

## Relationships between the Molecular Structure of Lignins and the Performance of the Negative Plates of Lead-Acid Batteries

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Lignin-basis polymers obtained from plants have been used as additives for the negative plates of lead-acid batteries in order to improve the performance of the negative plates. Most of lignins for additives are made of by-products of pulping-processes. Since their molecular structure is complicatedly changed by high-energy treatment in pulping-processes, its detail remains unclear. Therefore, the effects on the molecular structure of lignins on the performance of the negative plates of batteries have hitherto been ambiguous. Then authors obtained lignophenols with controlled molecular structure from native lignins using the phase-separation system, and investigated the relationships between the molecular structure of lignins and the performance of batteries by adding lignophenols to negative plates. It was found that the discharge performance of the negative plates of batteries improved because the active materials of the negative plates got finer, leading to larger surface area. It was considered that dimethoxyphenol units contribute to the improvement of both the initial performance and the life performance of batteries. Then, it was found that there exists a suitable molecular weight of lignins for uses in batteries.

Key words: lignin, lignophenol, molecular structure, additive, lead acid battery

### 1. INTRODUCTION

In recent years, the higher output of stand-by powers has been required for telecommunications and computers. According as high capacity and long life are required for lead-acid batteries with high rate discharge. In the case of high rate discharge, the discharge capacity of batteries depends on the performance of the negative plates of batteries.

Lignin-basis polymers have been used as additives for the reaction materials (active materials) of the negative plates of batteries. Then, the active materials become fine particles and the surface area increases for the interactions between lignin molecules and the active materials. As a result, the discharge capacity of batteries increases with increased reaction area of the active materials. In short, lignins have the effects on the performance of batteries [1-3].

However, the relationship between the molecular structure of lignins and the performance of the negative plates has been unclear up to now. Since their molecular structure is complicatedly changed by high-energy treatment in pulping-processes, its detail remains unclear. [2].

Then authors obtained "lignophenol"s with controlled the molecular structure, which are derived from native lignins using the phase-separation system [4-7], and investigated the relationships between the molecular structure of lignins and the performance of the negative plates of batteries when adding the lignophenols to negative plates.

### 2. PHASE-SEPARATION SYSTEM

The phase-separation system was developed for

converting native lignins to phenolic functional polymers by Funaoka et al. in Mie University, Japan. [4-7]

At first, native lignins within cell wall are solvated with phenolic compounds. Next, concentrated sulfuric acid is added with vigorous stirring. The contact of lignin with sulfuric acid is limited only to the interface between both phenolic compounds and sulfuric acid. Phenolic compounds are introduced to reactive  $C_{\alpha}$  positions of side chains in lignin molecules. After stopping stirring, the reaction mixture is separated to an organic phase containing lignin and an aqueous (acid) phase containing carbohydrates. [4-7]

All reactions in the phase-separation system proceed without any heating and pressing. The lignin-based materials derived using this system are termed "Lignophenol".

### 3. LIGNOPHENOL

Lignophenols are composed of 1,1-bis(aryl)propane type unit and have a relatively linear type structure. They have important properties of both improved phenolic reactivity and decreased heterogeneity in lignin structure [4-7].

The various functions of lignophenols can be controlled. For example, the molecular weight of lignophenols can be controlled using their intramolecular switching functions and the phenolic activity and functional group ratio can be controlled by an optional change of phenolic compounds used for solvation on the phase-separation system.

