained with 0.2 M catalyst concentration at all three reaction temperatures, while only slight increases in yield were achieved by increasing the reaction temperature from 150 to 170°C for all three catalyst concentrations; however, the reaction time required for reaching optimal yield was reduced.

A relationship between acetic acid yields with xylose yields was found. At conditions where xylose yields were less than 35%, there were undetectable amounts of acetic acid in the liquid phase. This suggested that the preferentially released xylan fraction was not acetylated. A similar observation had been reported by Belkacemi et al. (1991), who confirmed

that the acetyl groups on the sugar ring stabilize the structure against hydrolysis (therefore the unacetylated xylan fraction was preferentially hydrolyzed). At all of the maximal xylose yield conditions (>85%), the total acetic acid yields were less than 50%. This observation differed from some previously reported results in which they claimed that acetyl group removal was at a rate similar to xylan removal (Maloney et al., 1985). The different result here may be because of the acid catalyst used is less severe than mineral acids used in other reports, where in the mineral acid cases the acetyl groups were removed at a much higher rate. The maximum final acetic acid concentration detected in the liquid phase was around 6 g/L (with 0.2 M catalyst concentration for 60 min at 170°C). This low level of acetic acid concentration should not pose inhibitory effects on down stream ethanol fermentation, according to the studies previously reported (Keating et al., 2006; Palmqvist et al., 1999).

Parameter Estimation

The experimentally obtained kinetic data for hemicellulose hydrolysis in corn stover was analyzed with the Saeman and biphasic hydrolysis models described above. The estimated parameters are tabulated in Table I. The selectivity factor ($S = k_1/k_2$, i.e., the ratio of xylan hydrolysis rate to xylose degradation rate) was used to evaluate the efficiency of the catalytic reaction condition (Mosier et al., 2002). To calculate the overall k_1 value for the biphasic hydrolysis model, the substrate fractional factor ($\alpha = 0.35$, i.e., 35% of the total xylan is slow-hydrolysis xylan) (Wyman et al., 2005b) was used and therefore the overall $k_1 = 0.65k_{1f} + 0.35k_{1s}$.

The Saeman model parameters in Table I suggested that the selectivity factor increased by as much as 36 times as the catalyst concentration increased from 0.05 to 0.2 M, which explained why maximal xylose yields were observed for the reactions with 0.2 M catalyst concentration while the H^+ concentration increased by 3.5 times. Among all the experimentally examined conditions, the 0.2 M catalyst concentration at 150 °C condition resulted in the highest selectivity factor ($k_1/k_2 = 50.0$). Meanwhile, k_1 values were strictly higher than k_2 values in all of the estimated kinetic constants, which implied that all the examined conditions favored xylan hydrolysis over xylose degradation. Two trends in the estimated kinetic constants were observed: at constant temperature, doubling catalyst concentration resulted in a roughly doubling of k_1 values, and in contrast, k_2 values decreased by 2–7 times as the catalyst concentration doubled. The first observation seemed reasonable, where the hydrolysis rate constant was likely proportional to the catalyst concentration; however, the decrease of k_2 could not be explained by our current knowledge on acidic sugar degradation. Based on these estimated k_2 values, the xylose degradation rate decreased as catalyst concentration increased (which corresponded to slightly lower pH conditions). However, it is generally known that at lower pH conditions

