

Optimization of Synthesis of Spherical Lignosulphonate Resin and Its Structure Characterization*

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Abstract Calcium lignosulphonate was used to synthesize a spherical lignosulphonate resin in a cheap and non-toxic disperse medium by reversed phase suspension polymerization. The process conditions were optimized by orthogonal experiments. Under the optimal conditions ($T=95^{\circ}\text{C}$, $c_{\text{HCl}}=3\text{ mol}\cdot\text{L}^{-1}$, $m_{\text{HCHO}}:m_{\text{CLS}}=7\%$, $w_{\text{CLS}}=50\%$), globulation took about 20 min and the product was featured with excellent spherical shape, narrow particle size range, 61.20% of water retention capacity, 0.83 $\text{mmol}\cdot\text{ml}^{-1}$ of total volume exchange capacity and 3.46 $\text{mmol}\cdot\text{g}^{-1}$ of total exchange capacity. The results of Scanning Electron Micrograph and Scanning Probe Micrograph indicate that spherical lignosulphonate resin has a rugged surface with porous microstructure in the gel skeleton. The average pore size of dry samples was determined to be 10.46 nm by the BET method.

Keywords spherical lignosulphonate resin, process optimization, structure characterization

1 INTRODUCTION

Besides coal, petroleum and natural gas, the biomass mainly including plant is an important and necessary resource to realize the sustainable development of the human society. And in the plant kingdom, lignin is the second abundant natural polymer after cellulose, and it is the sole aromatic compound that can be obtained from renewable resources. Nowadays, most lignin applications are based on technical lignin, which are mostly separated during pulping process [1, 2]. Lignosulphonate (LS) has found wide application in many fields such as surfactant, synthetic resin and adhesive industry [3–5]. Mostly obtained as a byproduct from the red liquor during sulphite pulping process, lignosulphonate is actually a mixture of the fragments degraded from lignin macromolecules and the condensation compounds of these fragments. It consists of both aromatic and aliphatic portions and comprises a variety of functional groups, such as hydroxyl, carbonyl, methoxyl and sulphonic groups. Due to these characteristics, lignosulphonate appears to be a promising material to prepare ion exchange resin by chemical modification such as oxidation, condensation and amination, etc.

The preparation of lignosulphonate ion exchange resin has been studied since 1950s. In the beginning, the spent sulfite liquor was polymerized with formaldehyde to get a cation exchange resin with an ion exchange capacity of only 0.3–0.35 $\text{mmol}\cdot\text{L}^{-1}$ [6]. Later, the condensed or pure lignosulphonic acid was used and the ion exchange capacity increased to 2.1–2.34 $\text{mmol}\cdot\text{L}^{-1}$ [6]. However, all these works were confined to amorphous gel type resin with low yield, poor column performance and low exchange capacity. Spherical lignin based ion exchange resin were studied from the late 1970s. Zhu *et al.* [7] prepared the spherical lignosulphonic acid cation exchange resin with condensed lignosulphonic acid, but the repro-

ducibility was not good enough and the exchange capacity was still low (1.8–2.5 $\text{mmol}\cdot\text{g}^{-1}$). Zoumpoulakis and Simitzis [8] synthesized the lignin-novolac resins through partially substituted phenol by Kraft lignin or hydroxymethylated Kraft lignin, which were sulphonated with excessive concentrated H_2SO_4 and then cross-linked with formaldehyde to get the cation exchange resins. The products showed higher ion-exchange capacity (2.6–2.7 $\text{mmol}\cdot\text{g}^{-1}$) than typical sulfonated phenolic resin (2.4 $\text{mmol}\cdot\text{g}^{-1}$). Liu *et al.* [9] prepared spherical lignin beads by reverse-phase suspension polymerization with magnesium lignosulphonate in the mixture of electric insulation oil and chlorobenzene, but chlorobenzene is known to be a toxic substance. The reports on the ion exchange resin preparation with lignosulphonate as a main raw material are scarce.