## 4. EXPERIMENT

## 4.1 Synthesis of lignophenol (2 step process I)

Extractive-free wood meals were completely soaked with *p*-cresol or the mixture of 2,6-dimethoxyphenol and 2,6-dimethylphenol (3 mol equivalent/ phenylpropane unit) -acetone solution for 24 h to solvate lignin. After the acetone was evaporated, sulfuric acid (72wt%) was added to the reactive mixture and then it was stirred for 1h at room temperature. After phenol-benzene solution was added to the reaction mixture, the organic phase was dropped into excess diethyl ether with vigorous stirring. The precipitate was centrifuged. After drying, the precipitate was extracted with acetone. The soluble fraction was dropped into excess ethyl ether with vigorous stirring again. The precipitate (lignophenol) was collected by centrifugation, and dried. [4-7]

## 4.2 Test samples

Table I shows all kinds of lignophenols used for this study. Lignocresols were obtained from softwood and hardwood native lignins using *p*-cresol. Lignocresols were used mainly for evaluation of the difference between the molecular structure of softwood lignins and that of hardwood lignins. Lignophenols with different methoxyl group content were obtained from softwood and hardwood native lignins using the mixture of 2,6-dimethoxyphenol and 2,6-dimethylphenol.

Further, lignocresols have intramolecular switching functions, by which the molecular structure of lignocresols such as molecular weight and phenolic activities can be controlled under mild alkaline conditions (ex. 1N-NaOH at 170°C) [7]. Hardwood lignodimethoxyphenol was cross-linked to give high molecular weight materials by heating after hydroxymethylation [7]. The low and high molecular weight lignophenols were used to investigate the influences of molecular weight on the performance of batteries.

The amount of methoxyl and methyl groups in lignophenols were determined by <sup>1</sup>H-NMR spectra (JNM-A500 : made by JEOL, solvent (pyridine : chloroform) = (1:3vol), 500MHz). Their average molecular weight of lignophenols were measured by GPC (made by Shimadzu, solvent THF, Column: KF804, KF803, KF802, KF801).

Table I Lignophenols and their average molecular weights.

Lignocresols				
Name	Softwood lignocresol	Low molecular weight softwood lignocresol	Hardwood lignocresol	Low molecular weight hardwood lignocresol
Plant	Softwood		Hardwood	
Solvation	<i>p</i> -cresol			
Second treatment	-	Alkaline treatment[7]	-	Alkaline treatment[7]
Molecular weight	8000	2000	4000	1000
Lignodimethoxyphenols				
Name	Softwood lignodimethoxyphenol	Hardwood lignodimethoxyphenol	High molecular weight hardwood lignodimethoxyphenol	
Plant	Softwood		Hardwood	
Solvation	2,6-dimethoxyphenol: 2,6-dimethylphenol (10:0, 7:3, 5:5, 3:7, 0:10 mol ratio)		2,6-dimethoxyphenol : <i>p</i> -cresol (7:3 mol ratio)	
Second treatment	-	-	Thermal linking[7]	
Molecular weight	8000	4000	High molecular weight	

## 4.3 Lead-acid batteries for the test

At first, a lignophenol 0.2wt% per lead oxide, sulfate barium and plastic fiber were added to lead oxide, and the powdery mixture was mixed with water and sulfuric acid (35wt%). Then the mixture of paste was applied to grids consisting of Pb-Sn-Ca alloy by hand. The plates were cured at 40°C/98% RH for 24 h, and were dried at 50°C for 16 h. The negative plates for batteries were formed from the cured plates in sulfuric acid (28wt%) with electric capacity of 2.5 times theoretical capacity. The positive plates for batteries were produced under factory conditions.

Table II shows specifications and test conditions of these batteries. Then, the liquid type batteries (2 V-2.5 Ah) with a negative plate were made to examine initial performance at 2.1 CA discharge. The valve-regulated batteries (2 V-7 Ah) were assembled to examine life performance in the same design of the complete batteries, and were examined with trickle charge at 2.275 V at 60°C. Life performance was evaluated by checking the change of the discharge capacity at periodical 3 CA discharge during the trickle charge test.

The surface area of the negative active materials of batteries was measured. (ASA-2000: Shibata Scientific Technology, BET single point method, using pure N<sub>2</sub> gas)

Table II The specifications of batteries tested and the test conditions.