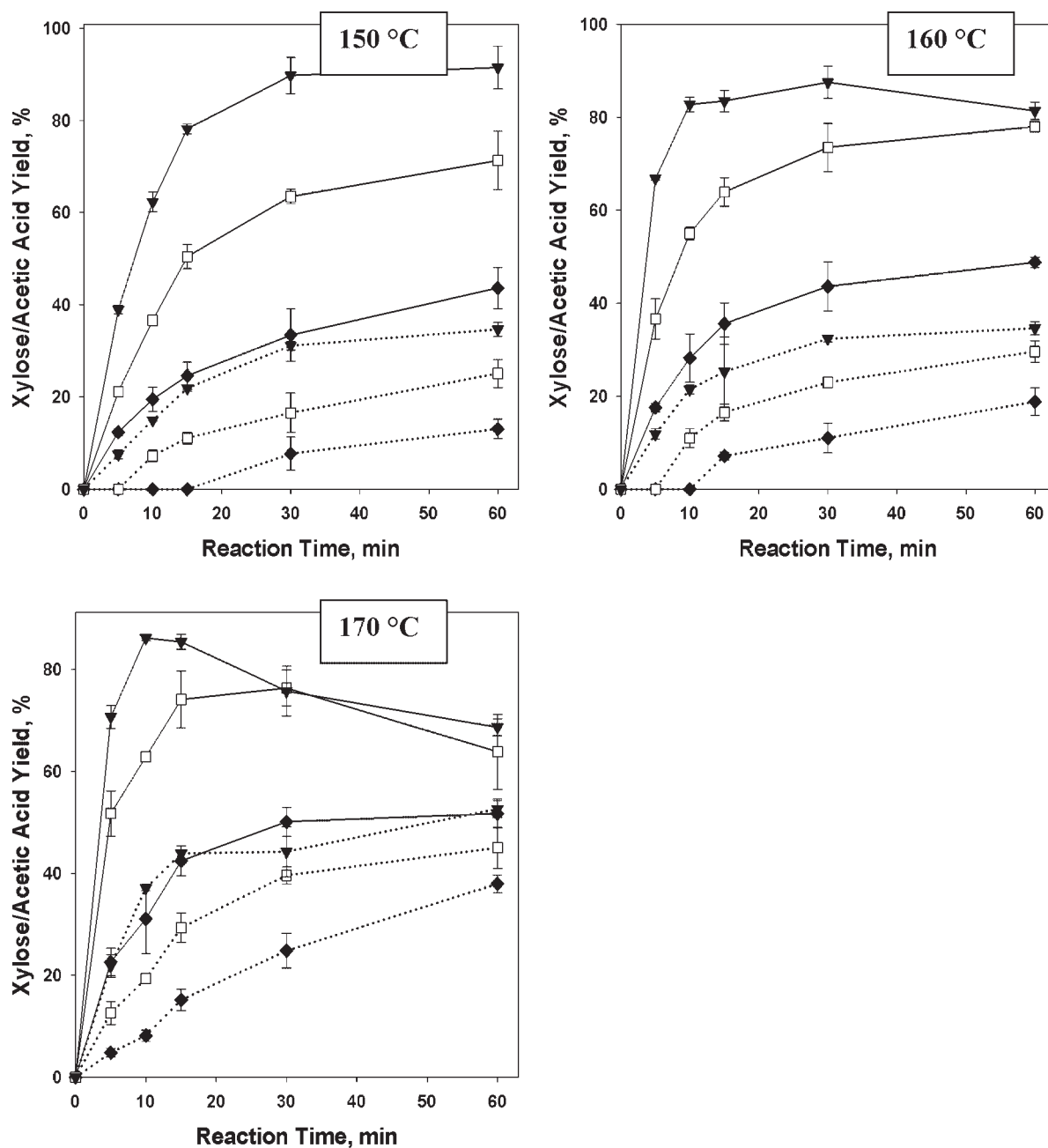


Figure 2. Hemicellulose hydrolysis profile in corn stover by maleic acid at 150, 160 and 170 °C (the error bars represent 95% CIs). Solid lines represent xylose yield, dotted lines represent acetic acid yield ($\blacklozenge$ 0.05 M; $\square$ 0.1 M; $\blacktriangledown$ 0.2 M).

(in the pH 1–3 region), the sugar degradation rate should be higher. Therefore, the estimated k_2 values may not accurately describe actual xylose degradation. Parameter estimation results for the biphasic model were slightly different from those for the Saeman model. The highest selectivity factor ($k_1/k_2 = 69.0$) was obtained at 0.2 M catalyst concentration at 160 °C. Meanwhile, the biphasic hydrolysis model resulted in higher R^2 -values, indicating a better fit to the experimental data. The k_2 values estimated based on the

Saeman and biphasic hydrolysis models were of indistinguishable difference.

Using the estimated kinetic constants listed in Table I, optimal conditions at different temperature and catalyst concentrations were determined (Table II). A severity factor ($\log R_0 = \log[t \exp((T - 100)/14.75)]$) (Abatzoglou et al., 1992) was used to compare the relative “severity” of these modeled optimal conditions. The severity factors fell in a narrow range of values from 3.0 to 3.7, and it was observed

Table I. Estimated kinetics constants for the Saeman and biphasic hydrolysis model.

<i>T</i> (°C) [MA] (M)	Saeman model				Biphasic model					
	<i>k</i> ₁	<i>k</i> ₂	<i>R</i> ²	<i>k</i> ₁ / <i>k</i> ₂	<i>k</i> _{1f}	<i>k</i> _{1s}	<i>k</i> ₂	<i>R</i> ²	<i>k</i> ₁ / <i>k</i> ₂	
150	0.05	0.019	0.014	0.94	1.36	0.015	0.029	0.014	0.95	1.42
	0.1	0.046	0.006	0.96	7.67	0.022	0.130	0.003	0.98	19.9
	0.2	0.100	0.002	0.99	50.0	0.109	0.086	0.002	0.99	50.5
160	0.05	0.032	0.017	0.93	1.88	0.003	0.138	0.001	0.98	50.2
	0.1	0.081	0.006	0.98	13.5	0.153	0.017	0.003	0.99	37.6
	0.2	0.194	0.004	0.98	49.0	0.361	0.079	0.004	0.99	69.0
170	0.05	0.043	0.017	0.97	2.53	0.020	0.118	0.012	0.98	4.52
	0.1	0.123	0.009	0.97	13.7	0.223	0.044	0.008	0.99	20.0
	0.2	0.252	0.008	0.98	31.5	0.433	0.119	0.008	0.98	40.4

that by increasing the overall severity, the reaction time required to reach the optimal yield was reduced. At the 0.05 and 0.1 M catalyst concentration conditions, the extent of final xylose yield increased with higher values of severity factors.

