

# Kinetics of Sawdust Hydrolysis with Dilute Hydrochloric Acid and Ferrous Chloride

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**Abstract :** With dilute hydrochloric acid as catalyst and promoted by ferrous chloride, hydrolysis of waste sawdust to produce monosaccharides was conducted by using an one-step method in a batch-wise operation reactor. Based on the model of first order consecutive irreversible reactions, the kinetics equation incorporating the term of catalyst concentration was obtained that is suitable for describing the hydrolysis of sawdust. Activation energies were calculated for hydrolysis of sawdust and decomposition of monosaccharides.

**Key words :** sawdust; acid hydrolysis; inorganic acid; kinetics

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## 1 INTRODUCTION

Energy resources, soil resources and water resources constitute the essential elements in sustainable development of human society. With rapid economic development of our country, the demand for energy has been continually increasing; therefore the situation of supply of fossil energy, for example, oil and coal, is becoming critical. From a long-term viewpoint, the shortage of energy sources, the liquid fuels in particular, is a crucial factor that would affect China's economic development at high speed. Cellulose and semi-cellulose as the components of biomass can be converted into monosaccharides through chemical or biochemical ways. Monosaccharides can be further processed into other products, e.g., fuel alcohol is produced through biotechnological fermentation. Monosaccharide in acidic media can readily degrade consecutively to other by-products such as furfural, hydroxymethyl furfural and acetic acid, which influence the fermentation efficiency<sup>[1,2]</sup>. Nevertheless, acidic hydrolysis of biomass at presents is still a preferential technology to hydrolysis by enzyme with respect to operation cost<sup>[3]</sup>.

Research<sup>[4]</sup> on hydrolysis of sawdust by catalyst HCl+FeCl<sub>2</sub> has been extensively reported, among which, however, kinetics of this system has seldom been introduced. The present work of hydrolysis of sawdust is particularly focused on the role of catalyst HCl+FeCl<sub>2</sub> by incorporating a concentration term in the kinetic expression.

## 2 EXPERIMENTAL

### 2.1 Test Material

Sawdust from saw mill was sieved and the portion under 40 meshes was collected for test. The

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composition of sawdust samples is listed in Table 1. Cellulose and hemi-cellulose were taken as the basis in calculating the yield of monosaccharide.

**Table 1 Composition of sawdust (% ,  $\omega$  dry)**

Components <sup>1)</sup>	Moisture	Ash	Extractives by benzene-alcohol	Hemi-celluloses	Cellulose	Lignin
Content (% , $\omega$ )	14.5	1.4	5.2	14.1	48.5	30.8

Note: 1) All components were on dry weight basis except moisture.

## 2.2 Analysis

Individual components in sawdust were determined through the gravimetric method<sup>[5]</sup>. Content of monosaccharides in hydrolysate was determined with the idiomatic analysis method<sup>[6]</sup>, but the hydrolysate must first be treated to remove  $\text{Fe}^{2+}$  and acidity the adjusted to  $\text{pH}=7$ . The yield of monosaccharides can thus be expressed as follows:

$$\text{yield} = \frac{\text{Total amount of monosaccharide in hydrolysate}}{\text{Total amount of cellulose and Hemicellulose in sawdust sample}} \times 100\%.$$

## 2.3 Experimental Installation and Method

The experimental installation shown in Fig.1 included a main component, percolating fixed-bed reactor. The reactor was made of stainless steel No. 316 L, having a capacity of 2.5 liter, with the designed pressure of 1.4 MPa and designed temperature of  $190^\circ\text{C}$ . Each run of tests started with sawdust and water in the reactor heated by an electric heater. As the temperature in the reactor reached the prefixed value, a catalyst solution was then quickly injected into the reactor under the pressure of  $\text{N}_2$  from the cylinder. Liquid product was sampled at certain intervals. In the tests, liquid-to-solid ratio was maintained at 30 to 40 L/kg (volume of catalyst solution/sawdust sample weight). Though the ratio decreased due to taking more liquid samples, the ratio still maintained above 30 L/kg.

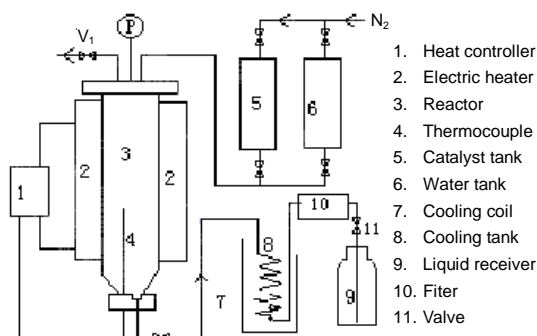


Fig.1 The process for biomass hydrolysis

Both cellulose and hemi-cellulose are polysaccharides that can be acidically hydrolyzed into monosaccharide (glucose, xylose). In hydrolysis of sawdust, monosaccharide was the desired product that is readily degraded consecutively into undesired products<sup>[7-9]</sup>.