		Initial performance evaluation test	Life performance evaluation test
Specification of test batteries	Battery type	2 V-2.5 Ah (Liquid type)	2 V-7 Ah (Valve regulated type)
	Number of plates	(-)/(+2)	(-)/(+3)
	Separator (Plates space)	Nothing(5 mm)	Retainer(1.8 mm)
	Electrolyte	40wt%-H <sub>2</sub> SO <sub>4</sub> Excess quantity	40wt%-H <sub>2</sub> SO <sub>4</sub> 0.8cm <sup>3</sup> /(Negative active material 1g)
Test conditions	Discharge current	2.1 CA	3 CA
	Life test	—	60°C, 2.275 V Trickle charge (Periodical 3 CA discharge)

## 5. RESULTS AND DISCUSSION

## 5.1 Initial performance

**Lignocresols:** Fig. 1 shows the surface area of the negative active materials and the discharge capacity of batteries with and without lignocresols at high rate discharge.

It is considered that lignins are adsorbed on the negative active materials, which become fine particles, restraining their crystal growth. Therefore, it is known that the surface area of the negative active materials increases and the performance of batteries improves [1-3]. It was proved that lignocresols worked as additives for the negative active materials, because the active materials with lignocresols had larger surface area and discharge capacity than that without lignocresols.

Lignocresols treated with alkalinity had low molecular weight, and the active materials with them had smaller surface area and discharge capacity than that with original lignocresols. Not only molecular weight is controlled low but also conjugate double bonds are produced in lignocresol molecules by alkaline treatment [6]. Though it is not clear whether conjugate double bonds in lignocresols influence the active materials of batteries, it does not seem that low molecular weight of

lignins is an effective additive for battery at least. On the other hand, the discharge capacity of batteries containing original hardwood lignocresol was larger than that containing original softwood lignocresol. Though the difference of molecular weight has not been taken account yet, it is assumed that the molecular structure of hardwood lignins was more effective than that of softwood lignins as additives for the negative active materials of batteries.

Fig. 2 shows the differences of the molecular structure of hardwood and softwood lignins. Their lignins are composed of two kinds of phenylpropane units. One is guaiacylpropane unit, another is syringylpropane unit. Softwood lignins are composed of guaiacylpropane unit only, but hardwood lignins are composed of both guaiacylpropane and syringylpropane units [8]. It is assumed that methoxyl group and dimethoxyphenol unit contents in lignin molecules contribute to the improvement of the discharge capacity of batteries.

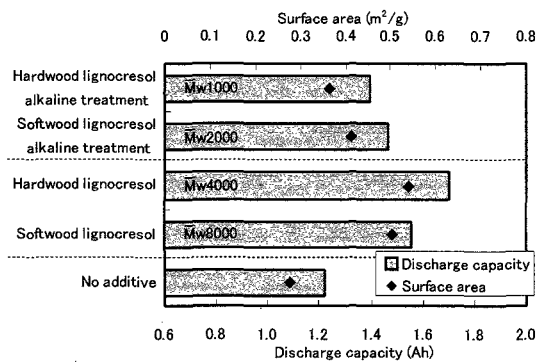


Fig. 1 The discharge capacities and the surface areas of the negative active materials with or without lignocresols.

	Softwood lignin	Hardwood lignin
Basic structure unit	Phenylpropane unit	
Structural characteristic		
Rider	$\alpha^*$ : -OH, =O, -Alkyl, -Allyl, =C. $\beta^*$ : -Alkyl, -Allyl, -O-Allyl, =C.	

Fig. 2 The difference of the molecular structures between softwood and hardwood lignins.

**Lignodimethoxyphenols:** We investigated how methoxyl group or dimethoxyphenol unit contents in lignin molecules influence the surface area of the active materials and the performance of batteries at high rate discharge. Lignodimethoxyphenols were synthesized by changing mixing ratio of 2,6-dimethoxyphenol and 2,6-dimethylphenol as lignin solvation agents in the phase-separation treatment in order to control methoxyl group or dimethoxyphenol unit content (Table I).

