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Dilute Acid Hydrolysis of Sugar Cane Bagasse at High Temperatures: A Kinetic Study of Cellulose Saccharification and Glucose Decomposition. Part I: Sulfuric Acid as the Catalyst

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Supporting Information

ABSTRACT: The kinetics of sugar cane bagasse cellulose saccharification and the decomposition of glucose under extremely low acid (ELA) conditions, (0.07%), 0.14%, and 0.28% H_2SO_4, and at high temperatures were investigated using batch reactors. The first-order rate constants were obtained by weight loss, remaining glucose, and fitting glucose concentration profiles determined with HPLC using the Saeman model. The maximum glucose yields reached 67.6% (200 °C, 0.07% H_2SO_4, 30 min), 69.8% (210 °C, 0.14% H_2SO_4, 10 min), and 67.3% (210 °C, 0.28% H_2SO_4, 6 min). ELA conditions produced remarkable glucose yields when applied to bagasse cellulose. The first-order rate constants were used to calculate activation energies and extrathermodynamic parameters to elucidate the reaction mechanism under ELA conditions. The effect of acid concentration on cellulose hydrolysis and glucose decomposition was also investigated. The observed activation energies and reaction orders with respect to hydronium ion for cellulose hydrolysis and glucose decomposition were 184.9 and 124.5 kJ/mol and 1.27 and 0.75, respectively.

1. INTRODUCTION

Climate change and rising oil prices combined with strategic needs for energy production have motivated an unprecedented effort to produce alternative fuels. Brazil stands out as the country with the most advanced alternative fuel-related technologies and policies in the world due to its pioneering use of sugar cane-based ethanol as fuel since the 1970s.[1]

In addition to the accumulated experience in ethanol production, highly selected crop varieties, sophisticated industrial processes, climate, and availability of arable lands may allow Brazil to continue to be a leader in ethanol production technology.[1] There are many strategies for the production of fermentable sugars from biomass. Therefore, it is very important to investigate and optimize strategies for processing the biomass in order to minimize the cost of production. The optimal strategy will depend on the availability, type (i.e., wood or nonwood), and composition of biomass that will be processed. In Brazil, the most abundant biomass is sugar cane bagasse. According to the last national crop survey released by the Brazilian National Company of Supply (CONAB), the estimated harvest during the 2010/2011 season is expected to reach 651.5 million tons, a 7.8% increase relative to the 2009/2010 season.[2] However, to maintain a leading position in a competitive field, Brazil needs to maintain consistent investments in generating new technologies to increase the production of ethanol per unit of planted area. Within this context, the conversion of lignocellulosic materials into fermentable sugars for ethanol production has been considered as a promising route to achieve the level of production necessary to supply world demand without increasing the planted area.[1]

The conversion of lignocellulosic materials into fermentable sugars can be achieved through acid or enzymatic hydrolysis. Acid hydrolysis can be classified into two categories: concentrated and dilute. Concentrated acid hydrolysis requires reactors that are resistant to corrosion, and the acid must be recovered after hydrolysis to make the process economically feasible. Enzymatic hydrolysis requires pretreatment of lignocellulosic material to improve accessibility and large investments in genetic engineering to develop modified microorganisms that are capable of synthesizing hydrolytic enzymes on a large scale at low cost. Therefore, dilute acid hydrolysis has many advantages compared with concentrated acid and enzymatic hydrolysis, such as reduced corrosion, shorter reaction times, and higher reaction rates.[3,4]

In pilot and industrial[5] scales, processes employing acid hydrolysis such as Dedini Rapid Hydrolysis[6] (DRH), Scholler,[7] Madison,[8] Grethlein,[9] and Two-Stage[10] have usually been performed with dilute sulfuric acid at temperatures ranging from 170 to 240 °C.[11] The lack of an operating commercial cellulosic ethanol plant is related to the technical and operational difficulties that result in a high cost of the final product, which is approximately US$0.80 per kg of ethanol.[1] This cost must compete with the cost of ethanol production from sugar cane sucrose (US$0.35 per kg),[1] referred to as first-generation ethanol

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and corn starch (US$0.27 per kg).[1] Part of the final product cost is based on the requirements of high temperatures and pressures for dilute acid hydrolysis. In a sugar and alcohol plant, this cost is minimized by bagasse burning, which provides steam for the boilers and electric energy consumed in the process.[1] Another difficulty arises from the need to neutralize the acid solution that contains the sugars, adjusting the pH to allow for the fermentation process. In general, calcium hydroxide is used to neutralize the acid solution, and it cannot be reused. In addition, the reaction between calcium hydroxide and sulfuric acid produces calcium sulfate (gypsum) that requires disposal. These are the main factors contributing to the high cost of the technology. In order to achieve acceptable levels of commercialization, the costs related to consumption and reuse of acid must be reduced, the efficiency in biomass conversion to sugars must be improved, and excessive formation of degradation sugar products that inhibit the fermentation process must be avoided.[12,13]

Within this context, the National Renewable Energy Laboratory (NREL) developed a dilute acid hydrolysis process for lignocellulosic biomass, which occurs under extremely low acid (ELA) conditions of sulfuric acid at low concentration, 0.07 wt %.[14−19] According to Torget et al.,[18] Kim et al.,[19] Xiang et al.,[14,15] and Ojumu et al.,[20,21] there are distinct advantages of using the ELA conditions. The low acidity minimizes gypsum production, and the corrosion characteristics of the ELA conditions are similar to those of neutral aqueous reactions so that standard-grade stainless steel equipment can be used instead of high cost nickel alloy equipment. The ELA conditions produce a significant cost savings in equipment relative to the other dilute acid hydrolysis processes. A process using the ELA conditions also qualifies as a "green technology" because it has a minimal environmental impact. Recent advancements in this technology have developed the acid hydrolysis process such that it can compete with the enzymatic hydrolysis process in overall process economics. In addition, recent findings at NREL have proven that yields of approximately 90% are attainable under the ELA conditions.[18,19] Therefore, the ELA hydrolysis process has great potential to produce fermentable sugars. The literature data on the acid hydrolysis of glucan under the ELA conditions are limited to those published by NREL and its co-workers[14−19] and Ojumu et al.[20,21] at the present time.

The aim of this study was to investigate the saccharification kinetics of cellulose obtained from sugar cane bagasse and the decomposition of glucose under extremely low acid (ELA) at high temperature conditions, employing sulfuric acid as the catalyst. In addition, this investigation was undertaken to compare the kinetic data provided by the experiments using the ELA conditions (0.07% H_2SO_4) with 0.14% and 0.28% sulfuric acid, i.e., two- and four-fold increases in H_2SO_4 concentration relative to the ELA conditions. The comparison between these data may reveal possible further insights into the hydrolysis reaction mechanism, and consequently, the potential application of the ELA conditions in the production of fermentable sugars from sugar cane bagasse cellulose, one of the most abundant biomass materials available in Brazil.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Sodium hydroxide and sulfuric acid (95−98%) were purchased from Qhemis (Brazil). Anthraquinone (98%) was provided by Lwarcel Cellulose (São Paulo, Brazil). D-glucose was purchased from Vetec (Brazil). Chromatography standards cellobiose, D-glucose, D-xylose, L-arabinose, acetic acid (49−51%), formic acid (49−51%), 5-hydroxymethyl-2-furfuraldehyde (HMF), and 2-furfuraldehyde (furfural) were purchased from Sigma-Aldrich.

2.2. Sugar Cane Bagasse Preparation. Sugar cane bagasse was provided by the Ipiranga ethanol and sugar company, Descalvado, São Paulo, Brazil. Raw bagasse was treated with water at 70 °C for 1 h with mechanical stirring to remove sugars remaining after the milling process. Fiber and pith fractions were separated by submitting raw bagasse to a wet depithing procedure. The depithing was performed using a sieve system containing two screens of 16 (1.19 mm) and 60 (0.250 mm) mesh. A continuous water flow was used to force the pith fraction to pass through a 16 mesh screen while fiber fraction was retained on this screen. Depithed bagasse was air-dried until a 7.7% equilibrium moisture content was achieved. The chemical composition of depithed bagasse was analyzed according to TAPPI standard methods for extractives,[22] cellulose and hemicelluloses,[23] Klason soluble and insoluble lignin,[24] and ash.[25]

2.3. Hemicelluloses Extraction. Hemicelluloses extraction was performed in a 1000 mL Parr reactor. The reactor was loaded with 65 g of depithed bagasse containing 7.7% moisture content and 715 mL of distilled water. The water quantity added to the reactor was calculated considering the bagasse moisture content to produce a solid to liquid ratio of 1:12. The reactor was heated to 160 °C and maintained at this temperature for 1 h. The heating time required to reach 160 °C was 70 min. The reactor pressure at 160 °C was measured and found to be 80 psi. After hydrolysis, the heating was stopped, and the reactor was quenched in an ice bath and depressurized. The prehydrolyzed depithed bagasse was washed with water to remove sugars and oligomers released during the hydrolysis. In order to reduce moisture content, prehydrolyzed bagasse was centrifuged for 30 min in ARNO centrifuge equipment. Afterward, moisture content was determined by an OHAUS-MB 200 dry-weight scale set at 105 °C for 3 h and found to be 59.0%.

