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Filtration of Lignin in Hydrolysis Solution

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(Figs. 1–5; Tables 1–6; Appendix)

SPECIFIC FILTRATION RESISTANCE ON THE FOUNDAMENTAL TEST

1) Introduction

Preliminary attempts to calculate the specific filtration resistance on the constant pressure filtration for hydrolysis solution of saw dust with conc. sulfuric acid have already been described. The specific filtration resistance(α) which was shown as $\alpha_m = 1.225 \times 10^3 e^{-2.556R}$ (R; mixing ratio of sulfuric acid has been sugested by Kobayashi[1] and because it's value was over Grace's limits[2], therefore a filter press had to be used. Also it has been recognized that the velocity of filtration was affected the mixing of sulfuric acid.

2) Experimental method

The lignocellulose was prepared from oak chip in steam cooking at 180°C for 2 hr and drying 105°C for 2 hr. The centrifugal mixer was used for the hydrolysis of lignocellulose. The composition of the hydrolysis solution (slurry) was as following; lignin 15.1%, reducing sugar 15.3%, average degree of polymerzation 4.04 and concentration of sulfuric acid 31.3%. The filtration area of the experimental filter press covered with a cloth of polyvinylalcohol fiber (Tebilon # 215).

Ruth equation[3] which has to be applied in this experiments is given in the following equation.

$$\frac{\Delta\theta}{\Delta V} = \frac{2V}{K} + \frac{2V_\circ}{K} \quad (1)$$

$$K = \frac{2\Delta P g_c k A^2}{m} \quad (2)$$

$$V_\circ = R_m k A / a_m \quad (3)$$

Where, ΔP: pressure drop, $k=(1\text{-}mc)\cdot\rho c$ (m; ratio of wet cake against dry cake, β; concentration of solid in solution, ρ; density of solution), g_c; gravitational coversion factor, A; area of filter, m; specific filtration resistance on weight bace, μ; viscosity, R_m; filtration resistant coefficient of filter medium. When the filtration pressure is smaller than several Kg/cm², the average specific filtration resistance α_m is solved by the following equation.

$$\alpha = \alpha_0 P^s \qquad (4)$$

Where, α_o is the initial specific filtration resistance, s is the compressiblity coefficient. θ / V which was calculated Table 1 is plotted in graph as in Fig. 1. $2V_o/K$ and V_o able to read from Fig. 1, and the value of K is calculated, the α_m is solved by using equation 2.

Table 1 Filtration of hydrolysis surry

pressure Kg/cm^2	time min	filtrate ml	weight of cake g	thickness of cake mm	water in cake %	void ratio	α exp.	α calced.*
2	15	30	50.0	3	76.4			
2	30	55	92.0	6	67.5			
2	60	85	123.0	9	68.5			
2	90	100	148.0	11	66.7			
2	120	130	172.0	13	65.7			
average		80	117.0	8.4	63.5	0.288	7.5×10^{11}	7.9×10^{11}
3	15	34	47.0	4	72.3			
3	30	58	81.9	7	67.0			
3	60	96	135.6	9	67.7			
3	90	103	147.5	12	64.5			
3	120	141	197.6	13	65.5			
average		86.4	121.6	9.0	67.4	0.293	9.98×10^{11}	10.45×10^{11}
4	15	42	87.5	6	63.5			
4	30	72	109.3	8	68.5			
4	60	110	150.8	11	63.7			
4	90	122	195.0	13	66.5			
4	120	146	200.0	15	64.7			
average		98.6	148.5	10.6	65.7	0.323	12.6×10^{11}	12.7×10^{11}
6	15	55	89.0	7	65.5			
6	30	86	102.5	9	61.5			
6	60	116	154.0	13	65.5			
6	90	150	189.0	15	63.5			
6	120	166	215.5	17	64.5			
total		114.6	150.0	12.2	64.1	0.294	18.0×10^{11}	16.9×10^{11}
8	15	65	94.3	8	63.5			
8	30	97	109.0	10	62.5			
8	60	126	171.8	13	62.5			
8	60	126	171.8	13	62.5			
8	90	166	207.4	15	61.0			
8	120	190	243.0	18	63.0			
total		128.8	165.1	12/8	62.4	0.323	20.5×10^{11}	20.5×10^{11}