## 3 RESULTS AND DISCUSSION

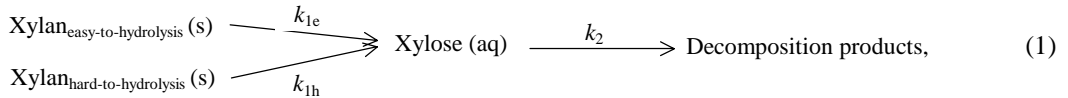
### 3.1 Kinetic Behaviors and Kinetics Model

Both cellulose and hemi-cellulose are polysaccharides that can be acidically hydrolyzed into monosaccharide (glucose, xylose). In hydrolysis of sawdust, monosaccharide was the desired product that is readily degraded consecutively into undesired products<sup>[7-9]</sup>.

A variety of kinetic models for acidic hydrolysis of hemi-cellulose and cellulose have been reported<sup>[10-12]</sup>. The commonly accepted kinetic behavior of hydrolysis model is consecutive irreversible reactions from cellulose (hemi-cellulose) to monosaccharides and then to decomposed products<sup>[10]</sup>.

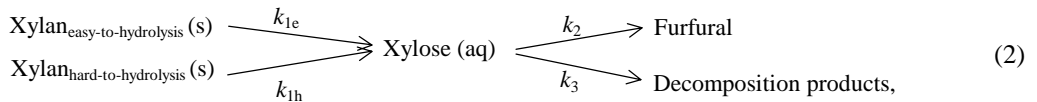
Hemi-cellulose is identified as the polysaccharides of xylan that can be classified into the

easy-to-hydrolysis fraction and the hard-to-hydrolysis fraction. For this reason, Kamiyama et al.<sup>[11]</sup> put forward a model for hemi-cellulose.



where,  $k_{1e}$  is the rate constant of easy-to-hydrolysis fraction of xylan,  $k_{1h}$  is the rate constant of hard-to-hydrolysis fraction of xylan,  $k_2$  is the rate constant of degradation of xylose.

Marton et al.<sup>[12]</sup> further proposed the mechanism by subdivision of decomposition of xylose. Furfural is separately listed as the major product from other products from decomposition.



where  $k_3$  is the rate constant of degradation of xylose.

But Lavarack et al.<sup>[10]</sup> studied the kinetics model by dilute acid hydrolysis of bagasse and held that scheme one is an accurate model to describe hydrolysis of monosaccharide to the desired product. Hydrochloric acid was found to be less active for the degradation of xylose than sulfuric acid. For this system with HCl+FeCl<sub>2</sub> as catalyst and monosaccharides as the desired product of hydrolysis of sawdust, Scheme No.1 is preferred to describe the kinetic behaviors.

The overall hydrolysis reaction can be expressed as



Conventionally, the kinetics of hydrolysis is expressed as first order<sup>[13]</sup>:



where  $k_1$  is the rate constant of hydrolysis of cellulose and semi cellulose,  $k_2$  is the rate constant of degradation of monosaccharide.

$$-\frac{dC_C}{dt} = k_1 C_C, \quad \frac{dC_S}{dt} = k_1 C_C - k_2 C_S, \quad \frac{dC_D}{dt} = k_2 C_S, \quad C_C + C_S + C_D = C_{C0},$$

where,  $C_C$  is the weight concentration of cellulose and hemicellulose,  $C_S$  is the weight concentration of monosaccharide,  $C_D$  is the weight concentration of decomposed products,  $C_{C0}$  is the initial weight concentration.

Analytical solution can be obtained as follows:

$$C_C = C_{C0} e^{-k_1 t}, \quad \frac{dC_S}{dt} = k_1 C_{C0} e^{-k_1 t} - k_2 C_S.$$

If  $C_S$  is from 0 to  $C_S$ , and  $t$  is from 0 to  $t$ , the yield of monosaccharides at any reaction time can be expressed as:

$$y_s = \frac{C_S}{C_{C0}} = \frac{k_1}{k_2 - k_1} [\exp(-k_2 t) - \exp(k_1 t)].$$

At the optimal reaction time:  $t_m = (\ln k_2 - \ln k_1) / (k_2 - k_1)$ , the yield of the desired product reached

its maximum value:  $y_m = (k_1/k_2)^{\frac{k_2}{k_2-k_1}}$ .

