

# Preparation of Cation-exchange Resin from Lignin

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## ABSTRACT

Lignin precipitated from black liquor of soda pulping of bagasse was used to prepare cation-exchange resin. The effect of sulfuric acid treatment, concentration of phenol and formaldehyde on the properties of the prepared cation-exchange resin was investigated. It was found that sulfonated resinified phenolated lignin gave a resin with an ion-exchange capacity higher than that of resin, which resulted from sulfonation of resinified lignin at zero phenol concentration. Infrared spectroscopy of the prepared ion-exchange resin shows new bands at 1060, 1160, 1280 and 1330  $\text{cm}^{-1}$  which indicated to the presence of  $\text{SO}_3$ .

*Keywords: lignin, ion-exchange resin, sulfonation, IR.*

## 1. Introduction

In nature, lignin is the second most abundant organic material, after cellulose. Lignin is a phenolic polymer so; it has potential as an alternative raw material for phenolic resins, adhesives, etc. Although a large number of works on conversion of lignin to useful materials have been done on hydrocracking, pyrolysis, and derivatization, there are no lignin products produced commercially except for lignin sulfonate, which can be obtained from black liquor of sulfite pulping (1).

Waste black liquor, which produced from soda or kraft pulping is thrown in stream water causing pollution or uses as a fuel for pulping chemical recovery in paper mills. So,

industrial usage of this waste black liquor is of great environmental and economical importance. Soda bagasse lignin has a high number of unsubstituted 3- and 5-positions on phenolic propanoid units (2). As a result lignin can be used successfully in different applications.

In the past 20 years, lignin showed potential for use as activated carbon (3), a binder as well as a coupling agent in particleboard (4, 5) and as a reactive component during the polymerization of phenol / formaldehyde resin (6). Also, the phenol was replaced by lignin on the preparation of novolac resins (7). Glassier (8), synthesized polymer from lignin and isocyanate combination, while Johns (9)

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employed lignin in formation of polyurethane, etc.

The most important polycondensates used to produce ion-exchange resins are derivatives of phenol and formaldehyde. Phenolic molecules that possess unsubstituted para- and both ortho- positions can react at three positions with formaldehyde and forming a network with terfunctional junction's (10). Yasuda et. al. (11) could be prepared strongly acidic cation-exchange resin from Klasion lignin of red pine by sulfonation of resinified sulfuric acid lignin. Also, ion-exchange resin was prepared from kraft lignin or hydroxymethylated kraft lignin of olive stone biomass by sulfonation of polymerization product of kraft or hydroxymethylated kraft lignin with phenol and formaldehyde under acidic conditions (12).

In this study, cation-exchange resin could be prepared from soda bagasse lignin. The effect of sulfuric acid treatment, concentration of phenol and formaldehyde on the properties of the prepared cation-exchange resin was investigated. Also infrared spectroscopy of lignin and sulfonated resin was investigated.

## 2. Experimental

### 2.1 Material

Lignin was separated from black liquor, which was obtained as a by-product from soda pulping of bagasse, by acidifying with HCl to pH 1.5, heated to 90°C, and then left for 1 hour. The crude alkali lignin was filtered, washed with water and dried in vacuum oven (13). Reagent grade formaldehyde of 37% concentration, phenol, chlorosulfonic acid, sulfuric acid; tetrachloroethane and sodium hydroxide were used.

### 2.2 Methods

#### 2.2.1 Preparation of cation exchange resin

Cation-exchange resin was prepared through three stages, namely, phenolation, resinification and sulfonation stages.

##### 2.2.1.1 Phenolation stage

A mixture of 1.0 g of lignin and 6.3 g of phenol in 15 ml of 72% sulfuric acid was stirred at 60°C for 5 hours. After quenching by dilution with 560 ml of water, the suspension was boiled for 3 hours. The solids were filtered out and were thoroughly washed with warm water to give phenolized lignin (14).

##### 2.2.1.2 Resinification stage

To a solution of 0.1g lignin or phenolized lignin in 1 ml 3M NaOH was added 0.5 ml of 37% formaldehyde. After heating at 60°C for 1 hour and then at 180°C for another 1 hour in a small autoclave heated in controlled electrical oven at a temperature which was 10°C above the stated reaction temperature. The solid contents were filtered of, washed with water, and then dried to give resinified phenolized lignin or resinified lignin (11).