Fig. 3 shows that methoxyl group content in hardwood lignodimethoxyphenols depend on the mixing ratio of lignin solvation agents. Fig. 4 shows the discharge capacity at high rate discharge using negative plates with various lignodimethoxyphenols. Fig. 5 shows the relationship between the surface area of the active materials and methoxyl group content of

dimethoxyphenol units in lignodimethoxyphenols.

It was proved that discharge capacity increased when methoxyl group and dimethoxyphenol unit contents increased. The surface area of the active materials increased with increase of methoxyl group and dimethoxyphenol unit contents.

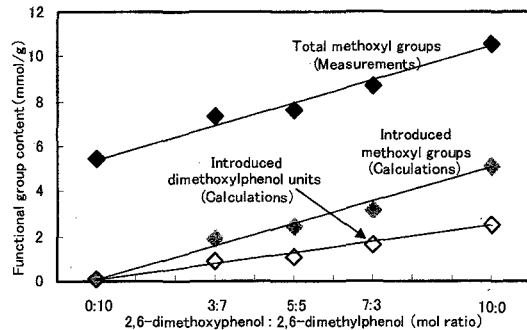


Fig. 3 Methoxyl group and dimethoxyphenol unit contents in hardwood lignodimethoxyphenols.

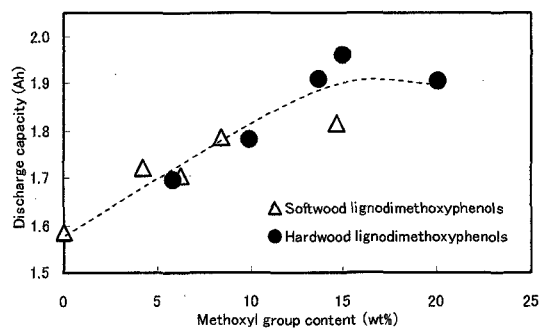


Fig. 4 Relationship between the discharge capacity of batteries and methoxyl group content of dimethoxyphenol units in lignodimethoxyphenols.

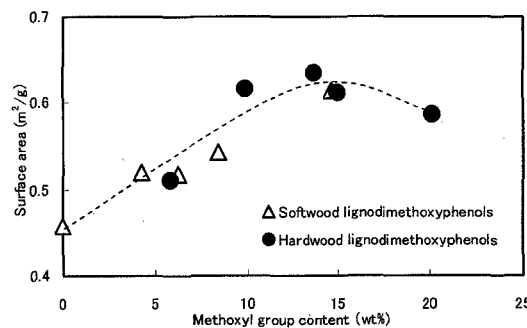


Fig. 5 Relationship between the surface area of the active materials and the methoxyl group content of dimethoxyphenol units in lignodimethoxyphenols.

It is never strange that methoxyl groups in lignin molecules were demethylated and change into catechol units by oxidation-reduction reaction in batteries, because methoxyl groups in lignin molecules are partly demethylated in pulping processes. Lignin molecules are negatively charged by demethylation, and affinities improve with lead ions ( $Pb^{2+}$ ) and other active materials. Lead ions and other active materials were probably adsorbed by catechol units in lignin molecules. Then, the crystal growth of the active materials was restricted. The active materials became fine particles, and the surface area (reaction area) of the active materials increased. Therefore, it was considered that the discharge capacity

of batteries improved.

But, the discharge capacity and the surface area of the active materials did not increase simply with increasing methoxyl group and dimethoxyphenol unit contents. There is a suitable range of them for the negative active materials of batteries. It is considered that the activation of lignin molecules was restrained because the steric hindrance in lignin molecules was emphasized for methoxyl groups or dimethoxyphenol units increased excessive. The methoxyl group and dimethoxyphenol unit contents must be precisely controlled.

### 5.2 Trickle life performance

*Dimethoxyphenol unit:* Fig. 6 shows the high rate discharge capacities of batteries containing softwood lignodimethoxyphenols with various methoxyl group contents while they are under life test by trickle charge.

