Alkaline Hydrolysis Kinetics Modeling of Bagasse Pentosan Dissolution

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The main pentosan components of sugarcane bagasse, which can be subjected to alkaline hydrolysis, are xylose, arabinose, glucose, and galactose. The pentosan reaction mechanism was considered for alkali-treated bagasse with variation of temperature and time. The kinetics of pentosan degradation were studied concurrently at temperatures of 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C, with a solid-liquid mass ratio of 1:15, a stirring speed of 500 revolutions/min, and different holding times for bagasse alkali pre-extraction. With respect to residual pentosan content and the losses of raw material, the hydrolysis rates of alkali pre-extraction and pentosan degradation reactions of bagasse all followed pseudo-first-order kinetic models. Finally, the main degradation activation energy was determined to be 20.86 KJ/mol, and the residual degradation activation energy was 28.75 KJ/mol according to the Arrhenius equation.

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INTRODUCTION

Bagasse is the residual by-product obtained after the extraction of juice from the crushed stalks of sugar cane (Nie *et al.* 2007). The production of bagasse has reached up to 200 million metric tons annually (Tu *et al.* 2006). It mainly grows in Brazil, Cuba, and India, *etc*. Within China sugar cane is grown mainly in the southern parts, and the supply of this renewable, easily stored, and easily transported resource has been described as "inexhaustible" (Sun and Peng 2003). The traditional approach used in most sugar mills is to burn most of the bagasses directly for the production of energy, an approach that wastes resources and pollutes the environment. Researchers have begun to advocate a positive development of biomass energy and materials through the use of bagasse.

Bagasse is rich in pentosans, with contents of 70% xylan and 30% poly-arabinose. After processing, pentosans can be converted into energy, chemicals, food, medicine, or beverages (Liu 2008). Because the production of hemicelluloses is second in amount only to the production of cellulose, the effective use of pentosans has a great potential value and significance in biomass feedstock applications. In a conventional pulp cooking process, most of the pentosans are present in the black liquor and are converted to heat, yielding only about 13.6 MJ/kg (Mabee and Saddler 2006). In other words, it is difficult to realize their economic value. Thus, the extraction of hemicelluloses before pulping has the potential to rationalize the use of resources and has opened up new possibilities (Aguilar *et al.* 2002; Binod *et al.* 2012; Gabrielii *et al.* 2000; Li *et al.* 2013; Roos *et al.* 2008; Shi *et al.* 2012; Tunc and van Heiningen 2008; Wyman *et al.* 2005; Zhang and Wei 2008; Xu *et al.* 2003). It is clear that the alkaline extraction hemicelluloses are the most

widely studied, and they could potentially achieve higher performance in hydrolysis compared to other methods from economic and environmental standpoints.

Many reports have discussed pentosan hydrolysis kinetics (Horwath *et al.* 1983; Maloney *et al.* 1985; Scully *et al.* 1986; Michniewicz *et al.* 1992; Luo *et al.* 2013; Zhao *et al.* 2013), yet there has been relatively little research concerning the pentosan hydrolysis kinetics of bagasse. So the present work is also focused on kinetic aspects. The aim was to develop an understanding of the complex carbohydrate degradation kinetic mechanisms involved and hence to optimize the system for a much improved efficiency of hemicelluloses extraction. A low-temperature alkali bath was used to extract hemicelluloses, and then the reaction time and reaction temperature were varied to determine the yield of pentosan extraction, while exploring a new method based on hydrolysis kinetics and degradation kinetics of pentosans with variation of temperature and time. The crucial part of this new technology was to build a pentosan dissolution kinetic model and to provide effective evidence for the control of alkali pre-extracted carbohydrates, and then through the Arrhenius equation to calculate the main degradation activation energy and the main residual degradation activation energy of pentosan (Bin 2009).

EXPERIMENTAL

To validate the proposed approach, practical experiments were carried out as follows.

