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Hydrolysis of Lignocellulose in Concentrated Sulfuric Acid

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(Figs. 1–5; Tables 1–3; Appendix)

INTRODUCTION

The hydrolysis rate of cellulose in concentrated sulfuric acid is very fast, but requires a large quantity of sulfuric acid. The weak point for making it a stable enterprise. Kobayashi has pointed out that a decrease of sulfuric acid decreases the hydrolysis rate (Fig. 1).[1] For example in a mixing ratio (calculated sulfuric acid of 100 %, g/ dried cellulose material, g) is 100, the hydrolysis goes until nearly 100 % at 1 minute. This experiment was made in a beaker by hand stirring. But when the mixing rate is 1, the hydrolysis goes unto about 80 % at 2700 minute. Therefore there are mixers of different mechanism by various authers, namely the vertical centrifugal;[2] the internal roll[3] ; the external roll[4][5], the screw mixer[6] and vibration.

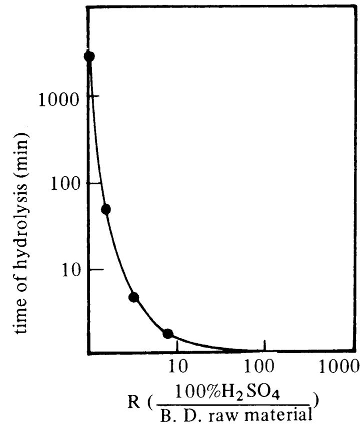

Fig. 1 Relation between hydrolysis reaction rate and used volume of sulfuric acid

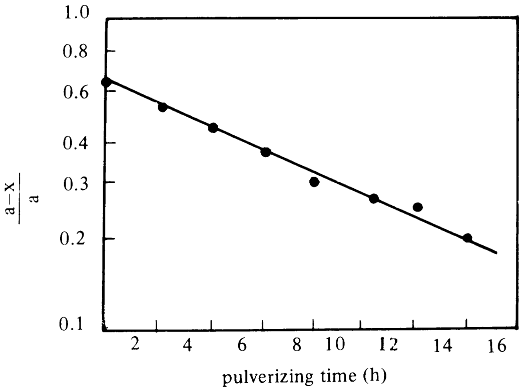

Fig. 2 Relation between (a−x)/a and pulverizing time.

In the screw mixer the reducing sugar had been controlled by the mixing ratio of sulfuric acid, and did not show the effects of the mechanical energy. But in the internal roll mixer, the relation between the pressure (ΔP) of roll and the proportion of hydrolysis (Y) was $Y = K\Delta P^{n}$ and the mixing ratio of sulfuric acid decreased till 0.8 in the internal roll mixer. On the other hand, Odincov reported that the mechanical energy of the vibrating mixer had a certain effect on the rate of hydrolysis the mixing ratio of sulfuric acid decreasing till 0.3 by the energy of the vibrating mixer.

The purpose of this paper is to make clear the effects of the mechanical energy which were reported by Odinkov for hydrolysis, and the effect of the centrifugal mixer which was developed for industrial use.

HYDROLYSIS OF LIGNOCELLULOSE ON THE SMALL RATIO OF SULFURIC ACID BY BALL MILL

1) Experiment method

The ligno-cellulose was prepared by digesting birch with steam cooking at 180°C, for 2 hr; drying it at 105°C for 2 hr. The lignocellulose (40 *g*) were totally immersed in kerosin (800 *ml*), then the lignocellulose were suspended in kerosin by stirring. 80 % sulfuric acid was put in the suspension till the ratio of 1 : 0.3 (dried lignocellulose, *g*: calculated sulfuric acid of 100 %, *g*). After stirring for 30 minutes, it was filtered by a Buchner filter. The filtrate was mainly kerosin without sulfuric acid. The filtration was stopped at the ratio of 1 : 2 (dried lignocellulose, g: sulfuric acid plus kerosin, *g*). The cake was pulverized in a ball mill (one ball type, gunmetal) of 130 mm diameter after ripening.