The predicted optimal conditions from the two models were similar: at 0.2 M catalyst concentration, lower reaction temperatures resulted in over 90% xylose yields. Therefore, under the studied experimental conditions, there was no strong support for the reaction to be modeled with the biphasic hydrolysis pattern, even though the introduction of an extra kinetic parameter improved the *R*²-values of the fitting. Therefore kinetic model expansion was performed with the Saeman model only.

Evaluation of Xylose Degradation Constants

The data in the previous section suggest that the xylose degradation kinetic constants ought to be experimentally determined, in order to be compared with those derived by model fitting. Pure xylose degradation experiments were carried out as described in Materials and Methods Section, with initial xylose concentrations set at 10 and 50 g/L. The xylose degradation time-curves are plotted (Fig. 3). By convention, the reaction was treated with first-order kinetic model for both initial concentrations; however, it was

Table II. Comparison of optimal conditions from Saeman and biphasic hydrolysis models.

[MA] (M)	<i>T</i> (°C)	Saeman model			Biphasic model		
		<i>t</i> (min)	Xyl (%)	log <i>R</i> ₀	<i>t</i> (min)	Xyl (%)	log <i>R</i> ₀
0.05	150	60	42.5	3.25	59.1	41.7	3.24
	160	42.5	49.2	3.40	60	49.0	3.54
	170	36.1	54.6	3.62	40.9	51.3	3.67
0.1	150	50	72.6	3.17	60	73.5	3.25
	160	34.1	80.4	3.30	60	76.2	3.54
	170	22.9	81.5	3.42	23.8	75.7	3.44
0.2	150	39.9	92.3	3.07	40.1	92.2	3.08
	160	18.9	91.9	3.04	25.5	94.4	3.17
	170	14	89.3	3.21	15.1	85.6	3.24

observed that the first-order kinetics assumption did not hold for both conditions. At 10 g/L initial xylose concentration, the *R*²-values for the first-order equations dropped from 0.99 at 170°C (Fig. 3a) to 0.86 at 150°C (at which temperature the extent of degradation was less than that at 170°C, data not shown in Fig. 3). Moreover, when 50 g/L initial xylose concentration was applied, the first-order treatment resulted in very poor linear correlation (*R*²-values around 0.56). The HPLC analysis of the reaction products showed a significant amount of xylose dimers formed by a second reaction, as has been noted previously (Fetzer et al., 1953). Since the dimerization reaction is a function of xylose concentration (higher than first-order kinetics), more sophisticated kinetics that include both reactions should be used to model xylose loss at higher xylose concentrations. However, in the present work, xylose concentrations from the hydrolysis of corn stover were low enough that first order kinetics could be used to describe the conversion of xylose to furfural.

Since at 10 g/L initial xylose concentration, the first-order kinetic treatment fit the data well and no condensation xylose dimers were observed by HPLC analysis, these *k*₂ values (shown in Table III) were substituted into the models to obtain the *k*₁ values. The experimentally determined *k*₂ values differed from the *k*₂ values estimated in the previous section (shown in Table I). The *R*²-values for the Saeman model decreased in some conditions; moreover, in two reaction conditions the biphasic model failed to converge. The lowering of *R*²-values may be due to the simplified assumption for xylose degradation kinetics (first-order treatment).

Parameter Expansion for Saeman Model Kinetic Constants

The rate constants (for both the hydrolysis and degradation steps) in the Saeman model were assumed to follow an Arrhenius-type expansion equation:

$$k = k_0[\text{H}^+]^n \exp\left(-\frac{E_a}{RT}\right)$$

where [H⁺] is the aqueous hydronium ion concentration on a molar basis. In order to expand the kinetic parameters, ln(*k*) versus 1/*T* (to obtain *E*_a) and ln(*k*) versus ln([HA] or [H⁺]) (to obtain *n*) curves were plotted, and representative plots are shown in Figure 4. The estimated xylose degradation kinetic constants from Table I could not be expanded to obtain a reasonable Arrhenius plot, which once again suggest that direct estimation of xylose degradation constants from hemicellulose hydrolysis data fails to accurately model the degradation reaction.