Material

Sugar cane bagasse was obtained from Yunnan Nan'en Sugar and Paper Co., Ltd. (Xinping, Yunnan Province, China) for this study. It was first air-dried and then ground to pass through a 0.2 to 0.4 mm screen. It was then depithed and air-dried before use. According to Chinese standards for the pulp and paper industry requirements, the bagasse chemical contents were determined as follows: 29.98% 1%-sodium hydroxide-extractives (GB/T 2677.8-1994), 51.52% cellulose (GB/T 5515-1985), 17.00% pentosans (GB/T 2677.9-1994), 80.54% holocellulose (GB/T 2677.10-1995), 19.07% Klason lignin (GB/T 2677.8-1993), 0.06% ash (GB/T 2677.3-1993), and 4.58% moisture content (GB/T 2677.2-1993).

Reagents

Sodium hydroxide, hydrochloric acid (12 mol/L), sodium bromide, sodium bromide, sodium chloride, potassium iodide, and sodium thiosulfate were purchased from Kelong Chemical Reagent Factory (Chengdu, China). All chemicals used in the study were of analytical-reagent grade.

Pre-extraction Methods

Combining the principles of dynamics theory and activation energy with variation of temperature and reaction time, the pentosan reaction mechanism was studied for pretreatment and extraction. The pentosan quality and content of bagasse were determined. The main steps are listed as follows:

(1) Pentosan reaction process

The process of bagasse pentosan extraction was carried out in a 1-L stainless steel reactor, which was placed in a 15-L thermoelectrical rotating autoclave. The oven-dried (105 ^{o}C) ingredients (50 g) were treated with an active alkali charge of 50% (w/w), and a solid-liquid mass ratio of 1:15 (w/v), at temperatures of 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C for 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, and 10 h to extract, and then the content of pentosans was measured.

(2) Dissolution regularity and kinetics reaction mechanism of hydrolysis process

The oven-dried (105 ^{o}C) ingredients (50 g) were treated with an active alkali charge of 50% (w/w), and a solid-liquid mass ratio of 1:15 (w/v), at temperatures of 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C with the variation of reaction time to extract pentosans. The 1-L stainless steel reactor was taken out and put into cold water for 5 min immediately according to different reaction times when reaching the set temperature. The bagasse samples were washed three times with hot water of 50 ^{o}C to 60 ^{o}C, then washed in cold water and air-dried.

Analysis Methods

In this study, the content of oven-dried (105 ^{o}C) bagasse pentosan was measured according to GB/T 2677.9-1994.

RESULTS AND DISCUSSION

Bagasse Hydrolysis Kinetics of Pre-extraction Process

Results of evaluation of hydrolysis kinetics showed how various factors (time, temperature, *etc*.) affected the hydrolysis reaction. The purpose of hydrolysis is to obtain maximum bagasse hemicelluloses. Poly-arabinose 4-O-methyl-glucuronic acid xylose is the main substance of bagasse hemicelluloses, and it is easily susceptible to alkaline hydrolysis (Bin 2009). Besides, the main factors of affecting alkaline hydrolysis are alkali type, solid-liquid ratio, temperature, and time. Other factors affecting the reaction speed are the reaction concentration and the reaction temperature. In order to study the hydrolysis reaction speed, tests were carried out at an active alkali charge of 50% (w/w), with a solid-liquid mass ratio of 1:15 (w/v), and with the reaction temperature reaching up to 90 ^{o}C during the reaction at first. Then the reaction vessel was kept tightly covered to prevent volatile loss of the solvent. It was found that the concentration of the solution remained substantially constant in this case.

For studying the influence of temperature on alkaline hydrolysis, the temperature was fixed at 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C, respectively, and the heating time was 20 min. The bagasse samples were put into the cuvette for hydrolysis pre-treatment.

Several processes are understood to take place, including hydrolysis of hemicelluloses, along with subsequent dissolution of water-soluble components, hydrolysis of insoluble polysaccharides, forming soluble oligosaccharides, dissolution of the oligosaccharides, and hydrolysis of oligosaccharides to monosaccharide under homogeneous conditions.

