

# A Novel Botany Phenol Thinner Derived from Lignin and Its Application in Polymer Drilling Fluid

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**ABSTRACT:** *In this work, a novel thinner derived from natural botany Chinese Larch Tree was obtained by combination lignin with phenol using  $H_2O_2$  as oxidant and the acting efficiency of lignosulfonate in the drilling fluids is greatly enhanced after oxidation with  $H_2O_2$ . Both the chemical structure and the adsorptive ability of the oxidation product are investigated. From experimental results, it was shown that lignin couple with polyphenol and the combination was greatly improved during the process of oxidation under  $H_2O_2$  in light of the increased molecular weight of the derivative and different major function groups content after oxidation. Furthermore, the oxidized derivative has the good adsorptive-warping ability on the outer surface of particulate clay, which gives great potential for developing novel polymer drilling fluid with good inhibitory and thinning properties.*

**KEYWORDS:** *Lignin; Polyphenol; Drilling fluid; Thinner; Oxidation.*

## INTRODUCTION

The problem of viscosity control and the clay swelling inhibition of drilling fluids by the action of thinners or dispersants have been studied by many investigators.

In past years, the use of chromium lignosulfonate in drilling fluids has been discontinued in certain areas because of possible harm to the environment [1].

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Recently, good inhibition of drilling fluid has been developed by adsorption of high-molecular-weight organic polymer on the surface of clay [2]. Clark greatly advanced the adsorbed polymer technique by showing that the use of a partially hydrolyzed polyacrylamide (PHPA) in conjunction with KCl was highly effective in stabilizing shales [3]. KCl was found to be an integral part of the polymer system and was used in high concentrations. The use of the potassium ion has proved to be highly effective in stabilizing shales, and its merit for this purpose is well known, however, the potassium ion is highly flocculating and its presence in the mud can adversely affect rheological and filtration control, thereby significantly influencing mud cost.

Lignosulfonates are refined lignin products made from spent sulfite liquor from which the fermentable sugars have been removed. The exact structure of lignin is not known; however, it is believed to be a phenolic propane type polymer which may exist as a branched chain or cross-linked structure. Based on the previous research of our group, we found that the combination of lignin and polyphenol is possible; however, a better understanding of the mechanism of adsorption of dispersants is essential before improvement and development of characteristics of drilling fluids and drilling fluid control [4]. For polymer drilling fluid, polymer concentration, molecular weight, and carboxyl substitution are important parameters affecting shale stability.

This paper develops a novel thinner using lignin and polyphenol as recourse and further investigates the characterization, such as molecular weight distribution, the content of major function groups, and the adsorptive ability of the sample on the outside surface of the particulate clay. Further application performance of obtained novel thinner in drilling fluid has also been investigated in detail.

## EXPERIMENTAL SECTION

### Material

Every material was crushed to 60~100 mesh and then defatted respectively. The crushed wood of Chinese Larch was labeled as LW (larch wood). The crushed bark of Chinese Larch was labeled as LB (larch bark). The crushed wood of *Pinus massoniana* Lamb (Mawei pine) was labeled as MW (Mawei wood). Crushed and purified tannin of *Casuar Equisetifolia* was labeled as T (tannin).

### Sample preparation

First, materials, LW, LB, MW, and T, were extracted using alkaline aqueous solution and sulfite respectively. The optimum conditions of extraction were as follows: the solid-to-liquid mass ratio of 1:6, the concentration of sulfate agent 2-3%, pH value 6-7, the reaction temperature 150-170°C, reaction time 2-3 h. The corresponding extractive was labeled as LWS (LW sulfite), LBS (LBS sulfite), MWS (MW sulfite) and TS (TS sulfite) respectively.

Next, the above extractives were coordinated with  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  respectively by mixing  $\text{Fe}^{3+}$  &  $\text{Zn}^{2+}$  solution of the total concentration from 1% to 4% at a reaction temperature of 70-80°C maintain pH value in the range from 4 to 7 under stirring. After about 100 minutes, the corresponding complexes were obtained and label as LWC (LW complex), LBC (LBC complex), MWC (MW complex) and TC (T complex) respectively.

Then, oxidations of obtained coordination complexes were carried out using  $\text{H}_2\text{O}_2$  as oxidant at reaction temperature 90-100 °C with about 12% concentrations of  $\text{H}_2\text{O}_2$  and 20-25% amount of obtained coordination complexes. The reaction time should be settled at the range from 1.0 to 1.5 h to allow the oxidation to carry out thoroughly. The corresponding oxides were obtained label as LWO (LW oxide), LBO (LB oxide), MWO (MW oxide) and TO (T oxide).