##### 2.2.1.3 Sulfonation stage

To a suspension of 0.1 g resinified phenolized lignin or resinified lignin in 2 ml tetrachloroethane was added 0.25 g chlorosulfonic acid. After stirring at 50°C for 0.5 hour and then at 100°C for another 1 hour, the suspension was made basic carefully by adding 20 ml 2M NaOH, then refluxed for 1 hour. The contents were filtered of and washed with distilled water then dried in vacuum oven to give sulfonated resin (Na<sup>+</sup> form) (11).

#### 2.2.2 Determination of sulfur content

The sulfur content of the prepared resins was determined quantitatively by using Vario El-Elementar.

### 2.2.3 Ion exchange capacity of sulfonated resin

To determine the ion-exchange capacities of the sulfonated resin, the  $H^+$  form of sulfonated resinified phenolized lignin or sulfonated resinified lignin was regenerated firstly by washing the  $Na^+$  form with 1M HCl then with distilled water. The washed sample was oven dried. 0.1 g sulfonated resin ( $H^+$  form) in 5 ml 0.05 M NaCl was allowed to stand for 2 hours at room temperature with stirring at intervals. After filtering out the resin with a glass filter, the combined solution of the filtrate and the washings was titrated with 0.05M NaOH using methyl orange as an indicator. By knowing the amount of alkali consumed, the ion exchange capacity was calculated (15).

### 2.2.4 Characterization

Infrared (IR) spectra of lignin and sulfonated resins were recorded on a Perkin Elmyer

Spectrometer (Model) using KBr disk pellet from  $4000-400\text{ cm}^{-1}$ .

## 3. Results and Discussion

Ion exchange resin can be formed from lignin by sulfonation of resinified lignin or resinified phenolized lignin which formed from the reaction of formaldehyde with lignin or phenolized lignin (Fig. 1). Firstly the effect of treatment of lignin by 72% sulfuric acid before phenolation process on the ion-exchange capacity and the effect of phenol to lignin ratio as well as formaldehyde to phenolized lignin ratio on the properties of produced resin will be study.

### 3.1 Treatment of lignin with sulfuric acid

The main reaction of lignin in 72% sulfuric acid treatment is intermolecular condensation

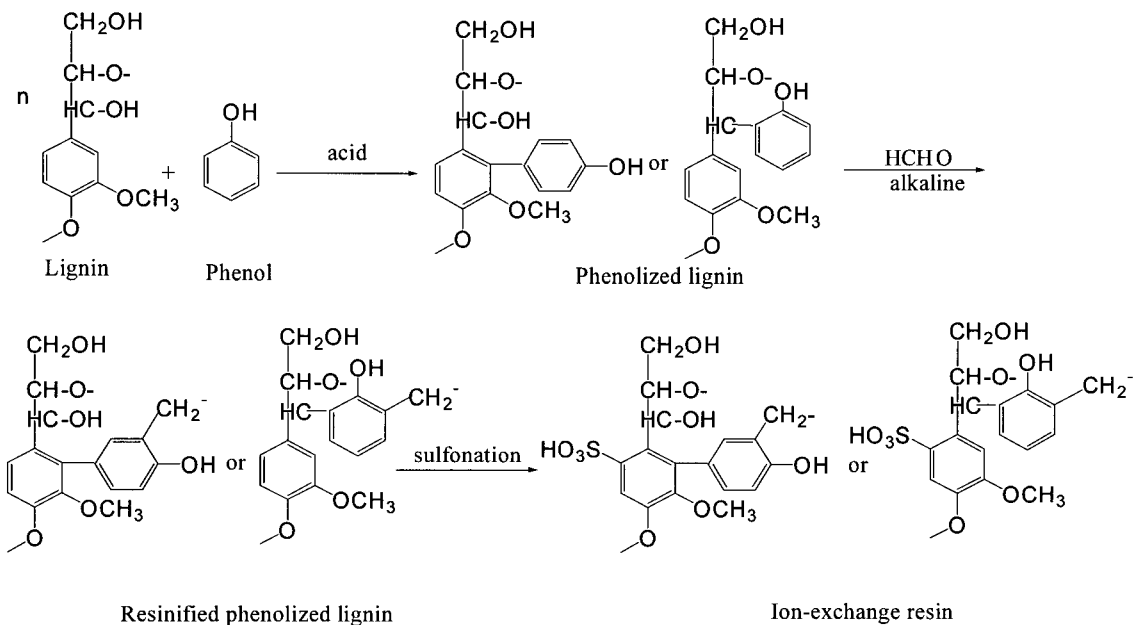


Figure 1 Preparation of ion-exchange resin from lignin.