Our previous study [10] indicated that a spherical lignosulphonate resin (RLS) with controllable size distribution could be developed in a cheap and non-toxic disperse medium with calcium lignosulphonate (CLS) as raw material, formaldehyde as cross linker, hydrochloric acid as catalyst by the reversed phase suspension polymerization technique. In this article, the suspension polymerization of CLS and formaldehyde in liquid paraffin were optimized by orthogonal experimental design in order to shorten the reaction time and improve the strength and ion exchange capacity of the product. The effects of temperature, concentration of hydrochloric acid, dosage of cross-linking agent and mass fraction of CLS on the rate of polymerization and the product quality were analyzed. In addition, the microstructure of RLS was revealed by scanning electron micrograph (SEM) and scanning probe micrograph (SPM). The pore size distribution of dry sample was determined by the BET method. And the thermal behavior of the product was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

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2 EXPERIMENTAL

2.1 Reagents and materials

CLS with the mass average relative molecular weight of 2505 is a by-product of sulfite pulping from Guangzhou Papermaking Company and used without further purification. HCl, HCHO and other reagents were analytical grade except that liquid paraffin was chemical grade.

2.2 Suspension polymerization

According to the mass fraction of CLS specified in Table 1, the aqueous solution of CLS was prepared by 30 g of CLS powder beforehand in a 500-ml three-necked flask equipped with an IKA RW 20 DZM.n digital stirrer and a reflux condensation tube. Certain amount of HCl (37% mass concentration) and HCHO (37% mass concentration) were added into the flask and stirred to mix well, and then 240 ml of liquid paraffin with 0.5 g of Span60 was added. The two-phase system was continuously stirred at 200 r·min⁻¹ and heated by an oil bath to reach the specified temperature, at which the mixture was stirred until the lignosulphonate beads were generated. The temperature was elevated and the beads were boiled at 105–110°C for 3–4 h, and parts of water and hydrochloric acid were discharged from the beads. As the reaction was finished, the mixture was cooled to room temperature and then filtered to get the reaction products and recover paraffin liquid. The products were washed thoroughly first by 2 mol·L⁻¹ NaOH solution and then by tap water and some surfactant. After wet sieving, the samples of spherical lignosulphonate resin with a size range from 0.20 to 1.20 mm were stored in water. The yield can reach 93% and the typical volume percent with size 0.2–1.2mm is higher than 95%.

2.3 Orthogonal experimental design

When the disperse medium, dispersing agent and the stirring conditions were specified, the effects of cross-linking reaction temperature (T), concentration of hydrochloric acid (c_{HCl}), dosage of cross-linking agent ($m_{\text{HCHO}} : m_{\text{CLS}}$) and mass fraction of CLS (w_{CLS}) on the rate of polymerization, water retention capacity [H_2O] and total volume exchange capacity (Q_v) of the product were investigated by the orthogonal experiment with four factors and three levels (Table 1). The experiments were conducted according to the orthogonal layout of $L_9(3^4)$.

Table 1 Factors and levels of orthogonal experiment

Level	Factor			
	A ($T/^\circ\text{C}$)	B ($m_{\text{HCHO}} : m_{\text{CLS}}/\%$)	C ($c_{\text{HCl}}/\text{mol}\cdot\text{L}^{-1}$)	D (w_{CLS})
1	75	4.2	1	0.50
2	85	7.0	2	0.40
3	95	14.0	3	0.33

2.4 Determination of fundamental performances

The fundamental properties of RLS including particle size range, water retention capacity, true and bulk density, and exchange capacity were determined after pretreatment according to relevant Chinese National Standards: GB/T5758-2001, GB5757-86, GB8330-87, GB8331-87 and GB8144-87, respectively. The ion-exchange capacity of the products was determined according to a standard method by converting the resin groups into the hydrogen form with excessive amount of acid, then rinsing off the excessive acid, equilibrating the resin with known volume of 0.1 mol·L⁻¹ NaOH and titrating of the excessive NaOH with 0.1 mol·L⁻¹ HCl.

2.5 Characterization of structure

The microstructure of RLS was characterized by S-510 SEM (Hitachi, Japan) and CSPM-2003 SPM (Benyuan, China). The pore size and specific surface area of dry sample were determined by an accelerated surface area and porosimeter system (ASAP2010, Micromeritics, USA).