### Sample analysis

The molecular weight distribution of the prepared samples, the content of groups ( $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$  and  $\text{Ph-OH}$ ) and the content of quinoid in the sample were examined according to the published determination method as reported in references [2-4].

The adsorptive ability of the prepared samples on the outside surface of particulate clay was determined using the UV method as described as follows [5]. The UV absorptivity of the prepared samples solution was determined before and after adsorbed on the outside surface of particulate clay at a wavelength of 280 nm. The UV absorption was assigned as  $A_1$  &  $A_2$  and the percent value calculated according to the following formula:  $a = (A_2/A_1) \times 100\%$ , which is a key parameter to evaluate the adsorptive ability of prepared combination compounds on the outer surface of the particulate clay.

Effect of the obtained samples on the properties of polymer drilling fluids has been also evaluated

by determine the apparent viscosity, dynamic stress and volume of water loss of the polymer drilling fluids before and after adding above oxidation samples.

#### **Rheology evaluation**

The performances of gums in the mud were investigated using prepared test mud according to the reported method [6-8]. Water-based base mud (Bentonite:  $\text{Na}_2\text{CO}_3$  :  $\text{H}_2\text{O}$  = 4: 0.2: 100 by weight) were aged for 24 h at room temperature to hydrate the bentonite. The required quantity of additive was added to the base mud under stirring at high speed for 20 min. Then, the rheological property of the treated mud as well as that of the base mud was measured to determine the rheological parameters such as apparent viscosity, dynamic stress and filtration quantity using a Fann35 viscosimeter (Chuangmeng Chemical Engineering Company).

## **RESULTS AND DISCUSSION**

#### **Content of quinoid**

As the properties of the compound is mostly dependent on the functional groups on it, the content of major functional groups in all of the prepared combinations of lignin and polyphenol before and after  $\text{H}_2\text{O}_2$  oxidation (LBO, LWO, TO) were determined according to a previous method [6]. Table 1 lists the results of the test. From Table 1, it can be seen that the content of  $-\text{SO}_3\text{H}$  group in four kinds of samples (LB, LW, MW, T) does not show obvious change after oxidation, while the content of  $-\text{COOH}$  group and  $\text{Ph-OH}$  group trends differently after oxidation by greatly increasing for  $-\text{COOH}$  group and decreasing for  $\text{Ph-OH}$  group. These testing results keep the good agreement with the properties of the function group, that is, the S in  $-\text{SO}_3\text{H}$  group on tree kinds of the resource has been the highest valence so to almost no any change of  $-\text{SO}_3\text{H}$  group content after oxidation, while further oxidation make  $\text{Ph-OH}$  group to its high oxidation state, quinoid, which can be further confirmed from the increased content of quinoid results after oxidation listed in Table 2. For polymer drilling fluid, the degree of carboxyl substitution in a polymer is a very important factor in the performance of drilling fluid because of carboxyl functional groups in a polymer can be adsorbed on clay particles and result in polymeric bridging. As shown in Table 1, an obvious increase of carboxyl substitution after oxidation derived from oxidation of hydroxyl groups of natural plants has been observed.

#### **Molecular weight**

For non-dispersed polymer drilling fluid, high-molecular-weight polymers are essential to be utilized to either encapsulate drill solids to prevent dispersion and coat shale for inhibition, or for increasing viscosity and reducing fluid loss [7]. Oppositely, low-molecular-weight polymers do not give good shale inhibition because of their short chain lengths and low solution viscosities [8]. From the results in Table 3, it can be seen that the molecular weight fraction higher than 5000 in all of combinations of lignin and polyphenol have been obviously increased after  $\text{H}_2\text{O}_2$  oxidation, especially for sample of LB, the molecular weight fraction higher than 5000 increases greatly from 30.01% to 58.97% after oxidation, which indicated that the polymerization between lignin and polyphenol has been greatly intensified by adding  $\text{H}_2\text{O}_2$  as oxidant.

As stated above that the molecular weight of the polymer is an important factor in the polymer drilling fluid and shales are immediately dispersed in low-molecular-weight polymer solutions (unless polymer concentration is very high) [9-10]. The molecular weight distribution of every combination compounds before (LBC, LWC, MWC, and TC) and after oxidation (LBO, LWO, MWO and TO) have been tested and display in Figs.1-3. From results, it can be seen that the volume of leaching out of every sample has been shifted to a low percentage range, indicating that phenols couple each other and low molecular weight increase after oxidation. Compared with other combination compounds, the great increase of low molecular weight in LB after oxidation has been observed due to its large hydroxyl group, which suggested that the combination between lignin and polyphenol under  $\text{H}_2\text{O}_2$  is intensified over the resource containing more hydroxyl groups.