remark; * Calculated from $K = 4.9 \times P^{0.69}$

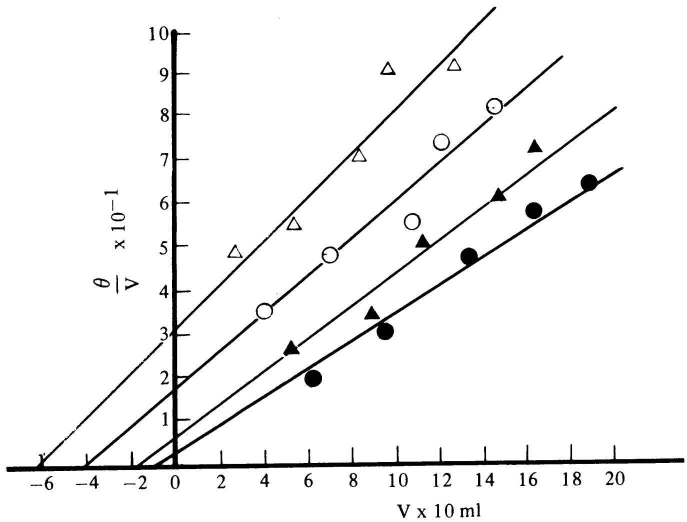


Fig. 1 Ruth plott

3) Results

The relation between specific resistance and pressure drop is shown in Fig. 2. When the average specific resistance is calculated from Fig. 2, the equation 4 may be taken as equation 5.

$$\bar{\alpha} = 4.9 \times 10^{11} \Delta P^{0.96} \qquad (5)$$

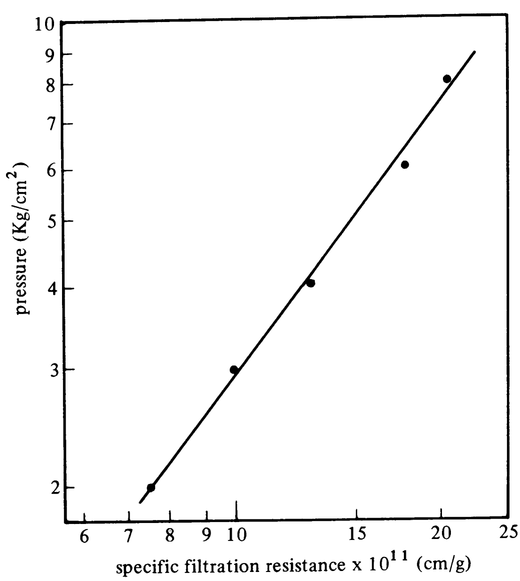


Fig. 2 Relation between pressure and specific filtration resistance

The specific resistance m, Ruth's filtration velocity constant K and $R_m / \alpha\rho_{wc}$ (ρ_{wc}; density of wet cake) which is calculated from Table 1 are shown in Table 3. When rearanged by a substituting equation (5) into equation (2), K is given in the following equation (6).

$$K = \frac{2A^2 \Delta P^{0.31}}{4.9 \times 10^{-11}} \qquad (6)$$

The filtration velocity affects very little the rise of pressure by compression of the cake as is evident from equation (6), and therefore it is not right to use a high pressure. The resistance of the filter cloth is loss than the resistance of the cake, therefore the filtration velocity is almost uninfluenced by using the filter.

AVERAGE DIAMETER OF LIGNIN

1) Experimental method

The purpose of this experment has been to calculate the filtration velocity for the washing of the cake. The particle size was determined in the constant settling period of the settling curve that was descrived by the size determination apparatus (Shimazu SA-2).

The conditions of lignin's preparation were like by to come, lignocellulose; steam cooking of birch 180°C, 2hr, hydrolysis; ratio of sulfuric acid 30%, filtration and washing 5 times, pH 6.0, drying; 105, 2 hr.

The lignin was put into sulfuric acid solutions which were fixed on 1, 2, 5, 10, 20, 30, 35, 40%. The measuring time was 10 hr at 20°C. The diameter of lignin was calculated by using Stock's $U_t = g(\rho_s - \rho_l) D_p^2 / 18\mu$ (U_t; terminal velocity, D_p; diameter of particle, ρ_s; density of lignin, ρ_l; density of sulfuric acid, μ; viscosity of sulfuric acid. The specific gravity of lignin was 1500 kg /m^3, and the viscosity of sulfuric acid was quoted Lange's Handbook[4]).