The discharge capacity was restrained in case of more dimethoxyphenol units. This shows that dimethoxyphenol units contribute to the improvement of not only the initial performance but also the life performance of batteries. As a methoxyl group in a phenylpropane unit was relatively stable due to the state of electrons, so it seems to be gradually demethylated in batteries as time went by. Therefore, the adsorption effect of lignin molecules was maintained in the active materials by slow demethylation. Then, the crystal growth of the active materials went to be restricted, and the reaction area of the active materials did not decrease. It was considered that the discharge capacity of batteries can maintain good life performance by a methoxyl group in a phenylpropane unit.

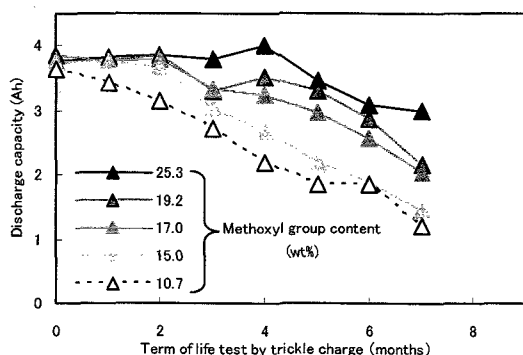


Fig. 6 The discharge capacities of batteries containing lignophenols with various methoxyl group contents under life test by trickle charge.

*Molecular weight:* Fig. 7 shows the high rate discharge capacity of batteries containing various lignophenols with different molecular weights while they are under life test by trickle charge.

Their dimethoxyphenol unit content was same except low molecular weight lignocresols (treated with alkalinity). As a result, discharge capacity was the largest from 2 to 7 months when molecular weight ( $\bar{M}_w$ ) was about 8000, though initial discharge capacity was the largest when molecular weight was about 4000.

It is considered that lignin molecule shows the effects as additives to the active materials by decomposition of themselves. After longer time, since lignin molecules gradually lose the effects on improving active materials, the discharge capacity of batteries was gradually declined.

As a result, it is expected that the polymerization of lignins contributes to the improvement of the life time of batteries. However, such lignodimethoxyphenol with high molecular weight did not dissolve in analytical solvent, and then the molecule activation of lignins was probably restrained. It is considered that lignodimethoxyphenol with high molecular weight did not contribute to the improvement of the life time of batteries. In short, we found that the molecular weight of lignins should be controlled within the suitable range for additives in the active materials of batteries.

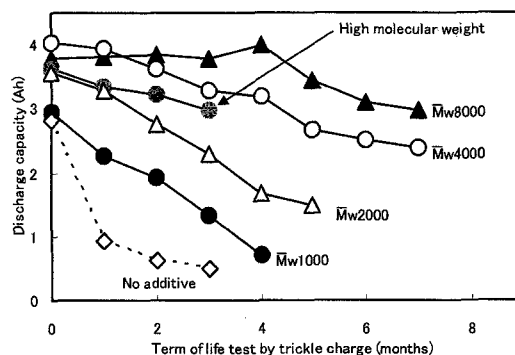


Fig. 7 The discharge capacities of batteries containing lignophenols with different molecular weights under life test by trickle charge.

It seems that the negative active materials are influenced by not only the molecular structures of lignins but also other characteristics. We will investigate the relationships between the performance of the negative plates of batteries and various molecular structure of lignins in future, too.

### 6. CONCLUSIONS

Lignophenols as well as industrial lignins have the effects on improving the active materials of lead-acid batteries. It is considered that methoxyl groups in lignin molecules are demethylated in batteries. The crystal growth of the active materials was restrained to adsorb lead ions and other active materials. It is considered that the discharge capacity of the active materials improved because the active materials got finer, leading to larger surface area (reaction area). In addition, it seems that both the initial performance and the life performance are improved by means of methoxyl groups of different stability when there are dimethoxyphenol units in the molecular structure of lignins. On the other hand, it was found that there was perhaps the suitable molecular weight of lignins to satisfy the uses of batteries.

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