2) Result

The ripening time and the pulverizing time varied in the first experiment untill 30, 60 and 90 minutes, and for the second experiment from 0.1 and 2 hours. The experimental results are shown in Fig. 2. Table 1 shows the experimental results for the case in which the pulverizing time was extended at a mixing ratio of 0.3.

Odincov has proved that the yield of reducing sugar increased with the ripening at

Table 1. Reducing sugar yield by pulverzing (r=0.3)

pulverizing time *hr*	reducing sugar yield %
0	32.0
2	47.1
4	56.4
6	63.4
8	70.0
10	73.5
12	75.4
14	80.3

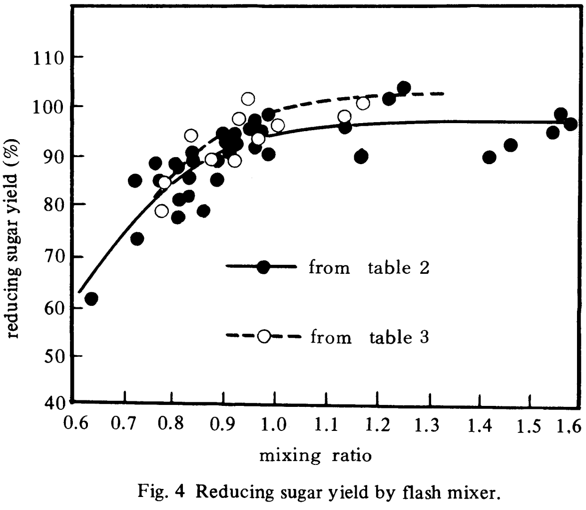

Fig. 4 Reducing sugar yield by flash mixer.

80°C, for 1 hr. As is evident from the Table 1, the yield of reducing sugar increased during first hour. The hydrolysis rate constant (k) was calculated from Table 1. Designating the maximum reducing sugar in lignocellulose is as and the formed sugar as x, $(a - x) / a$ was calculated for each pulverizing time. If the logarism of $(a - x) / a$ is plotted against pulverizing time a straight line appears as shown in Fig. 2, therefore this reaction is qualified as a first order reaction.

When the reaction rate constant k is calculated from $-k\theta = [\ \ln (a - x) / a\ ]$, k is 1.4×10^{-3} (1 / min). And when k is calculated from Odincov's report which used sawdust of spruce at a mixing ratio of 0.3 with the vibrating mixer, k values is 44.3×10^{-2} (1 / min). What is evident when comparing the two reaction rate constants is that the energy of Odincov's vibrating mixer shows 32 times as much as the energy of the ball mill. If the specifications of the vibrating mill are assumed as the pressure of vibrating mill 225 Kg / cm^2 ; vibrating number 1000 r.p.m. and stress velocity 50 cm / sec, the calculated electric power required per ton reducing sugar is about 2000 Kwh$^{7)}$. The mechanical energy from one unit operation is very large. This fact lead us to conclude to a strong economical interest.

PILOT PLANT TEST OF SULFURIC ACID MIXING BY CENTRIFUGAL MIXER

1) Experimental method

The centrifugal mixer was producted by way of a trial experiment for sulfuric acid mixing (Fig. 3). The principle of the mixing was the same flash mixer as that developed by Takarakoki Co. for the mixing of a paints. Namely, a double rotating disc rotating in high speed from opposite directions. The lignocellulose and the sulfuric acid are puted on the upper disc or the under disc from each hole, then they are blown off as film by the centrifugal force of each disc. Both films are collided and mixed. This mixing is able to