2.4. Soda Anthraquinone Pulping. Soda anthraquinone pulping of prehydrolyzed bagasse was performed in a 1000 mL Parr reactor. The reactor was loaded with 110.4 g of prehydrolyzed bagasse containing 59% moisture content, 9.34 g of NaOH (16% alkali expressed as Na_2O), 67.9 mg of anthraquinone (0.15%), and 523 mL of distilled water.[26] The water quantity added to the reactor was calculated considering the prehydrolyzed bagasse moisture content to produce a solid to liquid ratio of 1:13. The chemicals added to the reactor were calculated taking into account the prehydrolyzed depithed bagasse on dry weight basis. The reactor was heated to 160 °C and maintained at this temperature for 1 h. The heating time required to reach 160 °C was 75 min. The reactor pressure at 160 °C was measured and found to be 80 psi. At the end of the allotted time, the heating was stopped, and the reactor was quenched in an ice bath. The pulp was defibered, and the black liquor was removed with filtration. This procedure was repeated three times. The obtained pulp was washed with water until the water was at pH 6. In order to reduce the moisture content, the pulp was centrifuged for 30 min in ARNO centrifuge equipment. Then, the moisture content was determined using an OHAUS-MB 200 dry-weight scale set at 105 °C for 3 h and found to be 66.8%.

2.5. Batch Kinetic Experiments. All batch kinetic experiments were performed using sealed tubular reactors. The reactors (16.0 cm^3 internal volume) were constructed of stainless steel 316 L tubing (25.0 mm OD × 15.7 mm ID × 83.2 mm length).

Table 1. Chemical Composition of the Materials

material	cellulose (%)	hemicelluloses (%)	lignin (%)	ash (%)	extractives (%)
depithed sugar cane bagasse	49.49 ± 0.31	24.34 ± 0.78	22.69 ± 0.08	0.34 ± 0.03	1.8 ± 0.67
prehydrolyzed depithed bagasse	55.22 ± 0.25	17.54 ± 0.22	24.08 ± 0.30	0.59 ± 0.05	–
bagasse cellulosic pulp	88.32 ± 0.07	11.31 ± 0.09	1.45 ± 0.07	0.46 ± 0.04	–

The reactors were equipped with self-sealed O-ring closures made of polytetrafluoroethylene (PTFE) resistant to high temperatures (>250 °C), and the cap screw was made of aluminum.

For hydrolysis of the cellulosic pulp, the reactors were loaded with 0.6 g of cellulosic pulp (on dry basis) and 12.0 mL of 0.07%, 0.14%, or 0.28% H_2SO_4 to reach a solid to liquid ratio of 1:20. The samples were hydrolyzed at 180, 190, 200, 210, 215, 220, 225, and 230 °C for various reaction times. For glucose decomposition, the reactors were loaded with 5.0 mL of acid−glucose solution containing 0.07%, 0.14%, or 0.28% H_2SO_4. The glucose decomposition study was conducted at 200, 210, and 220 °C for various times.

The reactors were submerged in a glycerin bath set at the desired reaction temperature. The heat transfer experiments showed that the contents in the reactors achieved the desired reaction temperature in 3 min. After the desired reaction time had elapsed, the reactors were removed from the bath and rapidly quenched in an ice bath to stop the reaction. The contents of the reactors were collected and then analyzed by high performance liquid chromatography (HPLC) for cellobiose, glucose, xylose, arabinose, formic acid, furfural, and HMF. The remaining cellulose was filtered using a sintered glass funnel ASTM 10−15M, rinsed in distilled water, and then dried at 60 °C in an oven for 12 h and at 60 °C under reduced pressure (100 mbar) for further 12 h, stored in a desiccator and weighed. The cellulose remaining was calculated as follows

$$\text{Cellulose remaining, } \% = X \times 100 = \left(\frac{m_{\text{cel}_t}}{m_{\text{cel}_0}}\right) \times 100 \qquad (1)$$

where m_{cel0} and m_{celt} are the weights of cellulosic pulp at time 0 and t, respectively.

2.6. Analysis of the Hydrolysates. The chemical composition of the hydrolysates was determined by HPLC using Shimadzu chromatography equipment equipped with a pump (LC-10AD), a system controller (SCL-10A), a refractive index detector (RID-6A), an UV−vis detector (SPD-10A) set at 274 nm, and an oven (CTO-10A). Cellobiose, glucose, xylose, arabinose, and formic acid were separated and quantified using a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) at 45 °C with 0.005 mol/L H_2SO_4 as the eluent and a flow rate of 0.6 mL/min, while 2-furfuraldehyde (furfural) and 5-hydroxymethyl-2-furfuraldehyde (HMF) were separated and quantified using an RP 18 (C_{18}) Hewlett-Packard column (200 mm) at 25 °C with acetonitrile:water (1:8) with 1% acetic acid as the eluent and a flow rate of 0.8 mL/min. For the analysis of sugars and formic acid, the samples were filtered through a Sep Pak C_{18} filter (Waters) prior to chromatography, whereas for furfural and HMF analyses, the samples were filtered through a 0.45 μm membrane (Millipore) before injection (20 μL).

3. RESULTS AND DISCUSSION

Sugar cane bagasse is composed of two fractions: fiber bundles and pith. Pith contains higher ash content (5.4%) than the fiber fraction (1.1%).[27] According to the studies performed by Saeman,[28] biomass exhibits a buffering capacity for acids correlated with its ash content. As the ELA conditions employ low acid concentrations, it is expected that the ash content will interfere with the hydrolysis yields and sugar decomposition. Therefore, the study of the saccharification kinetics of sugar cane bagasse requires the separate study of the bagasse fractions: fiber and pith. The chemical composition of depithed bagasse was analyzed using TAPPI standard methods and is shown in Table 1.

Hemicelluloses are more easily hydrolyzed than cellulose in acidic media at high temperatures. In addition, sugars from hemicelluloses, xylose, arabinose, and glucose are degraded into furfural and 5-hydroxymethyl-2-furfuraldehyde (HMF), contaminating the hydrolysate with excessive amounts of degradation products.[29] Therefore, in order to investigate the saccharification kinetics of cellulose from depithed bagasse, it is necessary to remove the hemicelluloses fraction from the starting material. With this in mind, depithed bagasse was submitted to a hemicelluloses extraction process in order to remove the maximum possible percentage of hemicelluloses from the starting material without affecting the cellulose amorphous fraction. After the hemicelluloses extraction process, prehydrolyzed depithed bagasse was delignified using the soda anthraquinone method. The soda anthraquinone method is a pulping process that achieves a high degree of delignification for sugar cane bagasse.[30] Anthraquinone also acts as a protecting agent against the oxidation of end carbonyl groups of cellulose chains, preventing alkaline depolymerization. The chemical compositions of prehydrolyzed depithed bagasse and pulp obtained through the soda anthraquinone method were also determined by using TAPPI standard methods[22−25] and are shown in Table 1. A flowchart showing the pretreatment steps used to prepare sugar cane bagasse cellulose is shown in Figure 1. The cellulosic pulp, with low hemicelluloses and ash content, was used to investigate the saccharification kinetics of sugar cane bagasse cellulose.

3.1. Kinetic Models. *3.1.1. Cellulose Hydrolysis.* Saeman[28] proposed the first kinetic model for cellulose hydrolysis from experiments using wood free of hemicelluloses obtained from Douglas fir in a batch reactor. Dilute acid hydrolysis was described using two consecutive pseudohomogeneous first-order reactions as described by the reaction scheme as follows

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Degradation products}$$

The hydrolysis of the $\beta(1\rightarrow4)$ glycosidic bonds of cellulose follows first-order reaction kinetics, as is well established.[31,32] The first-order rate constant for acid hydrolysis of cellulose was evaluated by eq 2 as follows[33]

$$\ln X = -k_1 t \qquad (2)$$

where the term X is the cellulose remaining fraction (eq 1).