In contrast, the parameters estimated in Table III were readily expandable to obtain both *E*_a and *n* values (Fig. 4). The activation energy for the hydrolysis reaction was determined to be 83.3 ± 10.3 kJ/mol (Fig. 4a). Meanwhile, from the experimentally determined xylose degradation

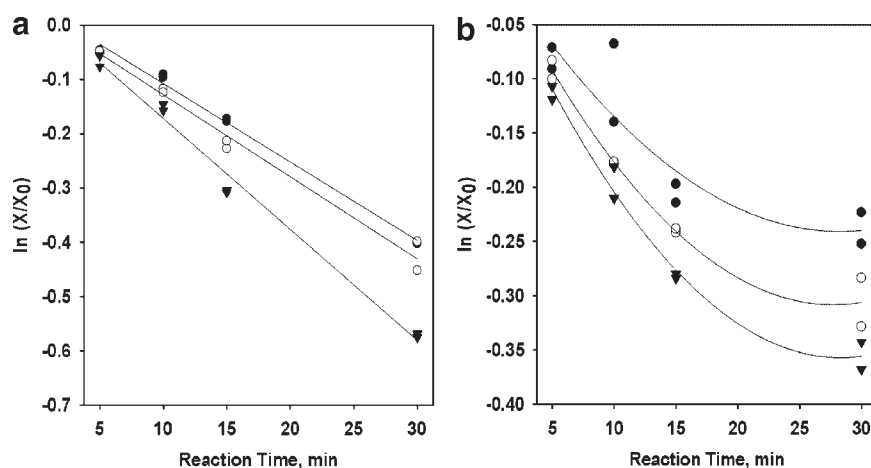


Figure 3. Xylose degradation profile at 170°C, with varying acid concentrations: (a) 10 g/L initial xylose concentration; (b) 50 g/L initial xylose concentration ((●) 0.05 M; (○) 0.1 M; (▼) 0.2 M).

kinetics the activation energy for the degradation reaction was 143.5 ± 9.9 kJ/mol. The activation energy for hydrolysis was significantly lower than the reported E_a values for dilute sulfuric acid catalyzed reaction reported by Bhandari et al. (1984) ($E_a = 171.6$ kJ/mol) and Esteghlalian et al. (1997) ($E_{af} = 129.8$ kJ/mol, $E_{as} = 167.6$ kJ/mol). The lower activation energy implies that maleic acid is a more efficient catalyst than sulfuric acid for hemicellulose hydrolysis, and it also explained why the experimental results suggested catalyst concentration to be much more influential than temperature for obtaining optimal xylose yield. A possible reason for the difference in E_a may be due to the differences in the acid strength between sulfuric and maleic acid. For sulfuric acid, the first proton is fully dissociated in the bulk water solution and the second proton is mostly dissociated at the pH range relevant here. Because the protons acid largely free of the Lewis acid donor (sulfuric acid), the mechanism of hydrolysis is likely to be through specific acid catalysis (rate dependent upon proton concentration, independent of Lewis acid concentration). In contrast, the protons are not fully dissociated from the two carboxylic

groups of maleic acid under similar pH conditions because of its higher pK_a . At pH between 1.5 and 2.5, at one end proton on the carboxylic group is nearly completely dissociated and at the other end the proton is retained. By our hypothesis, the free protons in solution acid act as specific acid catalysts to cleave the β -D-xylopyranosyl bonds while the retained undissociated carboxylic acid may also interact strongly with the -OH groups on the sugar ring to facilitate hydrolysis. The involvement of the undissociated acid form may lead to a change of catalysis mechanism from specific acid catalysis (proton-catalyzed) to general acid catalysis where the Lewis acid donor participates in the reaction. Additional experimental efforts to determine the exact mechanism(s) are required and a rigorous experimental investigation is currently underway.

To determine the n values (Fig. 4b), three different catalyst expressions were used: total catalyst concentration, theoretical proton concentration, and measured proton concentration (considering the buffer capacity of corn stover), all in molar basis. From the slopes of $\ln(k)$ versus ($[HA]$ or $[H^+]$) plots, the estimates for n were obtained

Table III. Estimated kinetics constants for the Saeman and biphasic hydrolysis models with experimentally obtained k_2 values.

T (°C)	[MA] (M)	Saeman model				Biphasic model				
		k_1 (min ⁻¹)	k_2 (min ⁻¹)	R^2	k_1/k_2	k_{1f} (min ⁻¹)	k_{1s} (min ⁻¹)	k_2 (min ⁻¹)	R^2	k_1/k_2
150	0.05	0.013	0.002	0.84	6.50	0.003	0.058	0.002	0.96	11.1
	0.1	0.038	0.002	0.92	19.0	0.020	0.140	0.002	0.98	31.0
	0.2	0.102	0.003	0.99	34.0	n/a	n/a	0.003	n/a	n/a
160	0.05	0.020	0.004	0.71	5.00	0.007	0.122	0.004	0.97	11.8
	0.1	0.080	0.005	0.97	16.0	0.134	0.031	0.005	0.99	19.6
	0.2	0.196	0.005	0.98	39.2	0.329	0.094	0.005	0.98	49.4
170	0.05	0.038	0.011	0.91	3.45	0.019	0.121	0.011	0.98	4.97
	0.1	0.127	0.014	0.92	9.07	0.169	0.080	0.014	0.92	9.85
	0.2	0.261	0.020	0.71	13.0	n/a	n/a	0.020	n/a	n/a

n/a represents conditions where the model failed to converge.