2) Results

Table 2 Relation between average diameter of lignin and concentration of sulfuric acid

concentration of H_2SO_4 %	specific gravity gravity of H_2SO_4	viscosity c.P.	terminal velocity mm/h	diameter of lignin μ
1	1.007	1.008	4.21	4.4
2	1.014	1.022	6.19	4.7
5	1.036	1.043	5.75	6.6
10	1.074	1.094	4.54	5.9
20	1.160	1.190	2.30	4.1
30	1.261	1.287	0.468	3.3
35	1.318	1.335	1.00	3.7
40	1.381	1.484	0.821	5.0

remark; specific gravity of H_2SO_4 at 20°C, viscosity at 20°C

The results are shown in Table 2 and Fig. 3. As is evident from Fig. 3, the relation between the diameter and the concentration of acid is rather complex, but the filtration velocity in washing may be explained by using this curve.

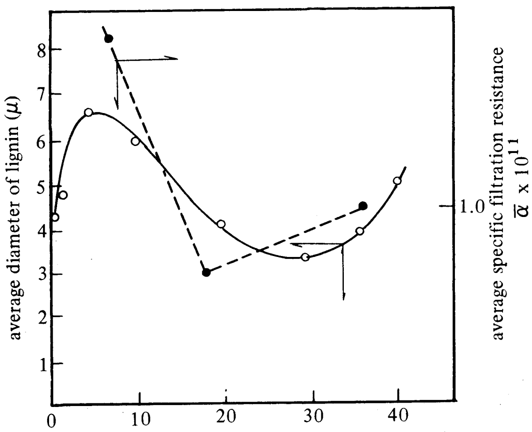


Fig. 3 Relation between average diameter of lignin and concentration of sulfuric acid

LIGNIN FILTRATION ON PILOT PLANT

1) Experimental method

The type of filter press used was the ordinary filter press with 16 chambers and a total filtration area of 1.5 m^2. The lignocellulose was prepared by steam cooking of birch at 150°C for 2 hr. The centrifugal mixer was used for the hydrolysis of lignocellulose. The filtration temperature was about 40°C, and the pressure used was 3, 4 and 6 kg/cm^2. The filtrate was measured every 15 minutes. A filter cloth was used of polyvinylalcohol fiber (Tebiron # 255). The viscosity was measured by Ostwald viscometer.

2) Results

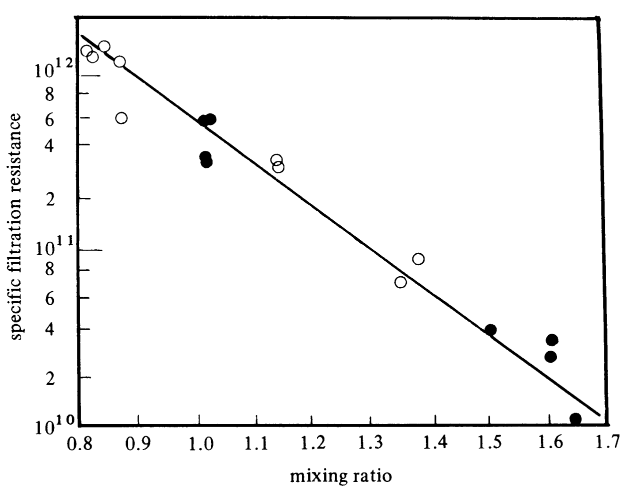
The specific filtration resistance which was calculated by using these experimental

Table 3 Filtration by pilot plant at pressure of $4 Kg/cm^2$

concentration of H_2SO_4 (%)	mixing ratio	reducing sugar (%)	polimerization degree	lignin (%)	specific filtration resistance (cm/g)
27.5	1.04	13.5	2.6	12.5	3.49×10^{11}
27.0	1.09	12.8	1.2	11.7	5.46 x "
27.5	1.06	12.8	1.5	12.7	5.40 x "
25.6	1.06	12.1	1.3	11.8	3.24 x "
32.1	1.60	11.3	2.5	8.5	0.325 x "
31.0	1.50	8.7	1.1	11.7	0.399 x "
29.6	1.61	8.1	1.1	10.2	0.276 x "
45.1	1.68	10.8	1.1	16.1	0.131 x "