### 3.2 Estimation of Parameters in Kinetics Expression

From Arrhenius equation  $k=k_0\exp(-E_a/RT)$ , pre-exponential factors  $k_{10}$ ,  $k_{20}$  and activation energies  $E_{a1}$ ,  $E_{a2}$ , were estimated from  $y-t$  (yield of monosaccharide vs. time) data at different reaction temperatures (Table 2). With the same composition of catalyst solution (2% HCl+0.5% FeCl<sub>2</sub>) shown in Fig.2 and Fig.3, the curves indicate that the calculated values from the kinetics expression can well agree with the data from experiment.

**Table 2** The activation energy and pre-exponential factor with catalysts

Catalysts	$k_{10}$ (min <sup>-1</sup> )	$k_{20}$ (min <sup>-1</sup> )	$E_{a1}$ (kJ/mol)	$E_{a2}$ (kJ/mol)	Temperature range (°C)
1% HCl+1.1% MgCl <sub>2</sub>	$1.239 \times 10^3$	$9.372 \times 10^2$	54.60	34.20	170~220 <sup>[7]</sup>
1% HCl+1.1% FeCl <sub>3</sub>	$1.483 \times 10^5$	$2.013 \times 10^2$	53.79	36.61	170~220 <sup>[7]</sup>
1% HCl+1% FeCl <sub>3</sub>	$1.634 \times 10^5$	$2.273 \times 10^2$	123.04	34.09	75~100 <sup>[7]</sup>
1.5% (HCl+ FeCl <sub>3</sub> )	$1.983 \times 10^8$	$5.0 \times 10^4$	96.52	54.36	155~210 <sup>[9]</sup>
2% HCl+0.5% FeCl <sub>2</sub>	$1.403 \times 10^{10}$	$7.189 \times 10^4$	87.57	50.52	125~160

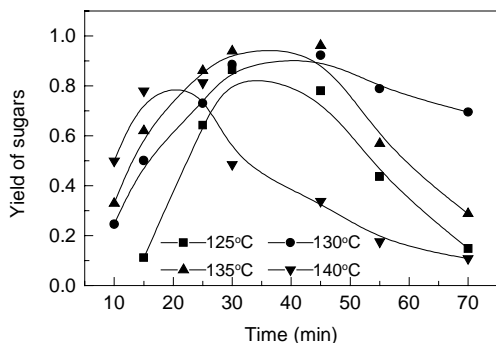


Fig.2 The correlation between calculated and experimental values

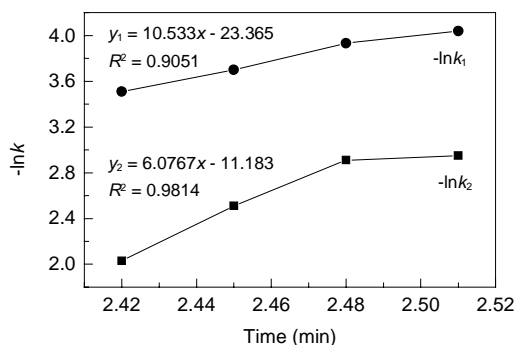


Fig.3 The relation between  $k$  and time

In order to describe the influence of catalyst composition on hydrolysis rate constant, it is assumed:

$$k_{10} = A[C_{\text{HCl}} + BC_{\text{FeCl}_2}]^m.$$

Experiments at 135°C with different catalyst compositions gave out the estimated values of the parameters:  $A=0.0895$ ,  $B=0.9413$  and  $m=0.97$ .

Permanents in the kinetics equation can be expressed as:

$$k_1 = k_{10} \exp(-E_{a1}/RT), \quad -\ln k_1 = \frac{E_{a1}}{R} \frac{1}{T} - \ln k_{10}; \quad k_2 = k_{20} \exp(-E_{a2}/RT), \quad -\ln k_2 = \frac{E_{a2}}{R} \frac{1}{T} - \ln k_{20}.$$

Therefore

$$k_1 = 1.48 \times 10^9 [C_{\text{HCl}} + 0.94C_{\text{FeCl}_2}]^{0.97} \exp\left(-\frac{87.57 \times 10^3}{RT}\right), \quad k_2 = 7.189 \times 10^4 \exp\left(-\frac{50.52 \times 10^3}{RT}\right).$$

### 2.3 Verification of Availability

The availability of kinetic expression was verified by the tests carried out at 135°C with catalysts at 3 concentration levels. The curves calculated from kinetic expression can satisfactorily agree with the data from experiment as Fig.4 indicated.