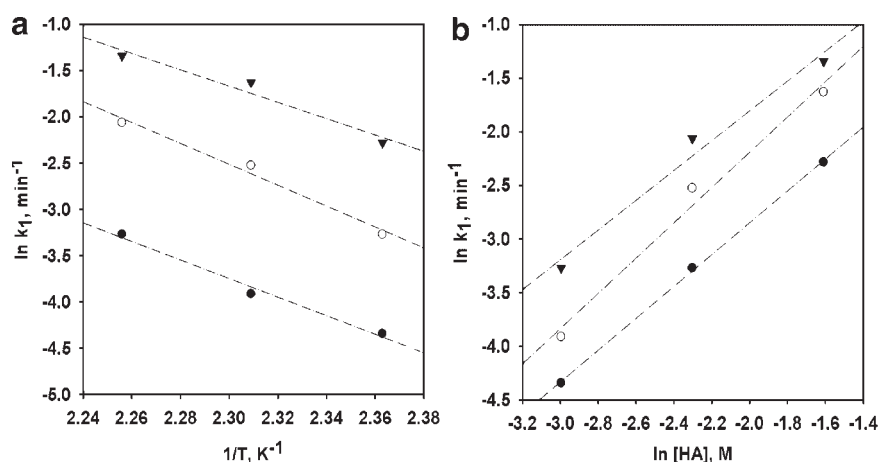


Figure 4. Representative Arrhenius plots for estimating the (a) E_a and (b) n values for kinetic constants expansion ((●) 0.05 M; (○) 0.1 M; (▼) 0.2 M).

(Table IV). The results suggest that using the theoretical proton concentration resulted in n values of 2.6, which did not match the physical interpretation of the hydrolysis reaction (should not be higher than second-order reaction). Meanwhile, the n values based on $[HA]$ and $[H^+]$ (measured) were surprisingly comparable. The n values determined for k_2 ranged from 0.15 to 0.47, which indicated that under minimal sugar degradation conditions (as in this study), the relative acidity or acid catalyst concentration did not affect the degradation behavior to a kinetically significant extent.

Through this series of data analyses, the kinetic constants for hydrolysis (k_1) and degradation (k_2) were expanded to the following forms:

$$k_1 = 2.37 \times 10 [HA]^{1.51} \exp(-83.3/RT) \text{ min}^{-1} \quad (10)$$

$$k_2 = 2.18 \times 15 [HA]^{0.29} \exp(-143.5/RT) \text{ min}^{-1} \quad (11)$$

These two expanded forms of kinetic constants were further fitted into the Saeman model:

$$[X] = \frac{k_1 [H]_0}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

An analytical treatment similar to the one employed by Esteghlalian et al. (1997) was adapted here: since at the optimal xylose yield condition $dX_{\max}/dt = 0$, by setting the Saeman model derivative (Eq. 4) equaling to 0, the reaction

time required to reach the optimal xylose yield could be calculated:

$$t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \quad (12)$$

Therefore, $t_{\max}$ can be determined at any combination of catalyst concentration and reaction temperatures. The determined $t_{\max}$ values were re-substituted into the Saeman model equation, and the corresponding optimal xylose yield was calculated. In this study, catalyst concentrations were varied from 0.05 to 0.2 M (within the range of the catalyst concentrations for the experiments). The temperatures were spanned between 120 and 200°C (whereas in the experiments the reaction temperatures were between 150 and 170°C). Therefore, the model assumed that experimentally determined activation energy (in the temperature window between 150 and 170°C) would not vary in the expanded temperature range. In the Arrhenius equation: $k = A \exp(-E_a/RT)$, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the reaction temperature in Kelvin. The above assumption was based on the fact that temperature dependence of the pre-exponential factor A has been compensated by the activation energy E_a , therefore the equation should be valid over 50°C with a deviation of less than 10^{-4} (Burnham and Braun, 1999). The simulation results based on the expanded Saeman model are shown in Figure 5.

The model suggests that a combination of higher catalyst concentration and lower reaction temperature lead to the optimal xylose yield (Fig. 5a). On the other hand, the only benefit of raising reaction temperature was that the time required to achieve optimal xylose yield could be reduced; however, high optimal xylose yield can also be achieved by increasing the catalyst concentration (Fig. 5b). The main reasons for the simulation results were explicit: the activation energy for hydrolysis being significantly lower

Table IV. Estimated n values for k_1 and k_2 terms.

