Hydrolysis Rate of Resistant Pentosan of White Birch Wood in Sulfuric Acid of Medium Strength

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The purpose of this study is to find optimal conditions for pre-hydrolysis in the new wood saccharification process with strong sulfuric acid. In the experiment, the hydrolysis rate of resistant fraction of pentosan of white birch (*Shirakamba*, *Betula platyphylla* SUKATCHEV var. *japonica* HARA) wood and the decomposition rate of xylose are measured in acid concentrations ranging from 30 to 60% at temperatures ranging from 30 to 90°C. The hydrolysis of resistant pentosan of white birch and the decomposition of xylose are the first-order reactions. The first-order reaction constant of hydrolysis of resistant pentosan, $k_B \text{ min}^{-1}$, is expressed by the following empirical equations as the function of percentage concentration of sulfuric acid, C , and reaction temperature described by absolute temperature, $T^\circ\text{K}$, ranging from 40 to 80°C:

$$k_B = 6.12 \times 10^{-7} C^{6.49} \exp [-9160/(RT)],$$

where sulfuric acid concentrations range from 30 to 50%;

$$k_B = 5.04 \times 10^5 \exp [-9160/(RT)]$$

where sulfuric acid concentration is 60%.

The first-order reaction constant of decomposition of xylose, $k_2 \text{ min}^{-1}$, is expressed by the following empirical equation as the function of sulfuric acid strength described by acidity function, H_0 , and reaction temperature described by absolute temperature, $T^\circ\text{K}$, in sulfuric acid concentrations ranging from 30 to 60% at temperatures within the range of 40 to 100°C.

$$k_2 = 7.01 \times 10^{14} \exp [-1.39 C - 31000/(RT)],$$

where C is sulfuric acid strength described by acidity function, H_0 .

INTRODUCTION

The new process of wood saccharification with strong sulfuric acid¹⁾ consists of three principal reaction stages and operations thereof.

Firstly, in the pre-hydrolysis, hemicellulose in wood chips is removed by the action of sulfuric acid of medium strength.

Secondly, the centrifugal separation of pre-hydrolyzed wood chips from sulfuric acid controls the mixing ratio of sulfuric acid to dry wood in main-hydrolysis described

below.

Thirdly, in a continuous through-circulation dryer, air or dry air blows at 45~65°C through a bed of pre-hydrolysis residues consisting of cellulose, lignin and sulfuric acid of medium strength. During this process²⁾ sulfuric acid is concentrated and the concentrated sulfuric acid converts cellulose into soluble glucose polymer which is soluble in water and easily hydrolyzed in dilute acid³⁾. This process is called main-hydrolysis.

Fourthly, in countercurrent extraction, the

1) T. Kobayashi, presented before the Second Meeting of the Working Party on Wood Hydrolysis, FAO Technical Panel on Wood Chemistry, held in Tokyo, Japan, 1960.

2) T. Kobayashi, K. Mitachi, K. Kikuchi and Y. Kamiyama, *This Journal*, **26**, 371 (1962).

3) T. Kobayashi and Y. Sakai, *ibid.*, **22**, 117, 277 (1958).

soluble in main-hydrolysis product is washed. The soluble contains soluble glucose polymer and sulfuric acid.

Fifthly, the recovery of sulfuric acid from the extract by a dialysis method⁴⁾ is carried out. Sulfuric acid recovered is readily adapted for reuse in further pre-hydrolysis process.

Sixthly, the post-hydrolysis in which the glucose polymer can be easily hydrolyzed by undialyzed sulfuric acid is undertaken.

In the new wood saccharification process using a strong sulfuric acid solution, experiments for finding optimal conditions of pre-hydrolysis have been desired since information on this subject has been hardly available in the literatures concerning wood saccharification.

The present paper deals with the kinetics of hydrolysis of pentosan in white birch wood in a sulfuric acid solution of medium strength ranging from 30 to 60% at temperatures ranging from 30 to 90°C.

MATERIALS AND METHODS

Samples of white birch wood (*shirakamba*, *Betula platyphylla* SUKATCHEV var. *japonica* HARA) ground to small pieces (20 to 40 mesh) were subjected to hydrolysis. The oven-dry sample contained 23.9% pentosan, 72.8% potential reducing sugar, and 22.6% lignin.