Under these conditions, the Saeman model[28] showed that the hydrolysis of cellulose is described by following

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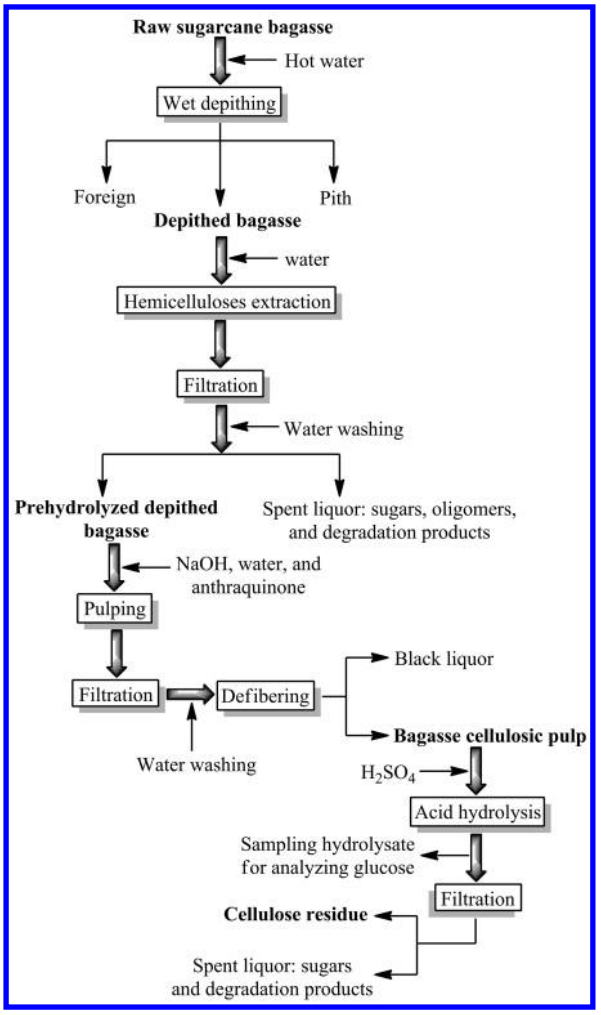

Figure 1. Flowchart of the steps used in the pretreatment of sugar cane bagasse.

equation

$$G = C_0\left(\frac{k_1}{k_2 - k_1}\right)(e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

where G (g/L) is the glucose concentration, C_0 (g/L) is the cellulose concentration expressed as potential glucose (C_0 = 48.3 g/L), k_1 and k_2 (min^{-1}) are the first-order rate constants for cellulose hydrolysis and glucose decomposition, and t (min) is the reaction time.

Residual cellulose decreases constantly during the hydrolysis reaction, and the amount of decomposition products also increases constantly, whereas the amount of glucose produced increases, reaches a maximum (given by eq 4), and then decreases. The maximum glucose concentration and the time in which the maximum concentration is reached are given by eqs 4 and 5

$$G = C_0\left(\frac{k_2}{k_1}\right)^{(k_2/k_1 - k_2)} \quad (4)$$

$$t_{max} = \left(\frac{\ln k_2 - \ln k_1}{k_2 - k_1}\right) \quad (5)$$

There have been several modifications for the kinetic model originally suggested by Saeman. According to the Saeman kinetic model (eq 3), glucose monomer is the only sugar product in the hydrolysate. In addition, cellulose hydrolysis cannot be treated as homogeneous, as it contains a crystalline and an amorphous fraction. The acid depolymerization of both cellulose fractions leads to a mixture of water-soluble oligosaccharides, such as cellobiose, cellotriose, and cellotetrose, which are further hydrolyzed in the aqueous homogeneous phase to glucose as follows

$$\text{Cellulose} \xrightarrow{k_1} \text{Cello}(m)\text{ose} \xrightarrow{k_{1,m}} \text{Glucose} \xrightarrow{k_2} \text{Degradation products}$$

where m is equal to bi, tri, tetr,..., and depends on the number of glucopyranose units in the oligosaccharide chain.[14,15,34]

Although cellulose depolymerization is a heterogeneous reaction, in the case of dilute acid hydrolysis at high temperatures, it has been shown that cellulose hydrolysis can be treated as homogeneous on the basis of that the diffusion of the oligosaccharides is relatively fast.[35] Therefore, the hydrolysis of oligosaccharides to glucose is expected to be faster than hydrolysis of cellulose to oligosaccharides.

An extended model was suggested by Conner et al.[36] in a study of the reversion reactions of glucose. These authors considered the formation of disaccharides, anhydrosugars, and degradation products from glucose. Abatzoglou et al.[34] and Sidiras and Koukios[35] also suggested modified models on the basis of the presence of oligomers during cellulose hydrolysis. Xiang et al.[14] studied the hydrolysis of yellow poplar in batch and BSFT reactors under the ELA conditions. These authors have demonstrated that significant amounts of oligomers were also found in the hydrolysate in addition to glucose monomer. Xiang et al.[14] also proposed a modified kinetic model by inserting a parallel pathway for the release of oligomers. This modified model assumes that during the catalytic acid hydrolysis process, the hydronium ions randomly attack the glycosidic bonds and consequently decrease the stability of hydrogen bonds. When both glycosidic and hydrogen bonds are cleaved, glucose and oligosaccharides are readily released into the solution.

3.1.2. Glucose Decomposition. McKibbins et al.[37] conducted a series of glucose decomposition experiments and verified that the decomposition of glucose at constant temperature and pH is also a first-order reaction. Pilath et al.[38] have demonstrated that 5-hydroxymethyl-2-furfuraldehyde (HMF) formation becomes significant at high temperatures (>140 °C) and at relatively low glucose concentrations (~10 g/L). The reaction scheme and first-order reaction rate equation are shown as follows

$$\text{Glucose} \xrightarrow{k_2} \text{HMF} \xrightarrow{k_3} \text{Degradation products}$$

$$\ln\frac{[G]_t}{[G]_0} = -k_2 t \quad (6)$$

where G_t and G_0 (g/L) are the concentrations of glucose at time t and 0.

3.1.3. Dependence of Hydrolysis and Decomposition Rate Constants on Temperature and Acid Concentration. The first-order rate constants obey the empirical Arrhenius equation with a modification to include the acid dependence term as follows[39]

$$k_i = A_i[H^+]^{n_i} e^{(-E_{a,i}/RT)} \quad (7)$$

where k_i (min^{-1}) is the first-order rate constant with i equal to 1 for cellulose hydrolysis and 2 for glucose decomposition,

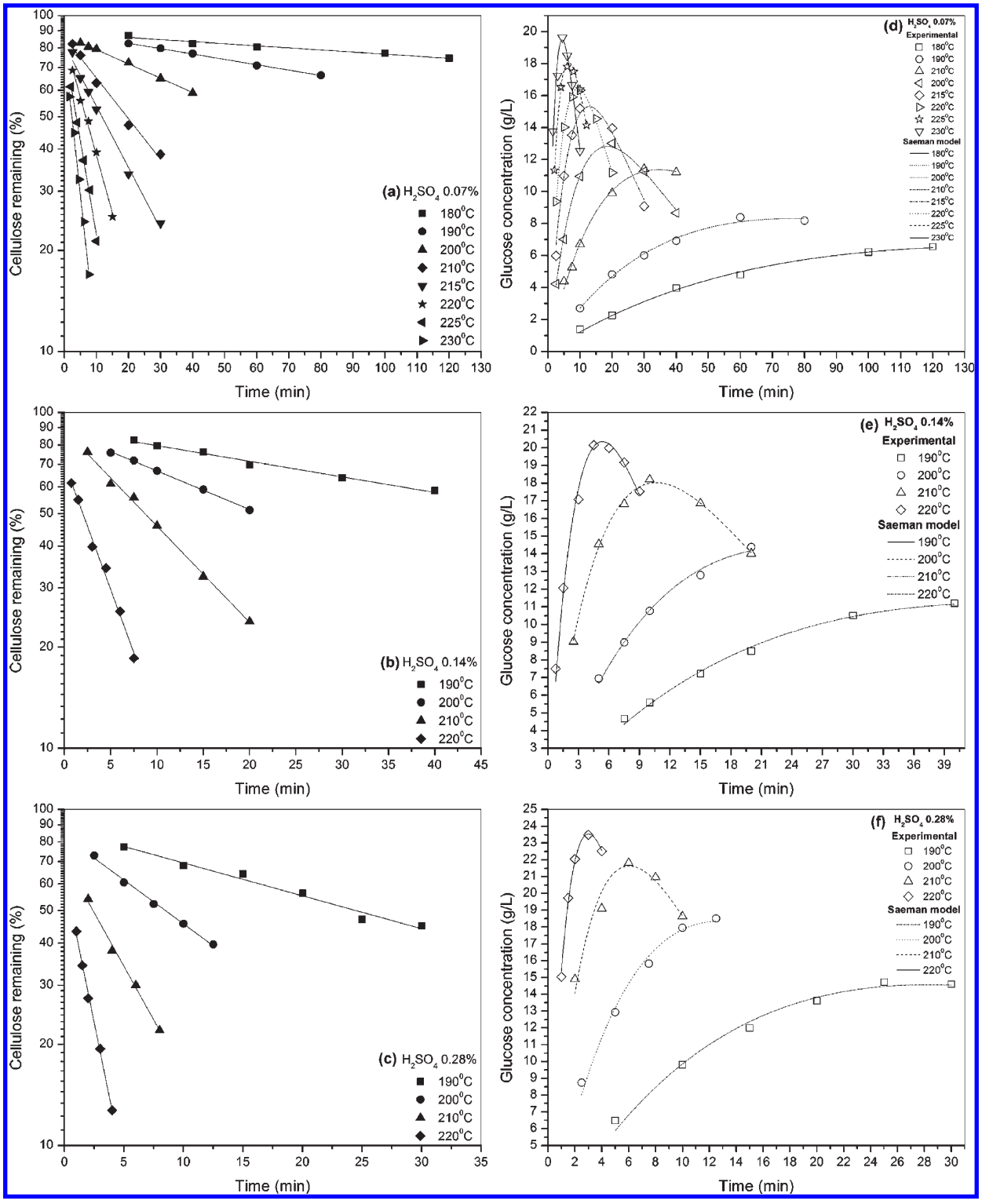

Figure 2. Effect of temperature on hydrolysis rate of cellulosic pulp obtained from weight loss data and profile of glucose concentration determined by HPLC (a) and (d) 0.07% H_2SO_4, (b) and (e) 0.14% H_2SO_4, and (c) and (f) 0.28% H_2SO_4.