N	$[HA]$	$[H^+]$ (theoretical)	$[H^+]$ (measured)
k_1^a	1.51 ± 0.13	2.57 ± 0.22	1.64 ± 0.15
k_2^b	0.29 ± 0.14	0.50 ± 0.23	0.32 ± 0.15

^aSlope R^2 -values between 0.96 and 0.99.

^bSlope R^2 -values between 0.72 and 0.98.

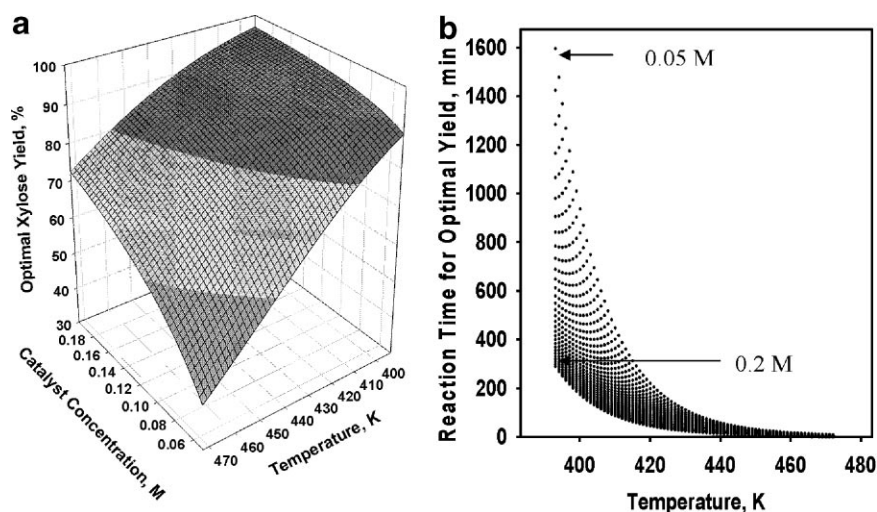


Figure 5. Simulation results of optimal xylose yield from the expanded Saeman model: (a) optimal xylose yield surface; (b) $t_{\max}$ for reach $X_{\text{opt}}\%$ with respect to temperature (120–200°C, 0.05–0.2 M maleic acid catalyst concentration).

than that for degradation, and the catalyst concentration term being much more influential than temperature on the hydrolysis reaction coupled with the minimal effect of catalyst concentration on xylose degradation. Compared to the reported results based on sulfuric acid, where the E_a for xylan hydrolysis was strictly higher than that for xylose degradation, maleic acid lowered the barrier for the hydrolysis reaction, and thus made possible a lower temperature hemicellulose process.

Because the model simulation was based on the assumption that activation energy would not change over a wide range of reaction temperatures, the modeled data, especially those indicating maximal xylose yields at lower temperatures, should be selectively examined by experiments to confirm the predictions. Since the highest xylose yield predicted from the model was reached at 120°C with 0.2 M catalyst concentration for about 5 h of reaction, this particular reaction condition was examined. On the other end, the 180°C reaction profile was also experimentally determined, and both are shown in comparison with the model prediction (Fig. 6).

The 120°C experimental data did not match well with the model predictions (Fig. 6b): the xylose yield reached 80% after 3 h of reaction, and the curve remained at this level from 3 to 5 h reaction time. The acetic acid detected in the liquid phase was less than 30% of potential yield, which corresponded well with the observations at the 150–170 °C reaction conditions. The experimental data being lower than predicted xylose yield may be attributed to the biphasic hydrolysis pattern becoming dominant at lower temperatures as removal of acetyl substitutions on the xylan backbone is significantly reduced, and the slow-hydrolysis xylan fraction being resistant to the catalyst action, thus leading to lower-than-predicted xylose yields. In Figure 6b, two xylan hydrolysis phases were shown and separated, with a fast-

phase between 0–2 h of reaction, and a slow-phase between 3 and 5 h; meanwhile, there was a transition zone between 2 and 3 h where the kinetics started to slow down. Therefore, inclusion of hydrolysis of the xylan side chains (acetate, arabinose, etc.) in future models of hemicellulose hydrolysis may help to improve the predictive power of this model. Our hypothesis was that biphasic or even multi-phasic xylan hydrolysis patterns may exist at even lower reaction temperatures, and this was illustrated by an additional set of experiment conducted at 100°C (Fig. 6a). A fast-phase of xylan hydrolysis between 0 and 12 h and a slow-phase between 12 and 18 h was observed. We believe that such biphasic pattern becomes overlooked at higher reaction temperatures as the reaction rate for the fast phase increases and is completed quickly. Therefore, at 150–170°C Saeman model fits the experimental data well. No biphasic xylan hydrolysis pattern was observed because the slow phase was completed before the first reaction time (5 min) was complete. This is illustrated in the 180°C reaction profile (Fig. 6c). The 180°C reaction profile matched quite well with the prediction curves based on the expanded Saeman model (Fig. 6c), indicating that the applicability of the expanded Saeman model for reaction temperatures higher than 150°C. However, furfural concentrations became more significant at 180°C (as high as 3.4 g/L at the end of 15 min of reaction). Therefore, it is not desirable to increase the reaction temperature to be higher than 170°C for optimization purpose.