The method by which the present experiment was conducted was similar to the procedure described in a previous report⁵⁾. The method of analysis used in this work was also similar to the method described in the said previous report. Pentose and pentosan were determined by a colorimetric method using benzidine⁶⁾, reducing sugar by Somogyi's method⁷⁾ and potential reducing sugar by the method of Saeman, Bubl and Harris⁸⁾.

4) I. Karaushi and T. Matsuno, *Report of the Hokkaido Forest Products Research Institute*, No. 15, 64 (1959); E. Tanaka and T. Kuwata, *ibid.*, No. 15, 106 (1959).

5) T. Kobayashi and Y. Sakai, *This Journal*, 20, 1 (1956).

6) Y. Sakai, *J. Agr. Chem. Soc. Japan*, 30, 256 (1956).

7) M. Somogyi, *J. Biol. Chem.*, 160, 61 (1945).

8) J.F. Saeman, J.L. Bubl and E.E. Harris, *Ind. Eng. Chem., Anal. Ed.*, 17, 35 (1945).

RESULTS AND DISCUSSION

Hydrolysis Rate of Pentosan Difficult to Hydrolyze.

After the sample of white birch wood was subjected to the measurements of extent of hydrolysis under various conditions, the loga-

FIG. 1. Hydrolysis of Hardwood Pentosan in 60% Sulfuric Acid at Different Temperatures.

○ 70°C ● 60°C
● 40°C ● 50°C

FIG. 2. Hydrolysis of Hardwood Pentosan in 50% Sulfuric Acid at Different Temperatures.

○ 80°C ● 70°C ● 60°C
● 50°C ● 45°C ● 40°C
△ 53°C

FIG. 3. Hydrolysis of Hardwood Pentosan in 45% Sulfuric Acid at Different Temperatures.

○ 80°C ◐ 70°C ● 60°C
● 50°C

FIG. 4. Hydrolysis of Hardwood Pentosan in 40% Sulfuric Acid at Different Temperatures.

○ 80°C ◐ 70°C ● 60°C
● 50°C

arithms of the ratios of residual potential pentose to initial potential pentose were plotted against time in minutes as shown in Figs. 1 to 6. These figures show that the pentosan hydrolysis is the first-order reaction. The reaction constants are obtained

FIG. 5. Hydrolysis of Hardwood Pentosan in 35% Sulfuric Acid at 70° and 80°C

○ 80°C ● 70°C

FIG. 6. Hydrolysis of Hardwood Pentosan in 30% Sulfuric Acid at 60° and 80°C.

○ 80°C ● 60°C

by multiplying the slopes of these lines by 2.303. The extrapolation of these lines to zero time of reaction does not pass through the point representing the initial potential pentose. Two lines having different slopes are observed with the lapse of time in the

pentosan hydrolysis as shown in Figs. 1, 5 and 6. This result agrees with the authors' previous experiments⁵). The notation k_B min⁻¹ is used in the description of reaction constant of hardly hydrolyzable pentosan fraction of white birch wood. The reaction constants, k_B , in a sulfuric acid solution ranging from 30 to 60% in concentration at temperatures ranging from 30 to 80°C are summarized in Table I.

TABLE I. HYDROLYSIS RATE CONSTANTS OF WHITE BIRCH WOOD PENTOSAN DIFFICULT TO HYDROLYZE IN SULFURIC ACID OF MEDIUM STRENGTH

H ₂ SO ₄ concn. %	Temp. °C	1st-order reaction constant, k_B (min ⁻¹ .)	
		Obsvd.	Calcd.*
60	70	0.663	
	60	0.458	
	50	0.326	
	40	0.237	
	30	0.110	
	30	0.128	
50	80	0.137	0.138
	70	0.106	0.0914
	60	0.0644	0.0631
	53	0.0447	0.0457
	50	0.0374	0.0398
	45	0.0346	0.0331
45	40	0.0263	0.0265
	80	0.0660	0.0697
	70	0.0443	0.0440
	60	0.0292	0.0318
	50	0.0204	0.0200
	80	0.0311	0.0324
40	80	0.0334	0.0324
	70	0.0208	0.0214
	60	0.0148	0.0114
	50	0.00803	0.00931
	80	0.0108	0.0137
35	70	0.00812	0.00904
	80	0.00541	0.00502
30	60	0.00274	0.00240

* Calculated from $k_B = 6.12 \times 10^{-7} C^{6.49} \exp [-9160/(RT)]$

When the logarithms of the reaction rate constants are plotted against the logarithms of the percentage concentrations of sulfuric acid, parallel straight lines are obtained in intervals proportional to the reciprocals of absolute temperatures within the range of sulfuric acid concentrations of 30 to 50% (Fig. 7). The slope of these lines is 6.49.