Table 4 Filtration by pilot plant at several pressure

pressure (Kg/cm^2)	mixing ratio	water in cake	thickness of cake mm	specific filtration resistance (cm/g)	times of measure
3.0	0.82	0.670	13	13.5 x 10^{11}	2
4.0	0.82	0.681	13	13.6 x "	2
6.0	0.82	0.685	13	18.5 x "	2
3.0	0.83	0.705	13	8.4 x "	1
4.0	0.83	0.710	13	13.7 x "	1
6.0	0.83	0.703	13	13.1 x "	1
2.0	0.84	0.708	13	5.07 x "	1
3.0	0.84	0.668	13	10.7 x "	2
4.0	0.84	0.675	13	13.6 x "	2
6.0	0.84	0.670	13	15.5 x "	2
3.0	0.84	0.718	13	14.4 x "	4
4.0	0.84	0.703	13	13.6 x "	4
6.0	0.84	0.691	13	14.3 x "	4
3.0	0.87	0.763	13	9.43 x "	1
4.0	0.87	0.758	13	10.8 x "	1
6.0	0.87	0.748	13	15.0 x "	1
3.0	1.14	0.738	13	2.40 x "	1
4.0	1.14	0.738	13	3.30 x "	1
6.0	1.14	0.729	13	3.87 x "	1
1.5	0.84	0.791	34	5.27 x "	1
4.0	0.87	0.715	34	5.40 x "	2
4.0	1.14	0.758	34	3.04 x "	1
5.0	1.39	–	50	1.05 x "	1



remarks; ●: from table 3, ○: from table 4

Fig. 4 Relation between mixing ratio and specific filtration resistance at 4 Kg/cm^3

results is shown in Table 3 and 4. The compressiblity factor of the cake was 0.55 ± 0.14, which is small as compared with the fundmental data. The cause is not clear, but it may be considerd that the kind of wood made a difference and that the particles of lignin coagulated only after 24 hr settling after the hydrolysis.

A nearly linear relation was obtained when the specific filtration resistance and the mixing ratio of sulfuric acid were plotted on semilogarimthmic graph paper.

The product of the concentration of the sulfuric acid, the concentration of reducing sugar and the average condensation degree could be assumed as functions of viscosity, namely, (concentration of sulfuric acid %) × (concentration of reducing sugar %) × (average condensation degree was calculated for 40°C) as an attempt. The result are shown table 5.

Plotted on semilogarithmic paper (Fig. 5), it appeared that they lay almost on a curve line which seems to have been done with some particular purpose. The significance of the curve line could not be made clear, but it will be useful to infer a round value of density.

It is conventional for recovering of surfuric acid that the resudial acid in lignin takes as small a volume as possible, therefore after filtration it was repulped two or three times. As the change of the specific filtration resistance has been considered in accordance to the concentration of the sulfuric acid and reducing sugar, the viscosity and arrother the physical property of lignin, the specific filtration resistance could be determined on every

Table 5 Relation between composition of filtrate and viscosity

viscosity c.p. 20°C	concentration of H_2SO_4 (%)	concentration of reducing sugar (%)	average degree of polymerization	(H_2SO_4 %) x (R.S. %) x (A.D.P.)
0.39	2.2	1.0	3.5	7.7
0.70	3.5	1.8	2.9	18.4
0.64	2.7	7.4	2.2	44.0
0.84	9.7	4.7	3.0	136.8
0.78	9.1	4.8	3.3	144.1
0.88	13.1	5.6	2.8	218.0
0.77	10.5	9.4	2.4	236.9
0.93	15.6	7.7	2.9	348.3
1.38	26.4	12.1	2.2	702.8
1.95	26.9	13.3	2.6	930.2
1.88	27.0	13.9	2.8	1050.6
1.92	26.6	13.5	3.1	1113.2
2.01	26.8	13.9	3.0	1117.6
2.52	30.1	16.1	2.7	1308.4
2.90	33.5	16.4	2.5	1373.5
3.32	35.5	16.8	2.5	1491.0
3.07	32.3	17.1	2.7	1491.3
2.62	36.4	16.1	2.7	1308.4
2.52	35.0	16.8	2.8	1646.4
3.86	32.1	16.7	4.1	2197.9
3.30	21.4	16.4	4.3	2214.3