Fig. 1. Preparation of ion - exchange resin from lignin.

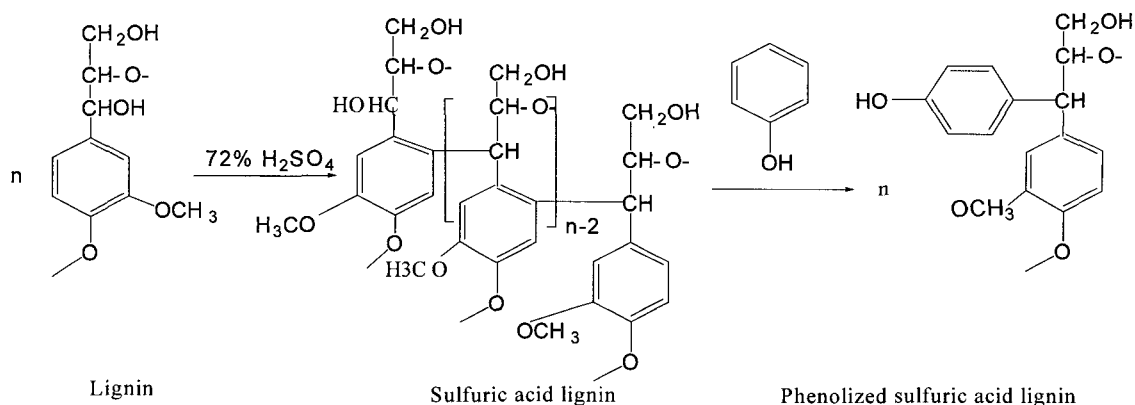


Figure 2 Phenolation of sulfuric acid lignin.

Fig. 2. Phenolation of sulfuric acid lignin.

between aromatic nuclei and side chain  $\alpha$ -carbons of lignin (16). Since, condensed lignin was easily exchanged their aromatic nuclei for those of simple phenolic compounds in the presence of sulfuric acid catalyst under mild condition (17), so the main mode of phenalization of sulfuric acid lignin in the presence of sulfuric acid as a catalyst as shown in Fig. 2.

To study the effect of treatment of lignin by sulfuric acid, 0.1 g of soda lignin was treated with 72% sulfuric acid in the usual manner. From Table 1 it is shown that the sulfur content and ionexchange capacity of untreated soda lignin were higher than that of treated soda lignin by sulfuric acid. This may be due to the steric hindrance of substituents, which were introduced during concentrated sulfuric acid

treatment, which lead to lowering the reactivity at the ortho position of the group.

So, the more detailed research in this work would be done on untreated lignin.

### 3.2 Effect of phenol to lignin ratio

The effect of phenol to lignin was studied, as shown in Table 2. The percent of formaldehyde used was 0.5 ml for each 0.1 g lignin or phenolized lignin. An increase of phenol percent increased the resin yield and accordingly increased the sulfonated yield. This may be due to the increase in the molecular weight of the obtained phenolized lignin, which is attained about 300. On the assumption that the molecular weight of lignin is 18618 on the basis of the empirical formula  $C_9H_{6.51}O_{1.62}(OH)_{1.01}(OCH)_{0.90}$  so, the reaction of one

Table 1. Effect of sulfuric acid treatment on ion-exchange resin

	Soda lignin		Treated soda lignin	
	Resin(S %)	Ion-exchange Capacity (mEq/g)	Resin(S %)	Ion-exchange Capacity(mEq/g)
Phenolized lignin	10.17	3.18	5.53	1.79
Non-Phenolized lignin	5.90	1.77	3.70	1.40

**Table 2. Effect of phenol % on ion-exchange resin**

Phenol (gm)	Resin yield (%)	Sulfonated yield (%)	Resin (S %)	Ion-exchange Capacity (mEq/g)
0.00	94.3	33.5	5.90	1.77
0.62	121.0	43.0	7.76	2.43
1.25	181.5	47.5	10.17	3.18
2.5	195.6	58.8	8.37	2.61
3.75	176.6	49.2	6.08	2.02
5.00	141.0	37.6	5.68	1.80

\* Resin yield based on lignin weight.

\* Sulfonated yield based on resin yield.