A_i (min^{-1}) is the pre-exponential frequency factor, n_i is the reaction order with respect to hydronium ion, $E_{a,i}$ (J/mol) is the activation energy, R (J/K·mol) is the ideal gas constant, and T (K) is absolute temperature.

The Arrhenius equation was wholly empirical in terms of its derivation. A related but more rigorous form of the theory is that of Eyring. The Eyring equation is[40]

$$\ln\left(\frac{k_i}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right) \quad (8)$$

where k_B is the Boltzmann's constant, h is Plank's constant, $\Delta H^{\ddagger}$ (J/mol) is the activation enthalpy change associated with

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Table 2. Hydrolysis of Cellulosic Pulp Obtained from Depithed Sugarcane Bagasse in 0.07%, 0.14%, and 0.28% Sulfuric Acid at Various Temperatures and Reaction Times

		first-order rate constant k_1 (min^{-1})				half-life $t_{1/2}$ (min)	
H_2SO_4 (%)	temperature (°C)	observed	R^2	calculated	R^2	observed	calculated
0.07	180	0.0014 ± 0.0002	0.9500	0.0027 ± 0.0001	0.9956	488.1 ± 55.0	254.8 ± 9.4
	190	0.0037 ± 0.0001	0.9980	0.0065 ± 0.0002	0.9918	188.4 ± 4.1	107.0 ± 3.6
	200	0.0098 ± 0.0002	0.9981	0.0189 ± 0.0006	0.9925	70.8 ± 1.4	36.6 ± 1.2
	210	0.0279 ± 0.0018	0.9833	0.0396 ± 0.0007	0.9964	24.8 ± 1.6	17.5 ± 0.3
	215	0.0420 ± 0.0018	0.9905	0.0672 ± 0.0019	0.9833	16.5 ± 0.7	10.3 ± 0.3
	220	0.0795 ± 0.0033	0.9933	0.0994 ± 0.0011	0.9965	8.7 ± 0.4	7.0 ± 0.1
	225	0.1290 ± 0.0061	0.9911	0.1584 ± 0.0022	0.9930	5.4 ± 0.3	4.4 ± 0.1
	230	0.2031 ± 0.0071	0.9951	0.2485 ± 0.0105	0.9349	3.4 ± 0.1	2.8 ± 0.1
0.14	190	0.0107 ± 0.0006	0.9832	0.0143 ± 0.0004	0.9931	64.8 ± 3.8	48.3 ± 1.4
	200	0.0264 ± 0.0005	0.9985	0.0342 ± 0.0011	0.9913	26.3 ± 0.5	20.3 ± 0.7
	210	0.0660 ± 0.0019	0.9958	0.0954 ± 0.0011	0.9967	10.5 ± 0.3	7.3 ± 0.1
	220	0.1734 ± 0.0079	0.9897	0.2148 ± 0.0061	0.9896	4.0 ± 0.2	3.2 ± 0.1
0.28	190	0.0226 ± 0.0017	0.9739	0.0291 ± 0.0012	0.9854	30.7 ± 2.3	23.8 ± 1.0
	200	0.0601 ± 0.0022	0.9948	0.0808 ± 0.0039	0.9829	11.5 ± 0.4	8.6 ± 0.4
	210	0.1469 ± 0.0077	0.9919	0.2033 ± 0.0103	0.9144	4.7 ± 0.3	3.4 ± 0.2
	220	0.4006 ± 0.0114	0.9968	0.4481 ± 0.0068	0.9940	1.7 ± 0.1	1.6 ± 0.0

forming the activated complex and $\Delta S^{\ddagger}$ (J/K·mol) is the activation entropy change. The logarithmic term ln (k_B/h) has a value of 23.76. Finally, the value of $\Delta G^{\ddagger}$ (J/mol) is obtained through the following relationship[40]

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (9)$$

Specific acid catalysis is observed when a reaction proceeds through a protonated intermediate that is in equilibrium with its conjugate base. Because the position of this equilibrium is a function of the concentration of solvated protons, only a single acid-dependent term appears in the kinetic expression.[40] For cellulose hydrolysis and glucose decomposition, the kinetic expression that shows the effect of acid concentration under conditions of constant temperature is given by eq 10

$$k_i = k_{H^+}[H^+]^{n_i} \quad (10)$$

where k_i (min^{-1}) is the first-order rate constant with i equal to 1 for cellulose hydrolysis and 2 for glucose decomposition, $[H^+]$ is the sulfuric acid concentration (in %), and n_i is the reaction order with respect to hydronium ion.

3.2. Hydrolysis of Cellulosic Pulp as a Function of Temperature and Acid Concentration. A kinetic study was undertaken to determine the factors that affect the rate of hydrolysis of cellulosic pulp obtained from prehydrolyzed depithed bagasse. This kinetic study was performed at temperatures ranging from 180 to 230 °C with a solid to liquid ratio of 1:20 and 0.07%, 0.14%, and 0.28% (w/v) H_2SO_4 for various reaction times. The experimental data for hydrolysis of cellulosic pulp is shown in Figure 2. Panels (a), (b), and (c) of Figure 2 show logarithmic plots of the percentage of cellulosic pulp remaining as a function of reaction time (Table 4 of the Supporting Information). The slopes of the straight lines (Figure 2a−c) represent the first-order rate constants obtained by weight loss data. The observed first-order rate constants ($k_{1,obs}$) for each acid hydrolysis conditions were determined from linear regression analyses of the data (Figure 2a−c) as described by eq 2 using Microcal Origin 8.1 software. As shown in panels (a)−(c) of Figure 2, the hydrolysis of cellulosic pulp obtained from depithed bagasse followed first-order reaction kinetics. Panels (d), (e), and (f) of Figure 2show plots of glucose concentration in the hydrolysates on the basis of HPLC analyses as a function of reaction time. The Saeman model (eq 3) was used to model the experimental glucose concentration profiles shown in panels (d)−(f) of Figure 2. From the glucose concentration profiles determined by HPLC analyses, it was possible to obtain the calculated first-order rate constants for both cellulose hydrolysis ($k_{1,calc}$) and glucose decomposition ($k_{2,calc}$) using Microcal Origin 8.1 software (Table 3 of the Supporting Information). These data were obtained using nonlinear fitting procedure in Microcal Origin and the Saeman model (eq 3) as a fitting function with $k_{1,calc}$ and $k_{2,calc}$ as variables.

Table 2 gives the first-order reaction rate constants for cellulose hydrolysis calculated from weight loss data, $k_{1,obs}$ and the Saeman model, $k_{1,calc}$. Table 2 also gives the half-life times, $t_{1/2}$, and coefficients of determination, R^2. As shown in Table 2, both methods used to obtain first-order rate constants for cellulose hydrolysis exhibited high coefficients of determination. However, the rate constants obtained from the weight loss data were smaller than those obtained by the Saeman model. For 0.07% H_2SO_4, from 180 to 230 °C, $k_{1,obs}$ differed from $k_{1,calc}$ by 92.9% to 22.4%. For 0.14% and 0.28% H_2SO_4, from 190 to 220 °C, $k_{1,obs}$ differed from $k_{1,calc}$ by 33.7% to 23.9%, and by 28.8% to 11.9%, respectively. These results showed that as the sulfuric acid concentration and reaction temperature were increased, $k_{1,obs}$ was closer to $k_{1,calc}$.