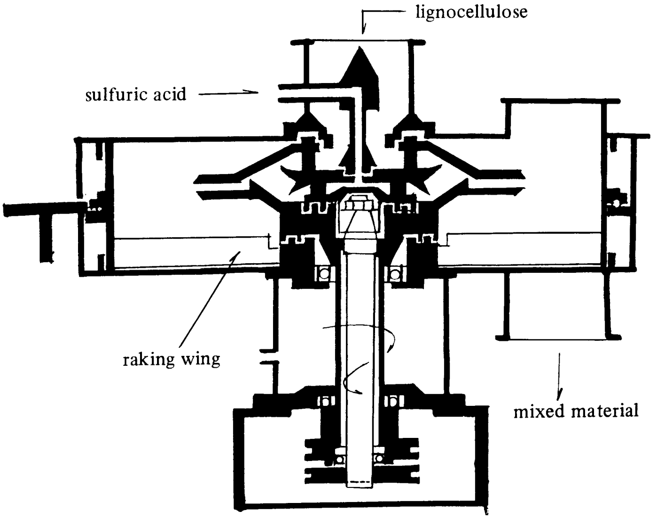

Fig. 3. Flash mixer

uniform, but the force of mixing is little.

The specifications of this mixer are as flowing; diameter of disc 400 mm; speed of rotating 2500 r.p.m.; horse power drive 2 Hp for each, horse power of wing for scrape on the outshirts 1.5 Hp, maximum treatment of dried lignocellulose 2000 *kg* / 24 hr. The mixing material used in the centrifugal mixer was brought to ripeness by using the mixer of a single helical screw type or of an extrude type. The mixing of the centrifugal mixer added instanty. The preparation of the lignocellulose and the analysis of the reducing sugar was made by the method as above.

The reducing sugar was 66.7 % and the lignin was 38.6 %. The ripening time was varied from 3 to 5 minitues for the screw mixer and from one to 3 minitues for the extruder mixer, then diluted immediately till 30 % sulfuric acid by the use water. After drying at 5 %, the lignocellulose was shifted between 40–80 mesh. The centrifugal mixer was operated for several hours, and the sampling was done after 30 minitues from the steady state operation.

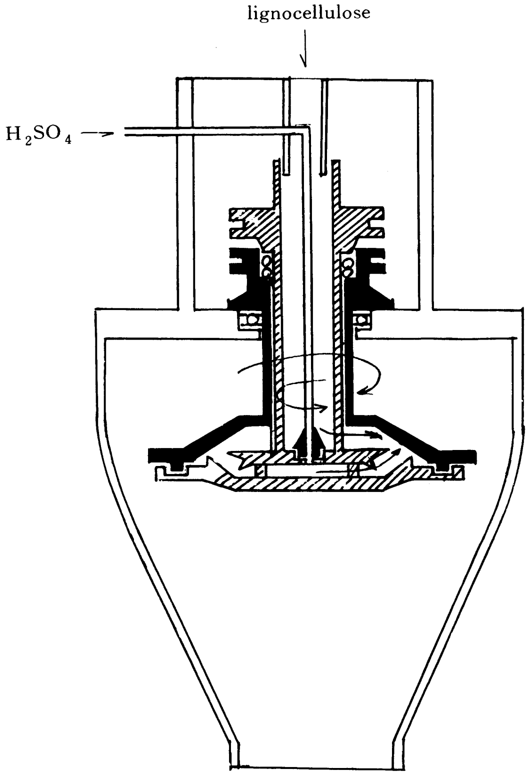

Fig. 5 Principle of centrifugal mixer on the commercial scale

The diameter of the mist of the sulfuric acid in the centrifugal mixer was 0.045 cm