The reaction constant in 60% sulfuric acid deviates from the straight lines described above, as shown in Fig. 7. It seems that the reaction of pentosan in 60% sulfuric acid

FIG. 7. Relation of First-order Reaction Constant to Sulfuric Acid Concentration in Hydrolysis of Hardwood Pentosan at Different Temperatures.

○ 80°C ◐ 70°C ● 60°C
◑ 50°C ● 40°C ⊗ 30°C

differs from those in 50% or less acid strength. This is in line with the fact that the mode of reaction of sulfuric acid of 60% or more concentration on cellulose differs from that of the acid lower than 56% in concentration. When the logarithms of these reaction constants are plotted against the reciprocals of absolute temperatures, parallel straight lines are obtained in intervals proportional to the logarithms of percentage concentrations of sulfuric acid. The activation energy calculated from the slope of these lines is 9160 cal/mol (Fig. 8). Using the equation presented by Saeman⁹), the experimental equation describing the first-order reaction constant in hydrolysis of hardly hydrolyzable pentosan of white birch wood, k_B , is calcu-

9) J.F. Saeman, *Ind. Eng. Chem.*, **37**, 43 (1945).

FIG. 8. Relation of First-order Reaction Constant to Temperature in Hydrolysis of Hardwood Pentosan in Sulfuric Acid of Different Concentrations.

○ 60% H₂SO₄ ● 50% H₂SO₄ ● 45% H₂SO₄
 ● 40% " ● 35% " ● 30% "

lated as follows: In sulfuric acid concentrations ranging from 30 to 50% within the range of temperatures of 30 to 80°C,

$$k_B = 6.12 \times 10^{-7} C^{6.49} \exp [-9160/(RT)],$$

in 60% sulfuric acid within the range of temperatures of 30 to 60°C,

$$k_B = 5.04 \times 10^5 \exp [-9160/(RT)],$$

where C is percentage concentration of sulfuric acid, R gas constant and T absolute temperature, °K.

Hydrolysis of Hexosan. Hydrolysis of pentosan was accompanied with hydrolysis of hexosan to some extent as the reaction time was extended. Hexosan content of the sample was obtained by subtracting its potential pentose content from its potential reducing sugar content. When the percentages of residual hexosan were plotted against time in minutes, concave curves were obtained as shown in Figs. 9 to 12. These curves show that the loss of hexosan during pentosan hydrolysis is inevitable except that the loss

in 40% sulfuric acid at 50°C is negligible.

Decomposition Rate of Xylose. The decomposition rate of xylose in sulfuric acid of medium strength was also observed. An

FIG. 9. Hydrolysis of Hardwood Hexosan in 60% Sulfuric Acid at Different Temperatures.

○ 70°C ● 60°C ● 50°C
 ● 40°C

FIG. 10. Hydrolysis of Hardwood Hexosan in 50% Sulfuric Acid at Different Temperatures.

○ 70°C ● 60°C ● 50°C
 ● 40°C

FIG. 11. Hydrolysis of Hardwood Hexosan in 45% Sulfuric Acid at Different Temperatures.

○ 80°C ◐ 70°C ● 60°C
● 50°C

FIG. 12. Hydrolysis of Hardwood Hexosan in 40% Sulfuric Acid at Different Temperatures.

○ 80°C ◐ 70°C ● 60°C
● 50°C

example of the results is given in Fig. 13. The straight line indicates that the reaction is of the first-order. The first-order reaction constants measured under various conditions are summarized in Table II.

When the logarithms of the first-order re-

FIG. 13. Decomposition of Xylose in 50% Sulfuric Acid at 45, 61 and 80°C.