As shown in panels (a)−(c) of Figure 2, cellulose hydrolysis was favored by increasing the acid concentration and reaction temperature, which indicates that the supramolecular structure of cellulose is very sensitive to reaction conditions. According to Xiang et al.,[14] who studied the hydrolysis of α-cellulose in a BSFT reactor at 205 °C and 0.07% H_2SO_4, at low temperatures (<210 °C) or low acid concentration (<0.07% H_2SO_4), the intra- and intermolecular hydrogen bonds between hydroxyl groups are relatively stable, and high-DP oligomers remain on the surface of the cellulose chains because of the strong hydrogen bonds until they are further hydrolyzed to glucose. Whereas at

Table 3. Influence of Temperature and Sulfuric Acid Concentration on the Maximum Glucose Yield for the Hydrolysis of Cellulosic Pulp

		observed[a]		calculated[b]	
H_2SO_4 (%)	temperature (°C)	time (min)	glucose yield (%)	time (min)[c]	glucose yield (%)
0.07	180	120	53.6	150	54.3
	190	60	60.0	77	59.4
	200	30	67.6	35	67.3
	210	20	54.8	19	50.2
	215	10	66.4	12.9	66.9
	220	10	55.6	9.3	55.9
	225	6	58.6	6.4	59.5
	230	4.5	60.2	4.4	59.8
0.14	190	40	55.9	45	56.0
	200	20	63.8	24	63.7
	210	10	69.8	10.6	69.1
	220	4.5	63.4	5.4	64.0
0.28	190	25	57.6	28	57.0
	200	12.5	67.3	12.8	66.7
	210	6	68.0	6	67.4
	220	3	60.3	3	60.5

[a] Glucose yields were calculated using the following relationships: $G_{yield} = [(G_t/G_{pot}) \times 100]$ and $G_{pot} = C_0[1 - (X/100)]$. Where G_{yield} is the yield of glucose (%), G_t is the maximum glucose concentration (g/L) at time t determined using HPLC analysis, G_{pot} is the potential glucose (g/L), X is the cellulose remaining (%) (Table 4 of the Supporting Information), and C_0 is the cellulose concentration expressed as potential glucose (C_0 = 48.3 g/L). [b] Glucose yields were calculated using eq 4, $k_{1,calc}$, and $k_{2,calc}$ (Table 2 and 5). [c] The times in which the maximum glucose yields occurred were calculated using eq 5 (Tables 2 and 5).

high temperature (>210 °C) or high acid concentration (>0.07% H_2SO_4), the intra- and intermolecular hydrogen bonds becomes progressively less stable, and low DP-oligomers are directly released to the solution and further hydrolyzed to glucose. The increase in the reaction temperature provided higher hydrolysis reaction rates, allowing for increased glucose formation at shorter reaction times. According to Table 2, an increase in the reaction temperature led to progressively more severe action of sulfuric acid on cellulosic pulp producing higher glucose yields.

Table 3 shows the maximum glucose yields observed experimentally and those calculated from the Saeman model. The observed and calculated glucose yields were quite similar, demonstrating that the experimental data were fit well by the Saeman model. The results displayed in Table 3 indicate that the ELA conditions applied for the hydrolysis of cellulosic pulp produced remarkable results in that unusually high glucose yields were achieved, such as 67.6% (200 °C, 0.07%, 30 min), 69.8% (210 °C, 0.14%, 10 min), and 68.0% (210 °C, 0.28% H_2SO_4, 6 min). These glucose yields were markedly higher than those of approximately 61% obtained by Ojumu et al.[21] The maximum glucose yields obtained by Kim et al.[19] for α-cellulose hydrolysis employing the ELA conditions were also approximately 60% for a temperature range of 205−220 °C and 0.07% H_2SO_4. However, glucose yields obtained in this study at high temperatures of 220−230 °C were lower than 61%. The same behavior was reported by Kim et al.[19] and Ojumu et al.[21], and it is contrary to the conventional concept of cellulose hydrolysis where glucose yields should increase as temperature increases. According to Kim et al.[19], this behavior is not unique to the ELA conditions, and it has been observed in hydrolysis with higher acid concentrations.

3.2.1. Activation Energy and Extrathermodynamic Parameters for Cellulose Hydrolysis from Experimental and Calculated Data. The first-order rate constants for cellulose hydrolysis obtained from weight loss data and the Saeman model were also entered into an Arrhenius plot, plotting ln k_1 versus 1/T (Figure 3a,b), and into an Eyring plot, plotting ln (k_1/T) versus 1/T (Figure 3c,d). Activation energies, enthalpies, and entropies were obtained from the straight lines (Figure 3a−d) for all acid concentrations and are shown in Table 4. Both the Arrhenius and Eyring plots were linear, exhibiting high coefficients of determination across the temperature and acid concentration ranges studied. As shown in Table 4, observed activation energies were very similar for all acid concentrations used in the hydrolysis experiments. The same behavior was observed in the calculated activation energies obtained from the Saeman model. These results suggest that the reaction mechanism for cellulose hydrolysis is the same across the acid concentration range studied, including the ELA conditions.

If the reaction mechanism is the same across the temperature and acid concentration ranges studied, it is possible to express the activation energy by using an average value. This findings are not consistent with those reported by Xiang et al.,[14,15] who reported an abrupt increase in the hydrolysis reaction rates between 210 and 225 °C for dilute acid hydrolysis of α-cellulose and pretreated yellow poplar in batch reactors. According to Xiang et al.,[15] this abrupt change in the reaction rates caused a break point in the Arrhenius plots near to 215 °C for acid hydrolysis of α-cellulose and between 210 and 225 °C for pretreated yellow poplar. Activation energies calculated from the hydrolysis rate constants obtained from weight loss data and the Saeman model were quite similar, indicating that the Saeman model can be used to estimate the overall hydrolysis process in a simplified manner.

Both the observed (184.9 kJ/mol) and calculated (172.6 kJ/mol) average activation energies are in good agreement with those obtained by Saeman[28] for the hydrolysis of Douglas fir free of hemicelluloses (179.3 kJ/mol) in a temperature range from

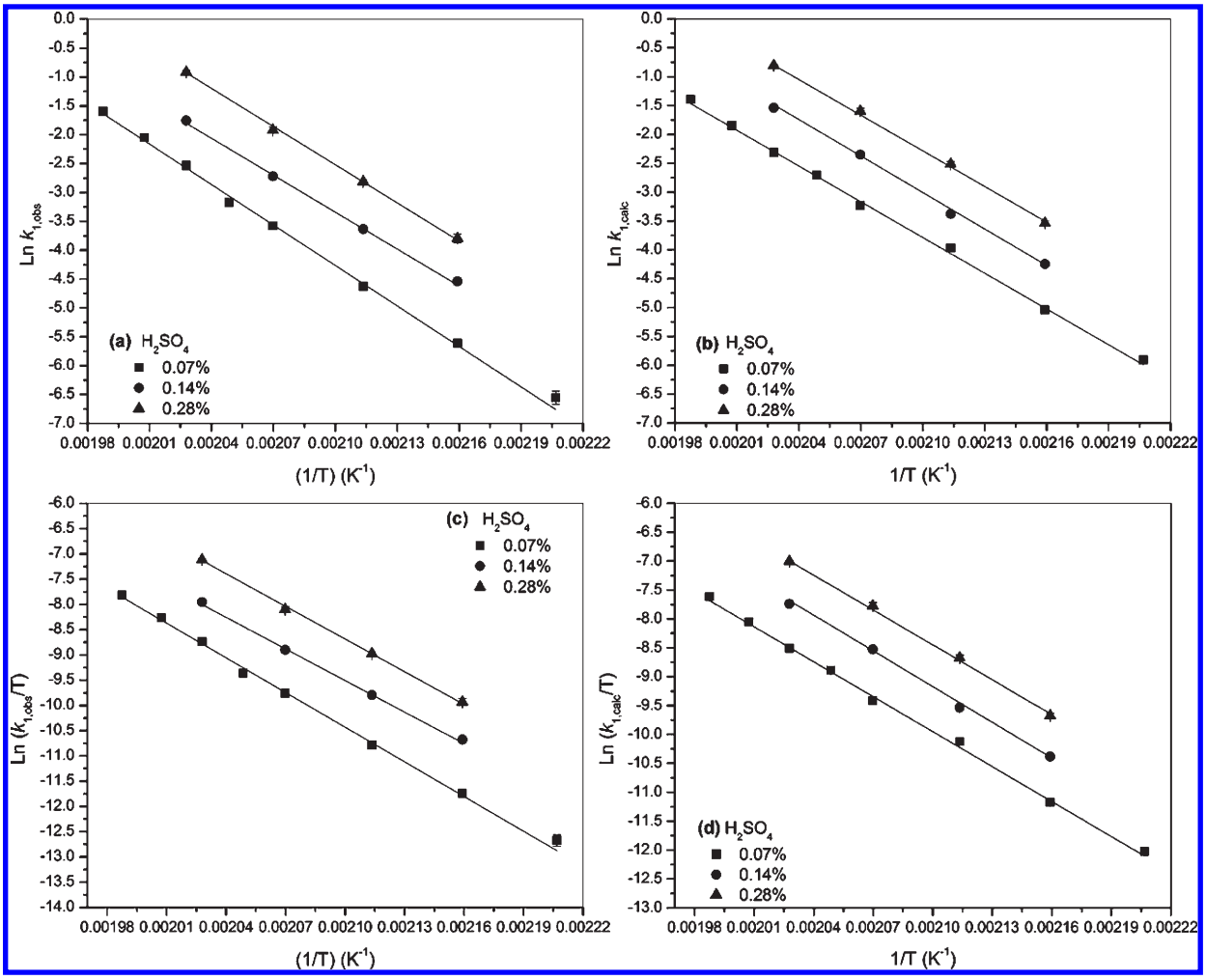

Figure 3. Arrhenius and Eyring plots for cellulosic pulp hydrolysis in sulfuric acid at high temperatures. Arrhenius plots for first-order rate constants obtained from weight loss data (a) and from the Saeman model (b). Eyring plots for first-order rate constants obtained from weight loss data (c) and the Saeman model (d).

170 to 190 °C and 0.4 to 1.6% H_2SO_4 and Lin et al.[39] for the hydrolysis of α-cellulose (178.5 kJ/mol) in a temperature range from 160 to 180 °C and 1.5% H_2SO_4. From Table 4, it is possible to notice that the activation energy predicted by the Saeman model differed by 7.1% from that obtained from the weight loss data.