To test and verify whether the hydrolysis reaction is a pseudo-first-order reaction, a plot was made showing ln (m_0 / m_t) versus extraction time *t*. Regression analysis was

carried out to test whether the data followed a linear relationship. The variable m_0 represents the initial quantity of raw materials (g), and m_t is the quantity of materials at t h, g. Experimental results are shown in Figs. 1, 2, and 3. It can be seen that coefficients of determination (R^2) were 0.9529, 0.9005, and 0.9184 at 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C, respectively, by regression analysis. Linear plots between ln (m_0/m_t) and t are shown in the figure; it can be concluded that the hydrolysis reaction was fairly well represented by a pseudo first-order-reaction model.
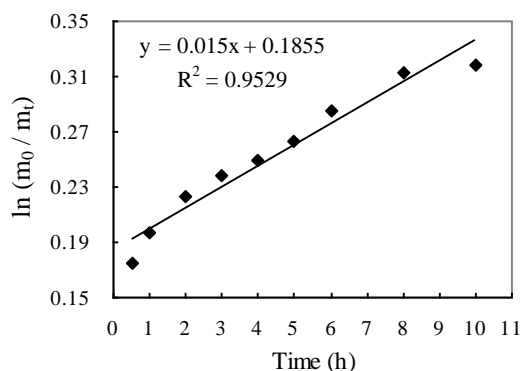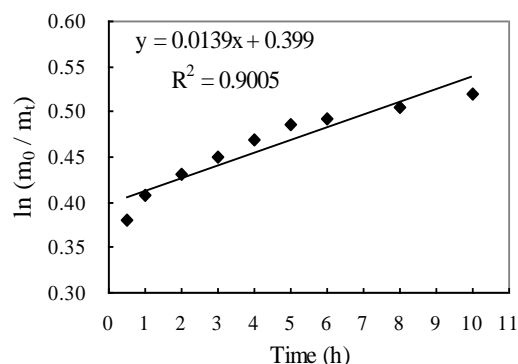
Fig. 1. 50 ^{o}C relation of ln (m_0/m_t) and time   **Fig. 2.** 70 ^{o}C relation of ln (m_0/m_t) and time
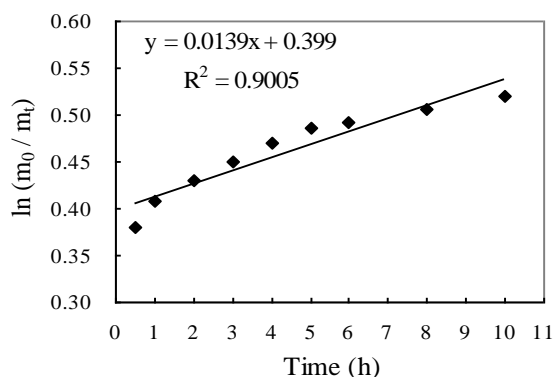
Fig. 3. 90 ^{o}C relation of ln (m_0/m_t) and time

Effect of Pentosan Yield and Extract Content of Bagasse in Alkaline Pre-extraction Process