○ 80°C ◐ 61°C ● 45°C

TABLE II. RATES OF DESTRUCTION OF XYLOSE IN SULFURIC ACID OF MEDIUM STRENGTH

H ₂ SO ₄ %	Concn. H ₀	Temp. °C	1st-Order reaction constant, min. ⁻¹	
			Obsvd.	Calcd.*
60	-4.32	80	0.0193	0.0190
		45	0.000148	0.000146
50	-3.32	80	0.00343	0.00408
		61	0.000320	0.000335
		45	0.0000460	0.0000330
46	-2.82	61	0.000221	0.000189
40	-2.28	100	0.0151	0.0113
		80	0.00116	0.00109
		61	0.000093	0.0000893
30	-1.54	100	0.00403	0.00404
		80	0.000407	0.000388
		61	0.0000193	0.0000319

* Calculated from $k_2 = 7.01 \times 10^{14} \exp [-1.39 H_0 - 31000/(RT)]$

action constants in Table II are plotted as the function of acidity function, H_0 , parallel straight lines are obtained in intervals corresponding to reciprocals of absolute temperatures as shown in Fig. 14. When the logarithms of the reaction constants are plotted against the reciprocals of absolute temperatures, parallel straight lines are ob-

tained at intervals corresponding to the acidity-

FIG. 14. Relation of First-order Reaction Constant to Sulfuric Acid Strength in Decomposition of Xylose at Different Temperatures.

FIG. 15. Relation of First-order Reaction Constant to Temperature in Decomposition of Xylose in Sulfuric Acid of Different Strengths.

○ 60% H₂SO₄ ● 50% H₂SO₄ ● 60% H₂SO₄
● 30% "

ty function as shown in Fig. 15. These facts indicate that the following equation fits well the first-order reaction constants in decomposition of xylose in sulfuric acid concentrations ranging from 30 to 60% within the range of reaction temperatures from 40 to 100°C.

$$k_2 = 7.01 \times 10^{14} \exp \left[\frac{-1.39 C - 31000}{RT} \right],$$

where k_2 is the first-order reaction constant, C sulfuric acid strength expressed by acidity function, H_0 , R gas constant, T absolute temperature, °K.

Yield of Pentose. In Table III, the first-order reaction constants in hydrolysis of resistant pentosan of white birch wood have been compared with the first-order reaction constants in decomposition of xylose. The values of k_r , the ratio of k_B to k_2 increases with decrease of the reaction temperature within the range of this experiment. Fig. 16 describes the relation between the value of

TABLE III. RATIO OF RATE OF PENTOSAN HYDROLYSIS TO RATE OF PENTOSE DESTRUCTION

H ₂ SO ₄ concn %	Temp. °C	Hydrolysis rate constant of pentosan Destruction rate constant of pentose $k_r = k_B/k_2$
60	80	46
	60	360
	40	3000
50	80	33
	60	210
	40	1800
40	80	29
	60	200
	40	1600
30	80	13
	60	85
	40	690
10	150	4.5*
	100	4.2*
1	150	3.7*
	100	3.5*

* Calculated from $k_2 = 1.27 \times 10^{18} C^{1.07} \exp \left[\frac{-29600}{RT} \right]^{10}$ and $k_B = 5.57 \times 10^{14} C^{1.15} \exp \left[\frac{-30900}{RT} \right]$

10) T. Kobayashi and Y. Sakai, "Kôbo Riyô Kôgyô", T. Asai ed., Tokyo, Kyoritsu Shuppansha, "Biseibutsu Kôgaku Kôza," 1957, Vol. IV, p. 191.

k_r and the maximum pentose yield (%), Z_m , which is calculated from the equation:

FIG. 16. Yield of Reducing Sugar as A Function of Residual Potential Reducing Sugar for A Variety of k_r Values ($k_r = k_B/k_S$, Z_m : Maximum Yield of Reducing Sugar).

FIG. 17. Value of k_r and Maximum Yield of Pentose as a Function of Sulfuric Acid Concentration and Temperature.

$Z_m = 100 \times k_r^{1/(1-k_r)^{29.11}}$. Fig. 17 shows the relation of sulfuric acid concentration and temperature to k_r value and to maximum yield.

When the pre-hydrolysis is carried out in 45% sulfuric acid at 70°C, the value of k_r becomes 42 and maximum yield of pentose attains 91% of theory in 125 minutes. The experiment of material balance of pre-hydrolysis of white birch wood using 45% sulfuric acid was carried out at 70°C for 60 minutes and the result is shown in Fig. 18. This result agrees well with the kinetical calculation described above.

The result calculated from the reaction constants presented above shows that when pre-hydrolysis of white birch wood is under-

FIG. 18. Material Balance for Prehydrolysis of White Birch (Shirakamba) Wood.

taken in 55% sulfuric acid at 40°C, pentose yield reaches 99.6% of the theoretical value in 152 minutes and the loss of hexosan is negligible.

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