Table 4 also shows extrathermodynamic parameters for the hydrolysis of cellulosic pulp obtained from weight loss data and the Saeman model. As shown in Table 4, the average observed and calculated activation entropies were found to be +103.0 and +80.2 J/K·mol, respectively. The activation entropy predicted by the Saeman model differed by 28.4% from that obtained by weight loss data.

Nelson[41] also provided a summary of activation energies calculated from literature data. According to Nelson's calculations, on the basis of weight loss data, the activation entropy for the hydrolysis of Douglas fir in 0.8% H_2SO_4 at an average temperature of 180 °C and wood cellulose in 2% H_2SO_4 at an average temperature of 160 °C were found to be +74.0 and +38.5 J/K·mol. Timell[42] studied the hydrolysis of various methyl α- and β-D-glucopyranosides, cellobiose, and xylobiose using four different mineral acids. The activation entropies were also found to be higher than +37.6 J/K·mol. On the basis of those results, Timell concluded that the hydrolysis of glycosides is a unimolecular reaction and that the rate-determining step is the formation of the oxynium ion. On the basis of the results obtained here, the literature data and considering that the plots of log $k_{1,obs}$ and log $k_{1,calc}$ versus log C_{H^+} were linear, with coefficients of determination higher than 0.98 (figure not shown), it is possible to conclude that the mechanism of hydrolysis of cellulosic pulp under the ELA conditions and 0.14% and 0.28% H_2SO_4 also proceeds through a unimolecular reaction.

As also shown in Table 4, the magnitude of the activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) reflected a transition state (TS) structure. The activation energy required for bond reorganization in cellulose hydrolysis was reflected in the values of observed and calculated activation enthalpies of the activated complex. The activation entropy is also a measure of the degree of organization resulting from the formation of the activated complex. Glucose formation led to an increase of translational, vibrational, and rotational degrees of freedom that resulted in high positive change in the observed and calculated activation entropies. The observed and calculated activation free energies ($\Delta G^{\ddagger}$) exhibited certain uniformity considering the estimated errors as the acid concentration was increased as shown in Table 4.

Table 4. Activation Energy, Pre-Exponential Factor, and Extrathermodynamic Parameters for Hydrolysis of Cellulosic Pulp and Decomposition of Glucose Obtained from Weight Loss, Glucose Decomposition Experiments, and the Saeman Model

H_2SO_4 (%)	$E_{a1,obs}$ (kJ/mol)	$A_{1,obs}$ (min^{-1})	R^2	$E_{a1,calc}$ (kJ/mol)	$A_{1,calc}$ (min^{-1})	R^2
0.07%	194.3 ± 3.1	$2.9 \times 10^{19} \pm 5.0 \times 10^{17}$	0.9982	171.6 ± 3.2	$1.5 \times 10^{17} \pm 3.0 \times 10^{15}$	0.9976
0.14%	177.2 ± 4.6	$9.6 \times 10^{17} \pm 2.7 \times 10^{16}$	0.9980	175.2 ± 6.0	$8.1 \times 10^{17} \pm 3.0 \times 10^{16}$	0.9965
0.28%	183.3 ± 3.7	$1.0 \times 10^{19} \pm 2.1 \times 10^{17}$	0.9988	170.9 ± 3.3	$6.1 \times 10^{17} \pm 1.2 \times 10^{16}$	0.9989
average	184.9 ± 5.0	$1.3 \times 10^{19} \pm 8.1 \times 10^{18}$	–	172.6 ± 1.3	$5.2 \times 10^{17} \pm 2.0 \times 10^{17}$	–
H_2SO_4 (%)	$E_{a2,obs}$ (kJ/mol)	$A_{2,obs}$ (min^{-1})	R^2	$E_{a2,calc}$ (kJ/mol)	$A_{2,calc}$ (min^{-1})	R^2
0.07	129.2 ± 0.4	$4.9 \times 10^{12} \pm 1.5 \times 10^{10}$	0.9999	102.4 ± 2.0	$8.3 \times 10^{9} \pm 1.8 \times 10^{8}$	0.9973
0.14	124.3 ± 5.2	$2.4 \times 10^{12} \pm 1.1 \times 10^{11}$	0.9965	104.5 ± 4.3	$1.9 \times 10^{10} \pm 8.4 \times 10^{8}$	0.9950
0.28	120.0 ± 3.9	$1.6 \times 10^{12} \pm 5.4 \times 10^{10}$	0.9979	110.4 ± 1.7	$1.2 \times 10^{11} \pm 1.9 \times 10^{9}$	0.9993
average	124.5 ± 2.7	$3.0 \times 10^{12} \pm 1.0 \times 10^{12}$	–	105.8 ± 2.4	$4.9 \times 10^{10} \pm 3.5 \times 10^{10}$	–
H_2SO_4 (%)	$\Delta H^{\ddagger}_{1,obs}$ (kJ/mol)	$\Delta S^{\ddagger}_{1,obs}$ (J/K·mol)	$\Delta G^{\ddagger}_{1,obs}$[a] (kJ/mol)	R^2	$\Delta H^{\ddagger}_{1,calc}$ (kJ/mol)	$\Delta S^{\ddagger}_{1,calc}$ (J/K·mol)	$\Delta G^{\ddagger}_{1,calc}$[a] (kJ/mol)	R^2
0.07%	190.3 ± 3.1	115.3 ± 6.4	135.1 ± 7.8	0.9982	167.6 ± 3.2	71.7 ± 6.5	133.3 ± 12.3	0.9975
0.14%	173.2 ± 4.6	87.1 ± 9.6	131.5 ± 14.9	0.9979	171.2 ± 6.0	85.7 ± 12.5	130.2 ± 19.6	0.9963
0.28%	179.3 ± 3.6	106.7 ± 7.5	128.2 ± 9.4	0.9988	167.2 ± 3.4	83.3 ± 6.9	127.4 ± 10.8	0.9988
average	180.9 ± 5.0	103.0 ± 8.3	131.6 ± 2.0	–	168.7 ± 1.3	80.2 ± 4.3	130.3 ± 1.7	–
H_2SO_4 (%)	$\Delta H^{\ddagger}_{2,obs}$ (kJ/mol)	$\Delta S^{\ddagger}_{2,obs}$ (J/K·mol)	$\Delta G^{\ddagger}_{2,obs}$[b] (kJ/mol)	R^2	$\Delta H^{\ddagger}_{2,calc}$ (kJ/mol)	$\Delta S^{\ddagger}_{2,calc}$ (J/K·mol)	$\Delta G^{\ddagger}_{2,calc}$[b] (kJ/mol)	R^2
0.07	125.2 ± 0.4	−14.3 ± 0.0	132.1 ± 0.5	0.9999	98.4 ± 2.0	−67.3 ± 0.3	130.9 ± 2.7	0.9971
0.14	120.3 ± 5.1	−20.1 ± 0.5	130.0 ± 6.4	0.9964	100.5 ± 4.2	−60.6 ± 0.5	129.8 ± 5.6	0.9947
0.28	116.0 ± 3.9	−23.9 ± 0.4	127.5 ± 4.8	0.9977	106.4 ± 1.7	−45.2 ± 0.2	128.3 ± 2.1	0.9993
average	120.5 ± 2.7	−19.4 ± 2.8	129.9 ± 1.3	–	101.8 ± 2.4	−57.7 ± 6.6	129.7 ± 0.8	–

[a] Activation free energy was calculated by using the average temperature (205 °C) from the study of hydrolysis of cellulosic pulp. [b] Activation free energy was calculated by using the average temperature (210 °C) from the study of glucose decomposition.

3.2.2. Effect of Acid Concentration on the Hydrolysis Rate Constants for Cellulose Hydrolysis. The effect of acid concentration on the hydrolysis rate constant was also investigated by varying the sulfuric acid concentration from 0.07 to 0.28% (w/v) at fixed temperatures of 190, 200, 210, and 220 °C. The first-order rate constants obtained from weight loss data and the Saeman model were also plotted as log $k_{1,obs}$ and log $k_{1,calc}$ versus log C_{H^+} (figure not shown). Both plots were fit to straight lines with high coefficients of determination. The reaction orders with respect to hydronium ion were obtained from the slopes of the straight lines of log $k_{1,obs}$ and/or log $k_{1,calc}$ versus log C_{H^+} (eq 10) and are summarized in Table 1 of the Supporting Information. The observed and calculated effect of acid concentration on hydrolysis rate obtained from weight loss data and the Saeman model were similar, 1.27 and 1.11, respectively. The difference between $n_{1,obs}$ and $n_{1,calc}$ was 14.4%. The observed effect of acid concentration on the hydrolysis of cellulosic pulp under the ELA conditions (0.07%), 0.14%, and 0.28% H_2SO_4 was similar to that reported by Saeman[28] (1.34) for the hydrolysis of Douglas fir.