3 RESULTS AND DISCUSSION

3.1 Results and analysis of orthogonal test

The laboratory results of the orthogonal experiments are listed in Table 2. Among them, the reaction time for globulation (Time) in the 5th test is the least, while Q_v is the highest and [H_2O] is near to the least, which indicate the quality of this product is the best.

The significance of the four major factors (A , B , C and D) can be evaluated by range analysis. In Table 2, K_i is the sum of the results of the tests at level i ($i=1,2,3$) for each factor. k_i is the corresponding average ($k_i=K_i/3$). R is the range, that is $R=k_i(\text{max})-k_i(\text{min})$. The factor with the larger range has more significant influence on a certain index, such as the reaction time for globulation, the water retention capacity or the total volume exchange capacity. The best level should be selected for the significant factor or general factor; while for the non-significant factor, the value of level should be decided by the economical and convenient principle [11].

The analytical results show that the significance of the four factors on the reaction time can be described in the order of $A>C>D>B$, and the better combination is $A_3-C_3-D_1-B_2$. Similarly, the significance of the factors on Q_v is in the order of $A>D>B>C$, and the better combination is $A_3-D_1-B_2-C_3$. While for [H_2O], they are $A>D>C>B$ and $A_3-D_1-C_2\approx C_3-B_2$. Based on the comprehensive consideration of the effects of all factors on the three indexes, it can be concluded that the most significant influencing factor is A , followed by D , C and B . The probably optimal combination is $A_3-D_1-C_3-B_2$, which hasn't occurred in Table 2, so the proof test was carried out in the probably optimal conditions: $T=95^\circ\text{C}$, $c_{\text{HCl}}=3 \text{ mol}\cdot\text{L}^{-1}$, $m_{\text{HCHO}} : m_{\text{CLS}}=7\%$, $w_{\text{CLS}}=50\%$. It took less than 20 min for

Table 2 Results and analysis of orthogonal test

Index	No.	A	B	C	D	Result		
						Time /h	Q_v /mol·L ⁻¹	[H ₂ O] /%
	1	1	1	1	1	8	0	100
	2	1	2	2	2	6	0.243	87.97
	3	1	3	3	3	8	0	100
	4	2	1	2	3	4	0.263	85.51
	5	2	2	3	1	0.3	0.793	62.52
	6	2	3	1	2	6	0.383	83.35
	7	3	1	3	2	0.5	0.538	75.6
	8	3	2	1	3	3	0.386	86.53
	9	3	3	2	1	0.3	0.672	62.35
Time	K_1	22	12.5	17	8.6			
	K_2	10.3	9.3	10.3	12.5			
	K_3	4	14.3	8.8	15			
	k_1	7.3	4.2	5.7	2.9			
	k_2	3.4	3.1	3.4	4.2			
	k_3	1.3	4.8	2.9	5			
	R	6	1.7	2.8	2.1			
	Q_v	K_1	0.243	0.801	0.769	1.465		
K_2		1.439	1.422	1.178	1.164			
K_3		1.596	1.055	1.331	0.649			
k_1		0.081	0.267	0.256	0.488			
k_2		0.532	0.474	0.393	0.388			
k_3		0.887	0.352	0.444	0.216			
R		0.806	0.207	0.188	0.272			
[H ₂ O]		K_1	287.97	261.11	269.88	224.87		
	K_2	231.38	237.02	235.83	246.92			
	K_3	224.48	245.7	238.12	272.04			
	k_1	95.99	87.04	89.78	74.96			
	k_2	77.13	79.01	78.61	82.31			
	k_3	74.83	81.9	79.37	90.68			
	R	21.16	8.03	11.16	15.72			

globulation. The size distribution of the product is very narrow (Fig. 1). The fundamental performances, presented in Table 3, were improved as compared with those of Test 5 in Table 2, including the lower water retention capacity and the higher total volume exchange capacity. The total exchange capacity was 3.46 mmol·g⁻¹ for dry sample of the products obtained at the optimal conditions, which was better than those reported by Zhu *et al.* [7] and Zoumpoulakis *et al.* [8], which were 2.5 mmol·g⁻¹ and 2.7 mmol·g⁻¹ respectively.