Both the experimental data and model suggest that higher acid loadings should produce higher xylose yields. Since the catalyst cost will be closely associated with final ethanol production economics, it is more desirable that lower catalyst loading to be applied. However, from a kinetic modeling analysis standpoint, it is of interest to see whether the model prediction holds true at higher acid loadings.

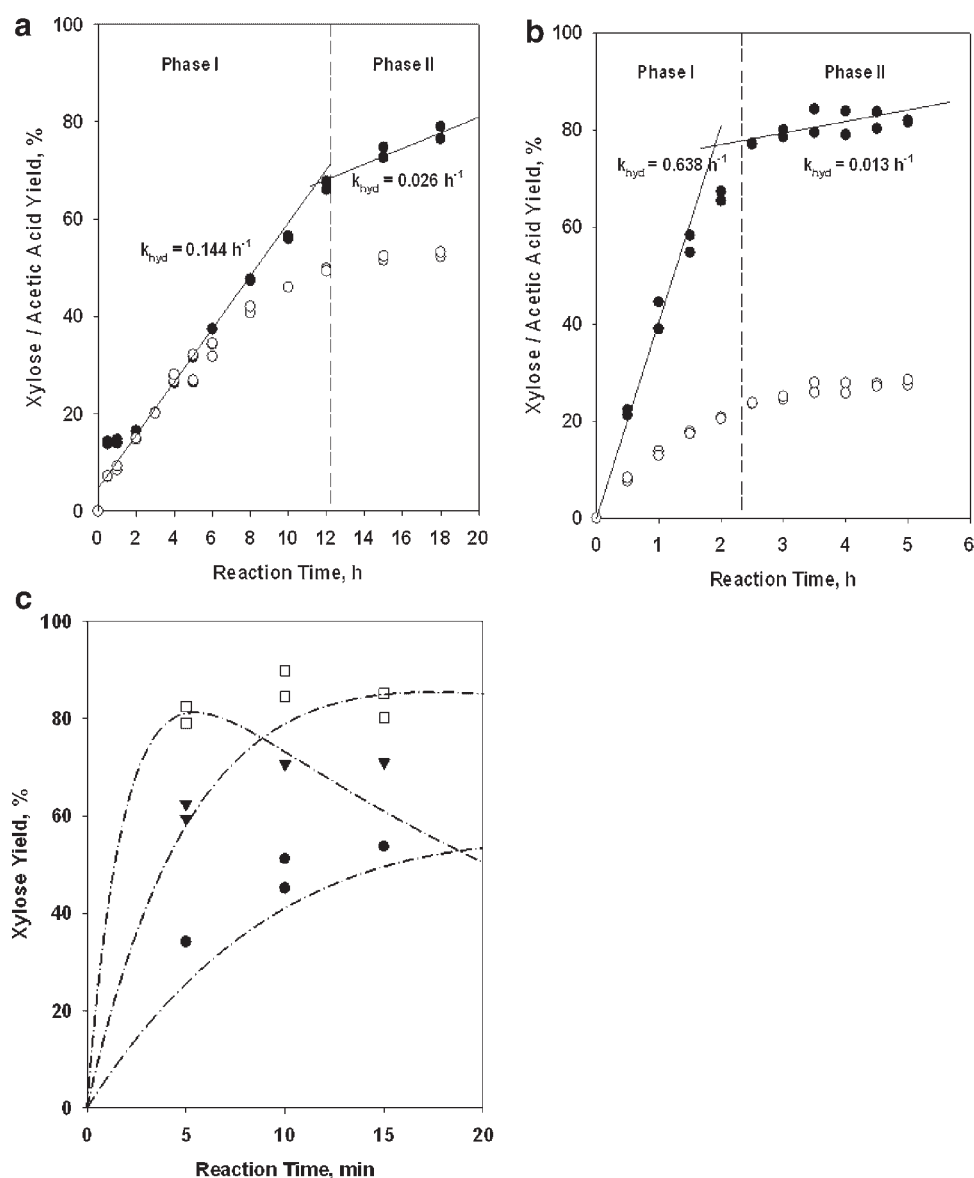


Figure 6. Xylose/acetic acid yields of hemicellulose hydrolysis reaction at (a) 100 °C ((●) xylose, (○) acetic acid) with 0.2 M maleic acid, where biphasic xylan hydrolysis pattern was observed (dotted line represents modeled xylose yield); (b) 120 °C ((●) xylose, (○) acetic acid) with 0.2 M maleic acid, where biphasic xylan hydrolysis pattern was observed (dotted line represents modeled xylose yield); (c) 180 °C ((●) 0.05 M, (▼) 0.1 M, (□) 0.2 M) with comparison to corresponding expanded Saeman model curves.