The empirical dependence of the rate constant for the hydrolysis of cellulosic pulp on acid concentration and temperature can be expressed by inserting the observed and calculated values (Table 4 and Table 1 of the Supporting Information) of reaction order with respect to hydronium ion, n_1, activation energy, $E_{a,1}$, and the pre-exponential frequency factor, A_1, in eq 7 as follows

$$k_{1,obs} = 1.32 \times 10^{19}[H^+]^{1.27} e^{(-184900/RT)} \quad (11)$$

$$k_{1,calc} = 5.23 \times 10^{17}[H^+]^{1.11} e^{(-172600/RT)} \quad (12)$$

These equations can be used to predict the rate constants for the dilute sulfuric acid hydrolysis of cellulosic pulp at different acid concentrations and temperatures.[39] Comparing eq 11 with eq 12 may indicate that the mathematical expression of eq 12 cannot be used to predict the rate constants with a high degree of accuracy due to the deviations between observed and calculated values for pre-exponential frequency factor, reaction order, and activation energy.

3.3. Glucose Decomposition as Function of Temperature and Acid Concentration. A kinetic study of the decomposition of a glucose solution was undertaken to determine the factors that affect the rate. The aim of this study was to provide glucose decomposition rate constants to compare with those obtained from fitting glucose concentration profiles using the Saeman model. The kinetic study was conducted at 200, 210, and 220 °C in 0.07%, 0.14%, and 0.28% H_2SO_4 (w/v) at a glucose concentration of 0.11 mol/L (20 g/L). The profiles of glucose decomposition as a function of time are shown in Figure 1 of the Supporting Information. When the logarithm of remaining glucose in percentage was plotted as function of reaction time, linear relationships were observed for all acid concentrations and temperatures. As expected, glucose decomposition obeyed the first-order reaction kinetics. The slopes of the straight lines represent the first-order rate constants for glucose decomposition as described by eq 6. The observed first-order rate constants ($k_{2,obs}$) for each glucose degradation conditions were obtained from linear regression analyses of the data (Figure 1 and Table 5 of the Supporting Information) using Microcal Origin 8.1. Table 5 shows the first-order rate constants for glucose decomposition obtained by measuring the remaining glucose, $k_{2,obs}$, and from the Saeman model, $k_{2,calc}$.

Using Table 5, it is possible to compare glucose decomposition rate constants obtained from linear regression analyses of

Table 5. Decomposition of Glucose in 0.07%, 0.14%, and 0.28% Sulfuric Acid at Various Temperatures and Reaction Times in Accordance with the Study of Glucose Decomposition and the Saeman Model

		first-order rate constant k_2 (min^{-1})				half-life $t_{1/2}$ (min)	
H_2SO_4 (%)	temperature (°C)	observed	R^2	calculated	R^2	observed	calculated
0.07	180	–		0.0131 ± 0.0009	0.9956	–	52.8 ± 3.5
	190	–		0.0229 ± 0.0012	0.9918	–	30.3 ± 1.6
	200	0.0266 ± 0.0002	0.9998	0.0418 ± 0.0019	0.9925	26.0 ± 0.2	16.6 ± 0.8
	210	0.0526 ± 0.0005	0.9995	0.0717 ± 0.0010	0.9964	13.2 ± 0.1	9.7 ± 0.1
	215	–		0.0893 ± 0.0026	0.9833	–	7.8 ± 0.2
	220	0.1006 ± 0.0022	0.9976	0.1157 ± 0.0011	0.9965	6.9 ± 0.2	6.0 ± 0.1
	225	–		0.1528 ± 0.0017	0.9930	–	4.5 ± 0.1
	230	–		0.2054 ± 0.0065	0.9349	–	3.4 ± 0.1
0.14	190	–		0.0322 ± 0.0018	0.9931	–	21.5 ± 1.2
	200	0.0464 ± 0.0011	0.9979	0.0509 ± 0.0035	0.9913	14.9 ± 0.3	13.6 ± 0.9
	210	0.0864 ± 0.0016	0.9989	0.0927 ± 0.0011	0.9967	8.0 ± 0.1	7.5 ± 0.1
	220	0.1685 ± 0.0046	0.9971	0.1616 ± 0.0044	0.9896	4.1 ± 0.1	4.3 ± 0.1
0.28	190	–		0.0423 ± 0.0027	0.9854	–	16.4 ± 1.0
	200	0.0882 ± 0.0047	0.9917	0.0757 ± 0.0066	0.9829	7.9 ± 0.4	9.2 ± 0.8
	210	0.1551 ± 0.0193	0.9551	0.1330 ± 0.0062	0.9144	4.5 ± 0.6	5.2 ± 0.3
	220	0.3042 ± 0.0175	0.9934	0.2390 ± 0.0053	0.9940	2.0 ± 0.2	2.9 ± 0.1

the remaining glucose in the glucose decomposition experiments, $k_{2,obs}$, and the rate constants obtained from glucose concentration profiles after cellulose hydrolysis using Saeman model, $k_{2,calc}$. For 0.07% H_2SO_4 (ELA conditions) and a temperature range from 200 to 220 °C, $k_{2,obs}$ was smaller than $k_{2,calc}$, whereas for 0.28% H_2SO_4, $k_{2,obs}$ was higher than $k_{2,calc}$. For 0.14% H_2SO_4 at 200 and 210 °C, $k_{2,obs}$ was smaller than $k_{2,calc}$, and at 220 °C, $k_{2,obs}$ was very similar to $k_{2,calc}$. Therefore, as acid concentration and reaction temperature were increased, i.e., the severity of the hydrolysis was increased, $k_{2,obs}$ was closer to $k_{2,calc}$. A similar tendency related to $k_{1,obs}$ and $k_{1,calc}$ values for dilute acid hydrolysis of cellulosic pulp was also observed. As mentioned earlier, Xiang et al.[15] demonstrated that oligomer formation increases as acid concentration and reaction temperature are increased. As the Saeman model does not take into account oligomer formation and estimates glucose decomposition rate constants using only glucose concentration, it is expected that the Saeman model underestimates k_2 values as acid concentration and reaction temperature are increased because the oligomers released were not converted into glucose and glucose concentration in the reaction medium is smaller than it was expected to be. If the oligomers concentration were taken into account and then converted into glucose concentration, glucose concentration will increase and probably $k_{2,calc}$ will be closer to $k_{2,obs}$. These findings justify the decrease in $k_{2,calc}$ relative to $k_{2,obs}$ as the reaction conditions become progressively more severe.

As shown in Table 5, it is possible to conclude that for all sulfuric acid concentrations studied, an increase in the temperature provided a greater effect on cellulose hydrolysis reaction rates than glucose decomposition rates.Therefore, comparing the obtained results, it is also possible to conclude that an increase in the acid concentration from 0.07% to 0.28% also provided a greater response in cellulose hydrolysis reaction rates than glucose decomposition rates.

The k_2/k_1 ratio was defined by Saeman[28] as the power of glucose formation. According to Saeman,[28] the maximum height of the curves shown in panels (d)−(f) of Figure 2 is a function of the k_2/k_1 ratio. Figure 4 shows the evolution of observed and calculated k_2/k_1 ratios on increasing temperature for the acid concentrations studied. Figure 4 also shows observed k_2/k_1 ratios obtained by Saeman[28] in the study of dilute sulfuric acid hydrolysis of Douglas fir in batch reactor. As shown in Tables 2 and 5 and Figure 4 (also Table 2 of the Supporting Information), an increase in the reaction temperature from 180 to 230 °C for 0.07% H_2SO_4 decreased the ratio $k_{2,calc}/k_{1,calc}$ from 4.827 to 0.827. For 0.14% and 0.28% H_2SO_4 from 190 to 220 °C, $k_{2,calc}/k_{1,calc}$ ratios decreased from 2.248 to 0.752 and from 1.452 to 0.533, respectively. If k_2/k_1 is less than the unity, the rate of glucose formation is higher than the rate of glucose decomposition. In these reaction conditions, the glucose yield is expected to be much higher. The difference between observed and calculated k_2/k_1 ratios also increased as the reaction temperature and acid

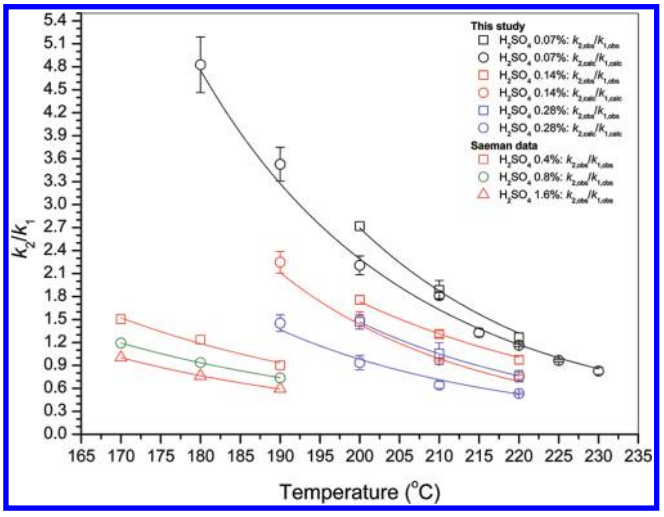

Figure 4. Profile evolution of the observed and calculated k_2/k_1 ratios on increasing temperature for the acid concentrations studied. Comparison with Saeman[28] data.

concentration were increased, except for 0.07% H_2SO_4 at 200 °C (Table 2 of the Supporting Information). This behavior is attributed to the Saeman model that underestimates glucose decomposition rate constants, decreasing the calculated k_2/k_1 ratios relative to the observed ratios.