Under the specified temperatures and different holding times, the pentosan content of extraction residues were measured respectively. According to the relation of time and extraction amounts of pentosan and based on the rules of hemicelluloses degradation, the extraction amount of pentose was measured, and the extents of dissolution of hemicelluloses (or carbohydrate) were found under different conditions of pre-extraction treatment. The results are shown in Figs. 4 and 5.
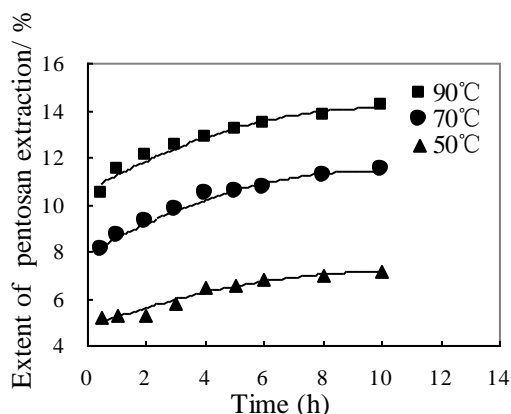
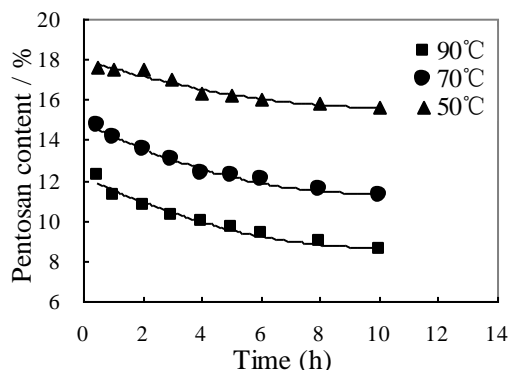**Fig. 4.** Effects of the temperature and time on yield of pentosan

Fig. 5. The change of pentosan extraction content of bagasse with NaOH

It can be seen from Figs. 4 and 5 that pentose extraction amounts rose when the extraction temperature was increased. Pentosan content kept rising when the holding time was extended. In addition, the pentose extraction amount grew faster over time while the treatment temperature was 90 ^{o}C, followed by 70 ^{o}C. The lowest temperature of 50 ^{o}C gave the slowest growth (in Fig. 5). Figure 5 indicates that temperature had a great influence on pentose extraction amount. As shown in Fig. 4, the pentose dissolution rate was higher at high temperature than at low temperature. At the same time, along with dissolution of carbohydrates, raw material sugar content gradually decreased and hydrolysis also showed a corresponding increase, which constituted a significant loss of raw materials.

Construction and Solution of Pentosan Dissolution Kinetics Model

Generally in research related to hemicelluloses kinetics it is assumed that the hydrolysis reaction complies with conservation of mass. Such conservation can be expected when using a large, constant liquid-to-solid ratio. The hemicelluloses hydrolysis reaction is considered to be pseudo-first-order reaction ($n = 1$), which can be expressed by,

$$\ln X = \ln X_0 - Kt \tag{1}$$

where t denotes the reaction time, and X_0 represents the pentosan content. Based on fitting of data to Eq. 1, one can determine whether pentosan degradation belongs to a pseudo-first-order reaction and one can then calculate reaction rate from Eq. 1.

According to the proposed method, the first step is to make a plot of $\ln X$ *vs. t* and to determine whether there is a linear relationship. Secondly, one calculates whether there is a nearly constant reaction rate, as represented by the value of k at different temperatures according the integrated form of the equation for a pseudo-first-order reaction. If $\ln X$ *vs. t* is a linear and k is also close to a constant, then it can be concluded that the reaction is a first-order reaction. Finally, it is pseudo-first-order reaction if $\ln k$ *vs. 1/T* gives a straight line, based on kinetic theory. Values of X and natural logarithm ($\ln X$) can be seen in Table 1.

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According to the data of Table 1, bagasse pentosan content followed a natural logarithm trend versus extraction time (ln$X$ *vs. t*). As shown in Fig. 6, there appeared to be two stages in the interaction. The filled symbols in the graph represent the first stage, and the hollow symbols in the graph represent the second stage.