Table 2. Reducing sugar yield in the hydrolysis by flash mixer

a) Ribon screw type

mixing ratio*	temp. °C	Conc. H_2SO_4 %	hydrolysis rate**	unreacted cellulose(%)***
0.64	43.0	83.2	62.3	13.4
0.73	61.0	79.2	73.3	17.1
0.73	52.0	78.9	86.0	18.5
0.77	52.5	78.9	88.7	14.9
0.78	51.5	78.9	89.4	17.5
0.80	51.5	78.9	89.4	13.2
0.81	56.5	83.2	78.8	11.1
0.82	53.0	79.1	87.5	13.5
0.83	60.0	82.3	83.2	15.4
0.84	53.8	81.2	84.9	12.3
0.86	56.3	81.0	75.9	16.3
0.88	47.5	81.0	80.6	18.3
0.89	51.5	80.8	88.4	11.6
0.91	50.5	78.9	95.4	8.7
0.92	55.0	83.0	93.6	7.4
0.93	54.0	79.1	92.5	9.2
0.94	52.5	78.9	96.2	9.4
0.95	55.0	82.4	95.2	7.0
0.96	62.0	79.5	91.1	14.3
0.97	52.0	79.1	95.4	9.0
0.98	43.0	79.1	98.2	10.9
0.99	52.5	78.9	90.5	14.8
1.14	55.6	82.5	96.6	5.1
1.17	71.0	80.0	90.6	11.7
1.23	61.0	79.9	101.0	4.2
1.25	50.0	79.7	104.0	0
1.42	64.0	80.0	90.2	9.1
1.55	68.0	80.0	95.0	6.2
1.57	71.0	80.0	97.8	4.2

b) Extruder type

mixing ratio*	temp. °C	Conc.H_2SO_4 %	hydrolysis rate**	unteacted cellulose(%)***
0.78	63.0	80.0	79.0	21.1
0.79	72.0	80.0	85.0	17.2
0.83	63.0	75.6	92.0	7.6
0.92	80.0	80.5	90.0	9.3
0.93	60.0	78.4	97.3	5.0
0.95	63.0	75.9	102.0	0
1.06	54.4	76.8	96.3	4.2
1.13	58.0	76.5	98.5	2.1
1.17	66.0	75.9	101.0	0

Remarks: * mixing ratio = 100% $H_2^2SO_4$ / B. D. lignocellulose
** hydrolysis rate = (reducing sugar / potential reducing sugar) x 100
*** unreacted cellulose = (unreacted cellulose / potential reducing sugar) x 100

Table 3. Hydrolysis of several woods by flash mixer

		oak	*tamo*	*elm*	*shina*	*maple*	*han*	*katura*	*birch*
potential reducing sugar in lignocellulose		66.3	62.8	62.0	69.1	69.4	64.5	61.2	66.7
reducing sugar yield per potential reducing sugar (%)[1]		88.4	78.4	89.1	93.0	77.1	89.1	90.6	90.5
composition of reducing sugar	reduction	trace	trace	0.1	0.6	0.6	trace	2.6	1.6
	xylose	3.2	2.4	2.7	2.2	3.1	2.6	1.8	2.2
	arabinose + mannose	0.2	trace		0.1	0.8	trace	trace	0.3
	glucose	91.0	93.0	94.6	90.4	89.8	90.7	90.4	90.3
	galactose	trace	0.6	trace	0.1	trace	0.1	trace	0.5
	di-triose	4.8	3.2	2.6	5.6	5.5	5.7	4.7	4.5
	oligosaccha.	0.8	0.8	trace	1.0	0.2	0.9	0.4	0.6

remarks: 1) mixing ratio 1 ; 1, temperature 40 ± 2.5°C, H_2SO_4 81%, water content in lignocellulose 5%.
2) post hydrolysis H_2SO_4 8%, 2 hours, 160°C, neutralization with $Ca(OH)_2$
3) hydrolysis of pentosan 185°C, 2 hours, steamcooking.

at the account. The equations to be used in this calculation is as following; $d = 160\,N\cdot g^{0.2}\cdot D^{-0.3}$[8]. · Where d signifies the average diameter of mist (cm); N stanes for the number of disc rotation (r.p.m.); g the volume of sulfuric acid (cm^3/sec) and D for diameter of the disc (cm).

2) Results

The experimental results obtained in the way described above are shown Table 2. The rate of hydrolysis reaction certainly is in relation to the temperature, the concentration of sulfuric acid and the time, but as is evident from Table 2, A difference in the rate did not appeare at a range of temperature 43.0–71.0°C in a concentration 75.9–83.2 %. Fig.4 was plotted from Table 2. It seems evident that the yield of reducing sugar is affected remarkably by the ratio sulfuric acid mixing.