3.3.1. Activation Energy and Extrathermodynamic Parameters for Glucose Decomposition from Experimental and Calculated Data. First-order rate constants for glucose decomposition obtained from experiments and the Saeman model were also used in an Arrhenius plot of ln $k_{2,obs}$ and ln $k_{2,calc}$ versus $1/T$ and into an Eyring plot of ln $(k_{2,obs}/T)$ and ln $(k_{2,calc}/T)$ versus $1/T$ (figures not shown). Activation energies, enthalpies, and entropies were obtained from the slopes of the straight lines and are shown in Table 4. As shown in Table 4, the observed and calculated activation energies for glucose decomposition were similar for all acid concentrations used in the glucose decomposition experiments. This result suggests that the glucose decomposition mechanism was the same for the ELA conditions, 0.14%, and 0.28% H_2SO_4. The average $E_{a2,obs}$ differed from the average $E_{a2,calc}$ by 17.7%. Xiang et al.[16] studied glucose decomposition under the ELA conditions and found an activation energy of 139 kJ/mol. The values of activation energies obtained from experiments monitoring the remaining glucose and predicted by the Saeman model for the ELA conditions in the present study were found to be 129.2 and 102.4 kJ/mol, respectively. These values are 7.6% and 26.3% smaller than that reported by Xiang et al.,[16] respectively. The average values of observed (124.5 kJ/mol) and calculated (105.8 kJ/mol) activation energies were also smaller than those reported in literature by Saeman[28] and McKibbins et al.,[37] who found activation energies for glucose decomposition in dilute sulfuric acid of 137.5 and 137.1 kJ/mol.

Table 4 shows extrathermodynamic parameters for glucose decomposition. Activation entropies for glucose decomposition under the ELA conditions obtained from the glucose decomposition experiments and the Saeman model were −13.3 and −67.3 J/K·mol, respectively, whereas the observed and calculated average activation entropies were −19.4 and −57.7 J/K·mol, respectively. The data reported by Saeman[28] and Pilath et al.[38] were used to calculate extrathermodynamic parameters for glucose decomposition. The activation entropies obtained in this study contradict those reported by Saeman[28] (+15.6 J/K·mol) and more recently by Pilath et al.[38] (+4.5 J/K·mol), who based their studies on glucose reversion reactions in 1.2 wt% H_2SO_4 at temperatures from 140 to 180 °C. The observed and calculated activation entropies found in this study were negative like those reported by Baek et al.[43] (−69.3 J/K·mol), who studied glucose decomposition in 0.5%, 1.0%, and 2.0 wt% H_2SO_4 at temperatures from 190 to 220 °C. Lu and Lü[44] have studied glucose decomposition kinetics catalyzed by copper chloride at temperatures ranging from 150 to 190 °C. From their reported kinetic data, the activation entropy was found to be −6.4 J/K·mol.

It is interesting to note that the glucose decomposition reactions described by Baek et al.[43] were performed in stainless steel 316 reactors, whereas the reactions developed by Saeman[28] and Pilath et al.[38] occurred in reactors made of inert materials, such as glass ampules and PTFE. In the present study, stainless steel 316 L was used to investigate both cellulose hydrolysis and glucose decomposition reactions. Xiang et al.[16] have also studied glucose decomposition in the presence of different metals and demonstrated how various metals used to construct industrial reactors may affect the overall degradation of glucose. In particular, iron had the strongest impact on glucose decomposition, causing the rapid disappearance of glucose in the reaction medium.

As demonstrated by Lu and Lü[44] and Xiang et al.,[16] glucose decomposition rates are affected by the presence of metals in the reaction medium. The positive values of activation entropy calculated from data reported by Saeman[28] and Pilath et al.[38] suggest the possibility that the rate-determining step for glucose decomposition, at least in reactors made of inert materials, is a unimolecular reaction. Nevertheless, the activation entropies calculated from data reported by Baek et al.[43] and Lu and Lü[44] and those obtained in this study suggest that the rate-determining step for reactions that occurred in reactors made of stainless steel is a bimolecular reaction. Overall, the influence of metals on glucose decomposition rates remains unclear, and no definite conclusions regarding mechanism can be drawn.

Stainless steel reactors are mainly used for industrial purposes. A stainless steel 316 L reactor was used by Dedini S/A in a pilot plant for saccharification of sugar cane bagasse. This process was called Dedini rapid hydrolysis (DRH) and consisted of a continuous process for acid hydrolysis of a lignocellulosic material, sugar cane bagasse, through which delignification and saccharification operations occur in a single reaction cycle by using a solubilizing organic solvent for lignin and a strong and dilute acid similar to the ELA conditions. The maximum yield achieved in stable and continuous operation mode was 88%, expressed as total reducing sugars (TRS).[6]

The observed and calculated values of the activation free energy ($\Delta G^{\ddagger}$) for glucose decomposition displayed a mild decrease as acid concentration was increased. The same behavior was observed for cellulose hydrolysis.

3.3.2. Effect of Acid Concentration on the Hydrolysis Rate Constants for Glucose Decomposition. The first-order rate constants for glucose degradation obtained from glucose decomposition experiments and the Saeman model were also plotted as log $k_{2,obs}$ and log $k_{2,calc}$ versus log C_{H^+} (figure not shown). Both plots were fit to straight lines with high coefficients of determination. The reaction order with respect to hydronium ion was obtained from the slopes of the straight lines of log $k_{2,obs}$ and log $k_{2,calc}$ versus log C_{H^+} (eq 10) (Table 1 of the Supporting Information). The observed and calculated effects of acid concentration on glucose decomposition under the ELA conditions (0.07%), 0.14%, and 0.28% H_2SO_4 were found to be 0.75 and 0.44 (Table 1 of the Supporting Information), respectively, and are smaller than those reported by Saeman[28] and McKibbins[37] for glucose decomposition (1.02 and 0.86) and higher than that reported by Baek et al.[43] (0.61). These results indicate that the Saeman model cannot predict glucose decomposition rates under the ELA conditions, 0.14%, and 0.28% H_2SO_4. Xiang et al.[16] also observed that the Saeman model cannot predict glucose decomposition rate constants under the ELA conditions. Another interesting point, considering the literature data and the results obtained in this study, is that the reaction order with respect to hydronium ion obtained from the glucose decomposition experiments conducted in reactors constructed from inert materials was higher than that obtained from the experiments performed in reactors made of stainless steel.

The empirical dependence of glucose decomposition rate constant on acid concentration and temperature can be expressed by inserting the observed and calculated values (Table 4 and Table 1 of the Supporting Information) of reaction order with respect to hydronium ion, n_2, activation energy, $E_{a,2}$, and the pre-exponential

frequency factor, A_2, in eq 7 as follows

$$k_{2,\mathrm{obs}} = 2.96 \times 10^{12}[H^+]^{0.75} e^{(-124520/RT)} \quad (13)$$

$$k_{2,\mathrm{calc}} = 4.85 \times 10^{10}[H^+]^{0.44} e^{(-105800/RT)} \quad (14)$$

These equations can be used to predict the rate constants for the dilute sulfuric acid degradation of glucose at different acid concentrations and temperatures.[39] Inspection of eqs 13 and 14 may indicate that eq 14 cannot be used to predict the rate constants with a high degree of accuracy due to the deviations between observed and calculated values for pre-exponential frequency factor, reaction order and activation energy.

4. CONCLUSIONS

The ELA conditions were successfully applied to the hydrolysis of sugar cane bagasse cellulose in batch reactors and produced remarkable glucose yields close to 70%. It was found that the reaction under ELA conditions obeyed Arrhenius theory, and no abrupt change in the rate constants have been found for the temperature range and acid concentrations studied. The higher activation entropies and the linearity of the plot of log k_1 versus log C_H+ suggest that hydrolysis of cellulose under the ELA conditions is a unimolecular reaction. However, the mechanism of glucose decomposition under the ELA conditions employing stainless steel reactors requires further clarification.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Profiles of glucose decomposition at 200, 210, and 220 °C in 0.07%, 0.14%, and 0.28% (w/v) H_2SO_4. Reaction orders with respect to hydronium ion for cellulose hydrolysis and glucose decomposition. The k_2/k_1 ratios obtained from experimental data and fitting glucose profiles using the Saeman model. Glucose experimental kinetic data for determination of $k_{1,\mathrm{calc}}$ and $k_{2,\mathrm{calc}}$ by fitting Saeman model. Remaining cellulose data for determination of $k_{1,\mathrm{obs}}$. Residual glucose data for determination of $k_{2,\mathrm{obs}}$. This information is available free of charge via the Internet at http://pubs.acs.org.

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