Table 1. Pentosan Content and Nature Logarithm of Bagasse Pentosan Content

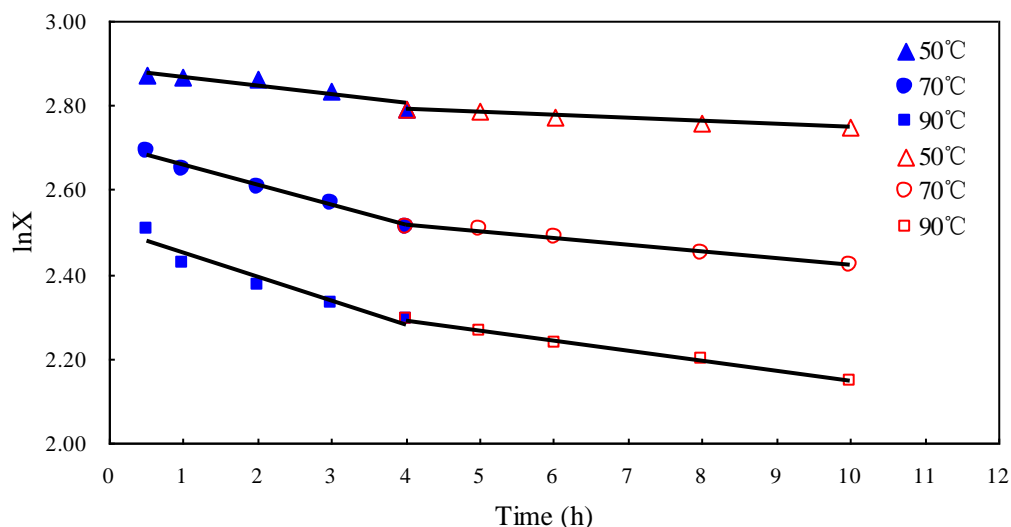| Temperature (℃)		Time (h)								
		0.5	1	2	3	4	5	6	8	10
50	X, %	17.63	17.56	17.48	16.98	16.33	16.26	16.01	15.78	15.65
	ln(X)	2.87	2.87	2.86	2.83	2.79	2.79	2.77	2.76	2.75
70	X, %	14.74	14.15	13.55	13.04	12.35	12.27	12.06	11.58	11.28
	ln(X)	2.69	2.65	2.61	2.57	2.51	2.51	2.49	2.45	2.42
90	X, %	12.29	11.30	10.75	10.30	9.93	9.63	9.35	9.00	8.56
	ln(X)	2.51	2.42	2.37	2.33	2.30	2.26	2.24	2.20	2.15

X: pentosan content in raw material.

Fig. 6. Variation of the natural logarithm of pentosan content and time

From Fig. 6, a linear relationship of ln$X$ *vs. t* was apparent. The hydrolysis reaction was divided into two stages under different holding temperatures, namely the main polyethylene pentose degradation phase and the residual polyethylene pentose degradation phase. These two phases were attributed to the different chemical structures of pentose, which generally fall into two classes. While most pentosans degrade easily, a small amount appears difficult to degrade. Therefore, the different classes of pentosan moiety have different activation energy. During the major part of the pentosan dissolution phase, when the temperature was 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C for 4 h, the pentosan dissolution rates were 34.68%, 50.60%, and 60.28%, respectively. Xylan was hardly soluble when the temperature was under 50 ^{o}C. As a non-wood raw material, bagasse is easily penetrated by NaOH. So it could be inferred that alkali infiltrated into the raw

materials during the main degradation stage of pentosan, along with partial dissolution of the hemicelluloses. Therefore, this stage can be explained as a process in which the dissolved chemical gets into the cell wall and has a reaction with pentosans, and then reaction products spread out from the cell wall (Zhang 1993).

The second stage is the residual pentose degradation phrase. Under the conditions of highest temperature 50 °C, 70 °C, and 90 °C, the pentosan dissolution rate was only 2.72%, 4.28%, and 5.48%, respectively, if one were to continue to hold the temperature constant for 10 h. Although this phase of dissolution was less than 6% of the pentose, it needed a longer cooking time, which showed that the structure and performance of residual pentosan removal stage and dissolution of pentose stage were different from the main degradation stage. It may be that dissolved pentosan is a type of macromolecule with stable structure, high molecular weight, and low reactivity, which made it harder for the pentose to dissolve (Zhang 1993).