\* Weight of lignin 0.2 g.

molecule of phenol results in a 50% weight gain of pheno lized lignin because molecular weight of P is 94.

The sulfur content and ion-exchange capacity of sulfonated resinified phenolized lignin or sulfonated phenolized lignin was determined. An increase of phenol percent increased the sulfur content and accordingly increased ion-exchange capacity of resin. By more increasing the percent of phenol, a drastic reduction in yields, sulfur content and ionexchange capacity was noticed. This may be due to the obtained phenolized lignin consists of phenyl propane units which are condensed with up to four molecules of phenol (19) and this lead to decrease the reactivity due to the steric hindrance.

### 3.3 Effect of formaldehyde to phenolated lignin ratio

The phenolized lignin was used to study the effect of formaldehyde on the properties of the obtained resin (Table 3) was prepared by reacting of 1.3 g phenol and 0.2 g lignin in the presence of sulfuric acid.

As shown in Figure 1 formaldehyde reacts at the ortho position of a phenolic hydroxyl group under the alkaline conditions. In Table 3, increasing formaldehyde ratio increasing the number of the introduced group which led to increasing the resin and sulfonated yields. Also, increasing formaldehyde ratio increased the sulfur content and ion-exchange capacity of sulfonated resins.

### 3.4 Infrared Spectra

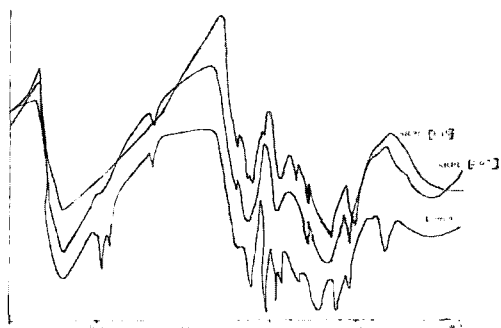
Fig. 3 shows the IR spectra of alkali lignin isolated from soda black liquor produced from pulping of bagasse and sulfonated resins (ion-exchange capacity 3.18 and 2.02). The

**Table 3. Effect of formaldehyde % on ion-exchange resin**

Phenol (gm)	Resin yield (%)	Sulfonated yield (%)	Resin (S %)	Ion-exchange Capacity (mEq/g)
0.5	149.1	44.1	6.82	2.95
1.0	181.5	47.5	10.17	3.18
1.5	183.3	50.0	11.42	3.88
2.0	179.4	49.1	12.44	4.20

\* Resin yield based on lignin weight.

\* Sulfonated yield based on resin yield.



**Fig. 3. IR spectra of lignin and sulfonated resin (SRPL).**

various bands of the IR spectra concerning these materials are summarized in Table 4. From this Table it is shown that, sulfonated resin (ion-exchange resin) does not show bands at 1510, 1410, 1270, 1130, 1040 and 815  $\text{cm}^{-1}$  while lignin shows them. So, the sulfonated resin does not exhibit the syringyl vibrations and the guaiacyl band but lignin shows them. Additionally, sulfonated resin shows bands at 1330, 1280 ( $\text{SO}_2$ ), 1160 ( $\text{SO}_2 \text{O}$ ) and 1060 ( $\text{S}=\text{O}$ )  $\text{cm}^{-1}$  whereas lignin does not show them because it is not sulfonated.

## 4. Conclusions

Sulfonation of resinified lignin gave a resin

with an ion-exchange capacity higher than that of sulfuric acid treated lignin. Increasing the phenol percent in phenolation stage and formaldehyde percent in resinification stage increased the ion-exchange capacity resin and sulfonated yields. The ion-exchange capacity of the prepared resin is superior to that of the corresponding commercial phenol-type resin (2-3 mEq/g).

IR spectroscopy of the sulfonated resin shows a new band that of  $\text{SO}_3$ .

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**Table 4. IR bands of lignin and sulfonated resin**

Band $\text{cm}^{-1}$	Group	lignin	sulfonated resin
3400-3200	OH	+	+
3024	C-H aromatic	+	+
1600, 1510	Aromatic ring	+	-
1410	COOH (combination vibration)	+	-
1330, 1280	$\text{SO}_2$	-	+
1320, 1270, 1130	Syringyl vibrations	+	-
1160	$\text{SO}_2 \text{O}$	-	+
1060	$\text{S}=\text{O}$	-	+
1040	Guaiacyl band	+	-
8152	neighboring H	+	-

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