#### **Adsorption ability**

Table 4 shows the adsorption ability of LB, LW, MW, and C before and after oxidation. From the UV adsorption intensity ratio of the prepared samples solution before and after adding clay, it can be seen the decrease of UV adsorptive intensity for all of the combination compounds of lignin and polyphenol after oxidation, which reflected the absorption ability to surface of clay particles. It is understandable to the decrease of spectral intensity for all of the combination

**Table 1: Content of major functional groups in LB, LW, MW and T before and after oxidation (mmol/g).**

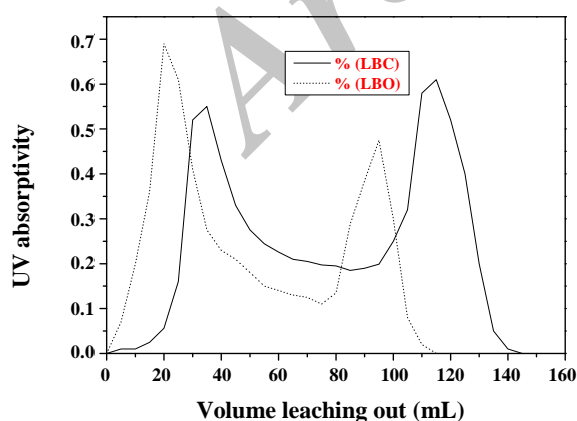
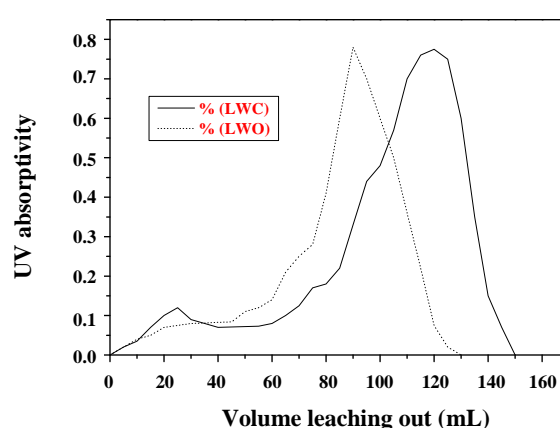
Major function groups	LBC	LBO	LWC	LWO	MWC	MWO	TC	TO
-SO <sub>3</sub> H	2.21	2.15	2.72	2.44	2.56	2.47	2.14	2.13
-COOH	1.16	2.14	1.62	2.14	1.21	1.86	0.95	1.34
Ph-OH	0.86	0.65	0.94	0.79	0.85	0.78	0.69	0.66

**Table 2: Content of quinoid in LB, LW, MW and T before and after oxidation.**

Phenol	Sample concentration (g/L)	Content of quinoid (10 <sup>-4</sup> mol/g.sample)
LBC	0.7383	0.4515
LBO	0.7383	1.6125
LWC	1.4765	0.1161
LWO	1.4765	0.8665
LMC	1.4765	0.1806
LMO	1.4765	0.6063
TC	0.7296	0.4623
TO	0.7296	1.7238
Reference	0	0

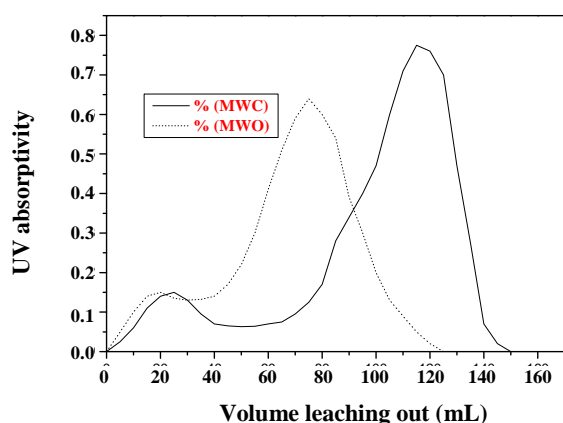
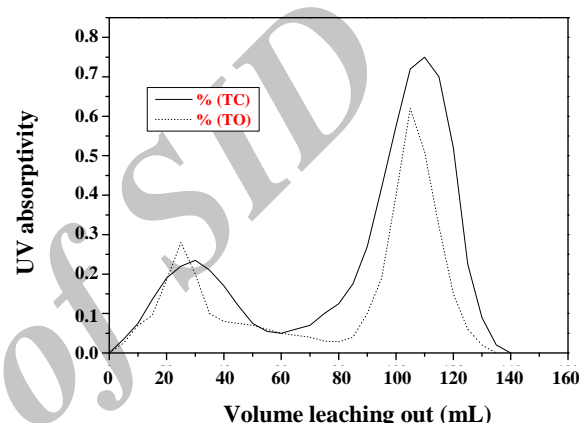
**Table 3: Molecular weight fraction higher than 5,000 in LB, LW, MW and T before and after oxidation (%).**