Table 2. Reaction Constant and Activation Energy of Pentosan

Temperature T/K	$1/T \times 10^{-3}$	Main degradation stage		Residual degradation stage		Correlation coefficient	
		$K \times 10^{-3}$	lnk	$K \times 10^{-3}$	lnk	R_1	R_2
323	3.10	22.80	-3.78	7.15	-4.94	0.8891	0.9605
343	2.92	48.54	-3.03	9.65	-4.64	0.8918	0.9872
363	2.75	54.60	-2.91	23.70	-3.74	0.9213	0.9935
Activation energy (kJ/mol)		20.86		28.75		0.8628	0.9141

R_1: Main degradation stage correlation coefficient.
R_2: Residual degradation stage correlation coefficient.

The Arrhenius equation is given by

$$k_i = Ae^{\frac{-Ea}{RT}}$$ (2)

According to Arrhenius equation, the infinitive integral can be defined as follows,

$$\ln k = -\frac{E_a}{RT} + \ln A$$ (3)

where E_a is the activation energy, A represents pre-exponential factor, T denotes the time, and R is constant coefficient. Depending on the rate constant k in different temperature, one can make a chart of $\ln k$-$1/T$, and then calculate activation energy E_a and pre-exponential factor A by the slope and intercept of the straight line.
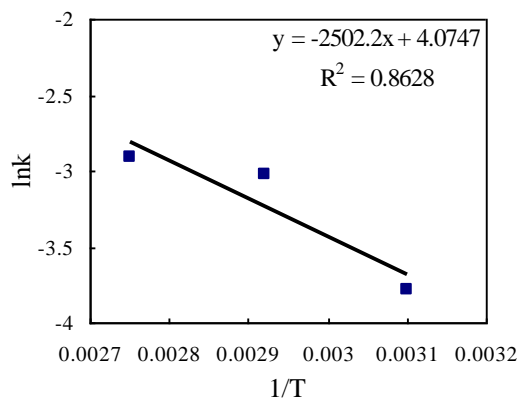
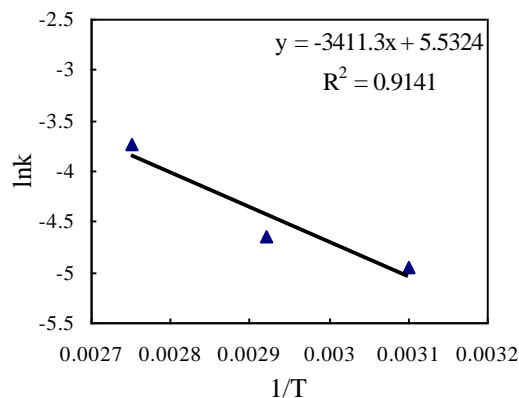**Fig. 7.** Relationship between ln*k* and 1/*T* of main degradation stage

Fig. 8. Relationship between ln*k* and 1/*T* of residual degradation

Using the least square method for regression calculation in Table 1, the results are shown in Table 2. Here, the curve of ln*K vs.* 1/*T* from Table 2 is shown in Figs. 7 and 8, respectively. It is clear that the pentosan main degradation stages activation energy was 20.86 kJ/mol and the residual degradation stage activation energy was 28.75 kJ/ mol.

CONCLUSIONS

In this study, considering a new approach related to pentosan hydrolysis kinetics of bagasse alkaline pre-extraction, one can conclude the following:

1. In the process of bagasse alkali pre-extraction, under the condition of the same amount of alkali and solid-liquid ratio, reaction temperature and reaction time have a great effect on pentosan extraction.

2. The hydrolysis kinetics of bagasse alkali pre-extraction and pentosan degradation reactions all can be classified as pseudo-first-order reactions.

3. Pentosan degradation kinetics can be expressed as two phases: a main degradation phase and a residual degradation stage; furthermore, the higher the dissolution temperature of pentosan, the more significant is the linear relationship of the pentosan degradation reaction.

4. The activation energy for the main degradation stage of pentosan was 20.86 kJ/mol, and the residual degradation stage activation energy was 28.75 kJ/ mol.

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