When ripening time of the screw mixer was changed one to 5 munitues, the difference of the yield of the reducing sugar was not visible. Therefore, the yield of reducing sugar did not affect very much the ripening time in the centrifugal mixer under a temperature of 43–70°C, and a concentration of sulfuric acid of 79–83 %. The ripening time was 1–5 minitures.

Kobayashi suggested the next experimental equation for the hydrolysis by using the extruder mixer : $Y = 31 \pm 48\,R$ (Y ; yield of reducing sugar, R ; mixing ratio).[9] The results calculated by using this equation are shown as a straight dotted line in Fig. 4. As compared with the dotted line, the centrifugal mixer increases the reducing sugar between 0.7 and 1.3 of the mixing ratio. This result of the extruder mixer seems a little better than that of the screw mixer. An exact answer to this contradiction has not been obtained yet.

8 kinds of broad leaf tree were experimented in the same way. The results are shown in Table 3. The yield of sugar was less for elm and maple, but there was difference for other tree as compared with birch the glucose in the reducing sugar solution almost about 90 %. Diameter of lignin which was calculated by Stock's law had a complicated relation for the concentration of sulfuric acid. This relation may be explanated by the filtration velocity in the washing of lignin.

The compressibility coefficient is 0.55 in case of this experiment of lignin filtration on the pilot plant. It is small as compared with the above fundamental data. The relation between the specific filtration resistance and the mixing ratio of sulfuric acid is evident, namely, a increase the mixing ratio and a decrease of the specific filtration resistance.

COMMERCIAL PLANT OF HYDROLYSIS

Hydrolysis by means of the centrifugal mixer was found to have two faults in long operation. One was that the small particles in the lignocellulose adhered in the rubbing area of axis and so increased the driving power. The other fault was that the lignocellulose which was mixed the sulfuric acid instantly coagulated to paste. and adhered to the wing, and then dropped down as dumplings. Therefore the lignocellulose which was carbonized by the delay adhered on the wing after several hours, so that it needed over haul cleaning every few hours.

The centrifugal mixer which was specially designed to eliminate these faults as shown in Fig. 5. The power part was on the upper side, then the sulfuric acid went out from the hole in the rotating axis. After the lignocellulose had been mixed the sulfuric acid, it dropped down into the under opening. The screw mixer or the extruder mixer are no needed for the ripening in case of an industrial scale. It is enough to convey the mixing material on the beltcoveyer within several minitus. This kind of mixer has been operated 200 hour non-stop at a commercial plant with good results.

CONCLUTION

Hydrolysis of the lignocellulose by mean of the ball mill decreased the sulfuric acid untill a ratio of 1; 0.3. But the mechanical energy was very large, therefore it led to a strong suspention for a economical effect.

The hydrolysis of the lignocellulose which used the centrifugal mixer was 90% of reducing sugar yield and spended a small amount of energy. The mixing ratio of sulfuric acid was optima at 1; 1. We have found that the screw mixer and the extruder mixer have an accelerating effect on the ripeing, but in case of the industrial scale, it is sufficient to convey the mixing material on the belt conveyer within several minutus.

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濃硫酸によるリグノセルローズの加水分解

保坂秀明

濃硫酸による鋸屑の加水分解において，Odincovは機械エネルギーの効果が認めているが，木材より脱ペントーザンされたリグノセルロースを原料とし，機械エネルギーとしてボールミルを用いて試験した結果，一次反応式によく従うことを認めたが，その反応速度は使用された動力に対して極めて低く，したがって膨大なる動力費を要することになることから，工業化に対して不満足なものであるとした。

従来研究された硫酸の混合機はいづれも一長一短があり，使用硫酸の節減と取扱い易い混合機として遠心法によるものを試作し，連続の装置試験を行い，濃硫酸との混合比1：1で90％以上の還元糖収率の好結果を得た。試験装置ではアメ状の混合物が掻取羽根に付着炭化し，長期運転の支障となったが，工業装置ではアメ状混合物を直ちに落下する方式で2週間程度の連続運転を可能にした。また，熟成は従来機械的撹拌が必要とされていたが，上方式の混合の場合は撹拌は全然不要であることが認められた。