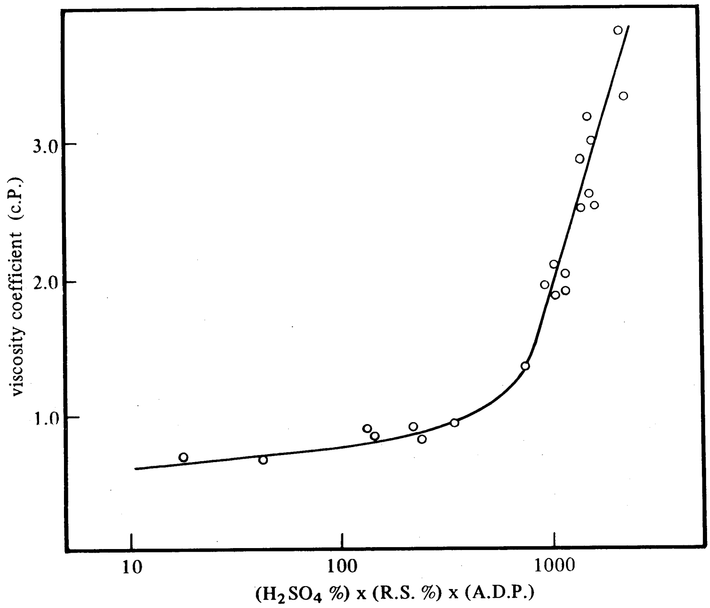


Fig. 5 Relation between viscosity and concentration of H_2SO_4 x concentration of reducing sugar x average degree of polymerization of filtrate at 40°C.

Table 6 Ratio of average specific filtration resistance at filtration and repulp

	number of experiment	average specific filtration resistance $\bar{\alpha}$	ratio of per filtration	concentration of H_2SO_4 (%)
	1	13.3×10^{11}	1	35.0
	2	8.30×10^{11}	1	34.0
filtration	3	3.03×10^{11}	1	34.3
	average	8.21×10^{11}	1	34.4
	1	8.11×10^{11}	0.66	17.1
	2	5.11×10^{11}	0.69	16.3
first repulp	3	2.12×10^{11}	0.69	17.0
	average	5.12×10^{11}	0.68	16.8
	1	33.6×10^{11}	2.44	7.6
	2	14.6×10^{11}	1.74	6.9
second repulp	3	4.35×10^{11}	1.43	6.9
	average	17.5×10^{11}	1.87	7.1

repulp. The results are shown in Table 6.

The used water was reajusted to the same volume on every repulp. The filtration velocity of second repulp was larger than the first repulp. The reason may be that the particles of lignin coagulated in the first or third repulp as is known from Fig. 3.

CONCLUTION

The average specific filtration resistance which was calculated is shown follow.

$$K = 4.9 \times 10^{11} \Delta P^{0.69}$$

The compressility coefficient is 0.69, therefore the filtration velocity has a very little affect for arising of pressure in order for compression of the cake.

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加水分解液中のリグニンの沪過

保　坂　秀　明

恒圧沪過の基礎試験の結果，比抵抗は grace の加圧沪過限界以上の 10^{11} オーダの比抵抗を圧力 2 ～ 8 kg／cm²で示した。したがって，リグニン炉過はフィルタプレスが至当であると結論した。

リグニンの粒子は，沈降速度の測定から算出したところ，硫酸濃度により複雑なる変化が認められた。ところが洗浄時のリパルプによる沪過の比抵抗は，第一リパルプでは初回沪過より低く，第三リパルプでは初回沪過より高い結果を得，この際の硫酸濃度をリグニン粒子の場合と比較すると，ほぼ同一の傾向がみられた。

テストプラントの試験結果では，比抵抗は硫酸混合比が支配的であり，混合比が少なくなれば，その比抵抗は増大する。また，粘度の目安として，（H_2SO_4%）×（還元糖%）×（平均重合度）との関係を求めたが，（H_2SO_4%）×（還元糖%）×（平均重合度）が 10 ～ 300 では粘度の変化はないが，300 以上で急激に粘度が増大する。これは実用的には利用できる目安とならう。