Therefore, 1.0 M maleic acid solution was prepared for examining the hemicellulose hydrolysis reaction at 150 °C, with experimental data shown in Figure 7. Under these conditions, a xylose yield of 96.8% of theoretical was reached within 15 min of reaction, while around 52% of acetyl was released into the liquid phase as acetic acid. The experimental data matches the model result well: from the model analysis, at a reaction temperature of 150 °C, increasing catalyst loading to 0.25, 0.5, and 1.0 M would result in xylose yields of 93.0%, 96.4%, and 98.2%, respectively; compared to 91.5% at 0.2 M catalyst loading. The theoretical values suggest that only 1.5–6.7% xylose yield improvements can be achieved by increasing the catalyst loading by $\frac{1}{4}$ to

5-folds. While near-quantitative xylose yields can be achieved, large increases of acid concentration are required. Optimization of a process using maleic acid to hydrolyze hemicelluloses must take these diminishing returns (xylose) for increased cost (maleic acid) into account.

Conclusions

The hemicellulose hydrolysis reaction in corn stover, catalyzed by maleic acid, was studied by kinetic modeling analysis. The monomeric xylose present in the liquid phase was a key indicator of the extent of the reaction, thus it was

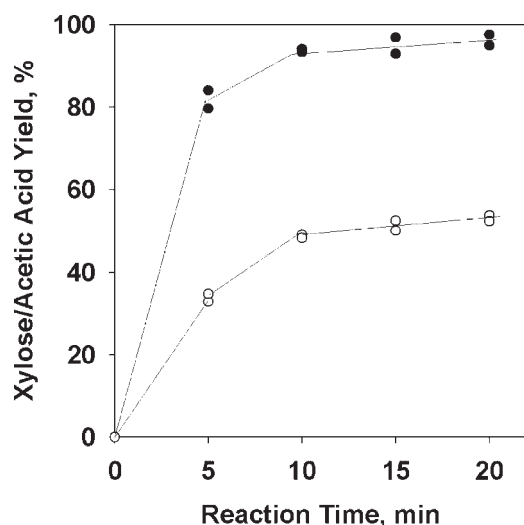


Figure 7. Xylose/acetic acid yields of hemicellulose hydrolysis reaction at 150°C ((●) xylose, (○) acetic acid), with 1 M maleic acid catalyst loading.

the target for the modeling analysis. Initially, both Saeman and biphasic hydrolysis models were applied to the experimental data. At higher temperatures (150–170°C) the Saeman model had the same predictive power as the bi-phasic model. However, experimental results at 120°C (0.2 M maleic acid) indicated that biphasic phenomena may become dominant at lower temperatures, due to insufficient acetyl removal. Nevertheless, near-quantitative xylose yields can be reached with a high catalyst loading (1 M). The results suggest that due to the complexity of hemicellulose composition, different models should be specifically developed for different temperature ranges (Saeman model for 150–200°C, and biphasic model for 100–140°C). A combination of experimental data and modeling analysis concludes that 80–90% xylose yields can be achieved at reaction temperatures between 100 and 150°C with maleic acid concentration 0.2 M or higher.

The xylose degradation constants directly estimated from hemicelluloses hydrolysis data decreased with increasing maleic acid concentration, which contradict the generally held view on sugar degradation. Additionally, Arrhenius-type expansion could not be made with the directly estimated parameters. Therefore, xylose degradation kinetic constants were determined experimentally using reagent grade xylose in the presence of aqueous acid solutions. When the experimentally determined degradation constants were integrated into a complete hemicelluloses hydrolysis the model, a drop in R^2 -values was observed. This could be explained by the loss of xylose to condensation reactions to form xylose dimmers at higher xylose concentrations (Ball and Jones, 1958; Nimlos et al., 2007) in addition to furfural formation. Condensation products were observed by HPLC analysis of pure xylose degradation solutions at high initial xylose concentration (50 g/L). The expanded Saeman model

suggests that a higher catalyst concentration and lower reaction temperature results in high xylose yield, because the E_a for xylan hydrolysis is significantly lower than the E_a for xylose degradation. A difference in activation energy for xylose degradation separates maleic acid from sulfuric acid catalytic behavior, which requires higher temperature and shorter reaction time to achieve optimal xylose yields. A difference in catalytic mechanism, either for hydrolysis or in sugar degradation, between maleic and sulfuric acids may explain these observations. Because maleic acid is a weaker acid than sulfuric acid, protons are only partially dissociated from maleic acid under the reaction conditions. The mechanism of general acid catalysis, proton mediated transfer associated with proton donor (maleic acid) may explain these results.

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