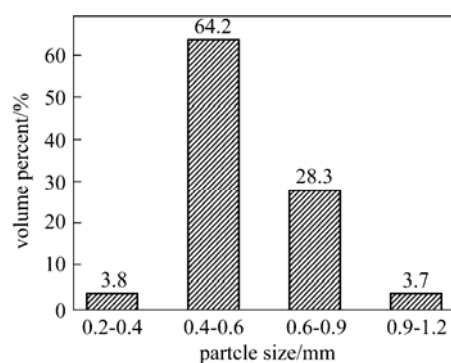


Figure 1 Size distribution of RLS produced under optimal conditions

3.2 Characterization of structure

The spherical lignosulphonate resin is dark brown opaque pellet of ideal spheric shape. The SEM and SPM photographs of RLS (Figs. 2 and 3) indicate that RLS has a rugged surface with porous microstructure in the gel skeleton.

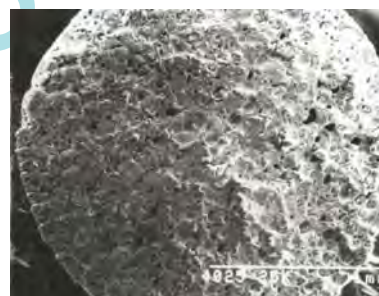
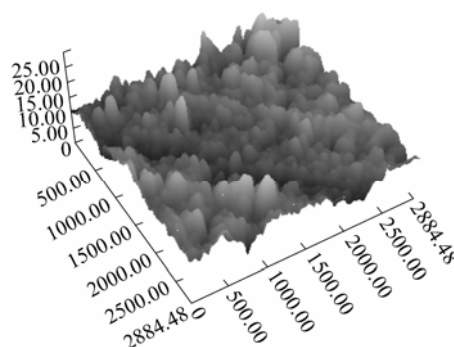
Figure 2 SEM photograph of RLS (×50) (Reaction conditions: $T=85^{\circ}\text{C}$, $c_{\text{HCl}}=2\text{ mol}\cdot\text{L}^{-1}$, $m_{\text{HCHO}} : m_{\text{CLS}}=7\%$ and $w_{\text{CL}}=50\%$)

Figure 3 SPM photograph of RLS (Reaction conditions are the same as Fig. 2)

Table 3 Fundamental performances of the product obtained at optimal conditions

Yield with size of 0.4-0.9 mm /%	Water retention capacity /%	Bulk density in wet state d_b /g·ml ⁻¹	True density in wet state d_T /g·ml ⁻¹	Total exchange capacity for wet resin Q_T /mmol·g ⁻¹	Total volume exchange capacity for wet resin Q_v /mmol·ml ⁻¹	Total exchange capacity for dry resin Q_T /mmol·g ⁻¹
92.5	61.20	0.68	1.08	1.34	0.83	3.46

The average pore size determined by the BET method was 10.46 nm, and the corresponding specific area was $4.6893 \text{ m}^2 \cdot \text{g}^{-1}$. However, the ion exchange resin is usually used in aqueous, and the BET method is only sound for dry samples, so the measured value is always lower than the true value because of the pore distortion or collapse during the drying of samples. The porosity of wet sample P can be calculated by Ref. [12]

$$P = 1 - \frac{d_b}{d_T}$$

According to the data in Table 3, the porosity of wet sample produced by the proof test was 43.27 %. Because the ion exchange resins is generally used in wet state, the further investigation on the pore structure of wet samples should be carried out in future research.

NOMENCLATURE

d_b	bulk density in wet state, $\text{g} \cdot \text{ml}^{-1}$
d_T	true density in wet state, $\text{g} \cdot \text{ml}^{-1}$
$[\text{H}_2\text{O}]$	water retention capacity, %
P	porosity of wet resin, %
Q_T	total exchange capacity for dry resin, $\text{mmol} \cdot \text{g}^{-1}$
Q'_T	total exchange capacity for wet resin, $\text{mmol} \cdot \text{g}^{-1}$
Q_v	total volume exchange capacity for wet resin, $\text{mmol} \cdot \text{ml}^{-1}$

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