Phenol	Molecular weight fraction higher than 5,000 (%)
LBC	30.01
LBO	58.97
LWC	7.53
LWO	16.45
MWC	8.03
MWO	19.38
TC	9.42
TO	19.87

**Fig. 1: Molecular weight distribution of LB before (LBC) and after oxidation (LBO).****Fig. 2: Molecular weight distribution of LW before (LWC) and after oxidation (LWO).**

**Table 4: Adsorption ability of LB, LW, MW and T before and after oxidation on the outside surface of particulate clay.**

	LBC	MWC	LWC	TC
A <sub>1</sub>	0.284	0.272	0.270	0.273
A <sub>2</sub>	0.162	0.167	0.171	0.169
a	44.4	61.4	63.3	60.5
	LBO	MWO	LWO	TO
A <sub>1</sub>	0.283	0.272	0.270	0.273
A <sub>2</sub>	0.067	0.149	0.152	0.151
a	23.7	54.8	56.3	54.5

**Fig. 3: Molecular weight distribution of MW before (MWC) and after oxidation (MWO).****Fig. 4: Molecular weight distribution of T before (TC) and after oxidation (TO).**

compounds because the strong absorptive functional group to surface of clay particles, carboxyl, formed after oxidation. For LBC and LBO, the decrease of spectral intensity is most dramatic indicating its much more effective absorption to a clay surface, which is further confirmed from its low molecular weight distribution listed in Fig.4.

#### **Performances of the sample in the polymer drilling fluids**

In Table 5 the performance of combination compounds derived from lignin and polyphenol into the polymeric drilling fluid as thinner, apparent viscosity, dynamic stress and volume of water loss, have been investigated. For comparison, the polymeric drilling fluid containing 0.4% of modified starch, 0.1% xanthan, and 0.1% CMC was also evaluated. From the results, it can be seen that 0.2% LBO can reduce the apparent viscosity of the polymeric drilling fluid effectively, from 36.5 mPa·s to 25.5 mPa·s, and it also can reduce the dynamic stress

from 9.5 Pa to 7.5Pa. Most of them, except 0.2%TC, can reduce the filtration. This fact showed that the thinning and inhibitory properties of combination compounds in the polymer drilling fluids are enhanced by modification of oxidation. The best performance of drilling fluid for LBO is reasonable according to molecular weight distribution and absorption ability test results showed above. We believe that the thinner and inhibition properties are mainly a result of major functional groups and molecular-weight effect.

#### **CONCLUSIONS**

A novel thinner for polymer drilling fluid has been developed by combination lignin with botany polyphenol and their intensified combination compounds after oxidation by H<sub>2</sub>O<sub>2</sub>. The characterizations on prepared combination compounds before and after oxidation have been investigated. From the test, it was found that the contents of major functional groups after oxidation

Table 5: Performances of the sample in the polymer drilling fluids.

Mud	Apparent viscosity /mPa·s	Dynamic stress /Pa	The volume of water loss/ml
Polymeric drilling fluid	36.5	9.5	7.0
Polymeric drilling fluid + 0.2%LBC	36.5	9.5	6.5
Polymeric drilling fluid + 0.2%LWC	42.0	10.0	6.5
Polymeric drilling fluid + 0.2%LMC	44.5	10.5	6.5
Polymeric drilling fluid + 0.2%TC	46.5	11.5	7.0
Polymeric drilling fluid + 0.2%LBO	25.5	7.5	6.5
Polymeric drilling fluid + 0.2%LWO	37.5	9.5	6.5
Polymeric drilling fluid + 0.2%LMO	39.0	9.5	6.5
Polymeric drilling fluid + 0.2%TO	41.0	9.5	6.5

were varied respectively except for  $-SO_3H$  groups, indicating the coupling between lignin and polyphenol during the process of oxidation. The molecular weight of all of the combination compounds obviously increase after oxidation, which is a major factor to the adsorptive-warping ability of thinner on the outer surface of particulate clay and resulting in their good thinning and inhibitory properties in the polymer drilling fluid.

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