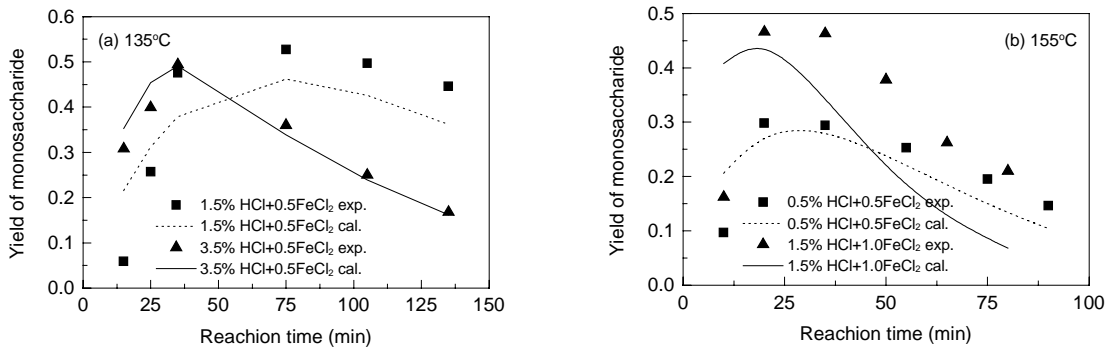


Fig.4 The yield of monosaccharide of experimental and calculated

## 4 CONCLUSIONS

(1) The kinetic model of consecutive reaction of the first order can be used to describe hydrolysis of sawdust. Activation energy  $E_{a1}$  was higher than  $E_{a2}$ . Therefore, an appropriate increase of temperature can improve the yield of desired product, monosaccharides.

(2) Rate constant  $k_1$  includes the factor of catalyst composition varying within the experimental range.  $\text{FeCl}_2$  acted as a promoter that was accounted for in the pre-exponential factor.

## REFERENCES

- [1] Pan J Q, Liu Y. Toxicity in Lignocelluloses Acid Hydrolysis to Fuel Alcohol [J]. *Biotechnology*, 2002, 12(1): 45–47.
- [2] Larsson S, Palmqvist E, Hähn-Hagerdal B, et al. The Generation of Fermentation Inhibitors during Dilute Acid Hydrolysis of Softwood [J]. *Enzyme and Microbial Technolnology*, 1999, 24: 151–159.
- [3] Kadam K L, Wooley R J, Aden A, et al. Softwood Forest Thinnings as a Biomass Source for Ethanol Production: A Feasibility Study for California [J]. *Biotechnol. Prog.*, 2000, 16(6): 947–957.
- [4] Yan Y J, Ren Z W. Continuous Catalytic Hydrolysis of Cellulose [J]. *Acta Energiæ Solaris Sinica*, 1999, 20: 55–58 (in Chinese).
- [5] Ministry of Light and Chemical Industry of Jiangsu Province. *Lignocelluloses Hydrolysis* [M]. Nanjing: Fuel Chemical Industry Publishing, 1974. 257–262 (in Chinese).
- [6] Wuxi Institute of Light Industry, Tianjin Institute of Light Industry. *Food Analysis* [M]. Beijing: Light Industry Publishing, 1987. 166–167 (in Chinese).
- [7] Dai Y S, Yan Y J, Chen P Y. Development of Energy from Biomass—II. Hydrolysis Reaction Kinetic of Bagasse with Inorganic Salts as Catalyst [J]. *Journal of East China Institute of Chemical Technology*, 1990, 16(3): 293–298 (in Chinese).
- [8] Choi C H, Mathews A P. Two-step Acid Hydrolysis Process Kinetics in the Saccharification of Low-grade Biomass: 1. Experimental Study on the Formation and Degradation of Sugars [J]. *Bioresource Technology*, 1996, 58: 101–106.
- [9] Li T C, Wang J, Yan Y J. Study on Technology Conditions and Kinetics about Two-step Hydrolysis of Rice Husk [J]. *Acta Energiæ Solaris Sinica*, 1995, 16(2): 143–149 (in Chinese).
- [10] Lavarack B P, Griffin G J, Rodaman D. The Acid Hydrolysis of Sugarcane Bagasse Hemi Cellulose to Product Xylose, Arabinose, Glucose and Other Products [J]. *Biomass and Bioenergy*, 2002, 23: 367–380.
- [11] Kamiyama Y, Sakai Y. Rate of Hydrolysis of Xylo-oligosaccharides in Dilute Acid Sulphuric Acid [J]. *Carbohydrate Research*, 1979, 73: 15–18.
- [12] Marton G, Dencs J, Szokonya L. *Handbook of Heat and Mass Transfer Principles of Biomass Refining* [M]. Houston: Gulf Publishing, 1989. 609.
- [13] Zhu B C. *Chemical Reaction Engineering* [M]. Beijing: Chemical Industry Publishing, 1993. 17–18 (in Chinese).