

Novel Modified Lignosulfonate as Drilling Mud Thinner Without Environmental Concerns

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ABSTRACT: A novel modified lignosulfonate was prepared by crosslinking lignosulfonate acid with naturally occurring tannin extract in the presence of formaldehyde and further chelating with ferrous ions. The modification reactions were verified by IR analyses and its performances as polymeric thinning agent for aqueous bentonite mud in oilfields were evaluated. Compared with commonly used FeCr–lignosulfonate thinner, the chrome-free modified lignosulfonate without environmental concerns has better thinning ability and can offer better resistance to elevated temperature, as well as matched tolerance to high salinity. In addition, its thinning mechanism was discussed by means of adsorption isotherms, zeta potential measurements, and SEM observations. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1662–1668, 1999

Key words: water-soluble lignin derivative; modified lignosulfonate; environmental acceptability; polymeric thinning agent; drilling mud

INTRODUCTION

Polymeric thinning agents used for controlling the rheological properties of water-based bentonite mud for oilfield drilling are varied, ranging from natural and modified natural products such as lignite, Cr–lignosulfonate, FeCr–lignosulfonate (FCLS), to fully synthetic materials such as maleic anhydride–styrene sulphonate copolymers, either homo- and copolymers of the acrylic acid.^{1–7} Among these additives, FCLS is the thinner most widely employed in dispersed bentonite mud formulations. As environmental regulations governing the disposal of drilling fluids become increasingly restrictive, however, the use of conventional FCLS as drilling mud thinner is being curtailed owing to the high toxicity of chrome.

Therefore, the search for alternative lignosulfonate-based thinner with environmental acceptability has always been an endeavor in oilfields.^{8–18}

In this work, a novel modified lignosulfonate thinner called FTLS (Fe-tannin-lignosulfonate) was prepared by crosslinking lignosulfonate acid with a naturally occurring tannin extract in the presence of formaldehyde and further chelating with ferrous ions; its performances and thinning mechanism were also examined. In comparison with widely used FCLS thinner, this chrome-free modified lignosulfonate without environmental concerns possesses better thinning ability and can offer better resistance to elevated temperature as well as matched tolerance to added NaCl.

EXPERIMENTAL

Materials

The lignosulfonate used was a commercial calcium lignosulfonate (CaLS), isolated from the

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spent liquor of sulfite pulping of softwood and obtained from Hongqi Chemical Factory in Heilongjiang Province, China. Dried tannin extract was a commercial product obtained from Chengdu Kaojiao Factory in Sichuan Province, China. Formaldehyde and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were of analytical grade. The clay used in this work was calcium bentonite provided by East Sichuan Oilfield, Xuling, China. The commercial thinner studied was FCLS provided by East Sichuan Drilling and Exploration Company, Xuling, China.

Preparation and Characterization

In each batch of experiments, 75 g CaLS was first dissolved in the required amount of aqueous H_2SO_4 solution for complete decalcification. After the precipitated CaSO_4 was removed by filtration, the obtained lignosulfonate acid (LS) was crosslinked with 25 g tannin extract in the presence of 4 mL HCHO (36%) at 105°C for 2 h. Then the crosslinked LS (TLS) was further reacted with 0.0375 mol aqueous $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at the same temperature for 30 min. The reacted mixture was then dried under vacuum at 40°C. For purification, the dry solid so obtained was extracted repeatedly with dimethyl formamide and dialyzed by semidialysis membrane to remove unreacted lignosulfonate, tannin, and ferrous ions. The prepared FTLS was a powdered material of brown-black color, readily soluble in cold or hot water with $\text{pH} = \sim 1\text{--}14$. The infrared spectra ($\sim 4000\text{--}400\text{ cm}^{-1}$) of purified LS, tannin, TLS, and FTLS samples were recorded on a Perkin-Elmer 1430 spectrophotometer by using the KBr disc technique.

Mud Property Tests

Mud property tests were performed according to American Petroleum Institute (API) specifications. Each batch of base mud used in this study was made up by adding 80 g bentonite clay, 4 g Na_2CO_3 into 1000 g fresh water with $\sim 80\text{--}85^\circ\text{C}$ and agitating strongly to form uniform dispersions. It was aged for more than 24 h at room temperature prior to use and its density was maintained at 1.05 g/cm^3 . For the base mud and the mud treated with FTLS or FCLS, a ZNN-D₃-type rotating viscometer was used to measure the viscosity at two rotating rates of 600 and 300 rpm (Φ_{600} , Φ_{300}), the gel strength after 10 s and after 10 min of setting (θ_1 , θ_{10}). Then the rheological parameters such as apparent viscosity (η_a), plastic viscosity (η_b), and yield point (τ_0) were determined as follows:

$$\eta_a = \Phi_{600}/2 \quad (\text{mPa s})$$

$$\eta_b = \Phi_{600} - \Phi_{300} \quad (\text{mPa s})$$

$$\tau_0 = 0.511(\Phi_{300} - \eta_b) \quad (\text{Pa})$$

API filtrate volume was measured by a ZNS-III-type medium-pressure filtration apparatus made in Lanzhou Oil Refinery, China.

Adsorption Measurements

The adsorption isotherms of LS, TLS, and FTLS on the bentonite clay were determined at room temperature ($30 \pm 1^\circ\text{C}$) and at pH 9.0 by putting the bentonite dispersions (0.9 wt %) into contact with various amounts of lignin derivative in 0.5% NaCl solution. The sample tubes were oscillated for 3 h to ensure reaching equilibrium and then centrifuged at a speed of 4000 rpm. The residual concentration of lignin derivative was determined on the supernatant by UV spectroscopy at the corresponding maximum wavelength. The amount of lignin derivative adsorbed was calculated from the difference between the initial and the equilibrium concentrations.

Zeta Potential Measurements

The zeta potential of the bentonite dispersions treated with lignin derivatives was determined by using a Model 501 Lazer Zee MeterTM made by Pen Kem, Inc. The suspensions were prepared by diluting adsorption test samples to 0.01 wt % of solid.

SEM Observations

The grain structures and morphologies in the clay slurry untreated and treated by FTLS sample were examined by a Hitachi S-430 apparatus at an accelerating potential of 10 kV. The SEM photos had been reproduced at magnification of $\times 2000$.

RESULTS AND DISCUSSION

Verification of Modification Reactions

Figure 1 presents the IR spectra of purified LS, tannin, TLS, and FTLS samples. The IR spectrum of LS shows obvious absorption bands at 3442 cm^{-1} for phenolic or hydroxyl groups, 1030 cm^{-1} for sulfonic acid groups, 1262 cm^{-1} for aromatic

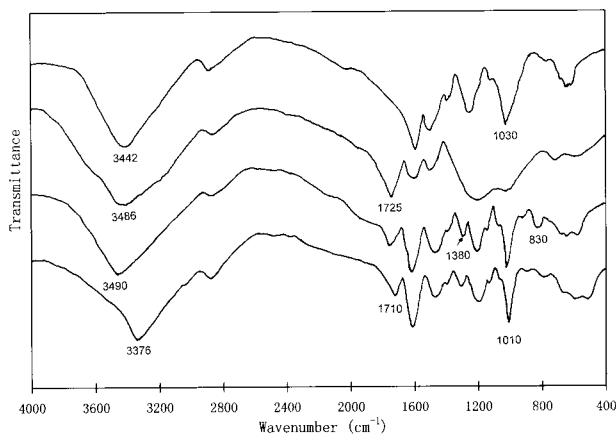
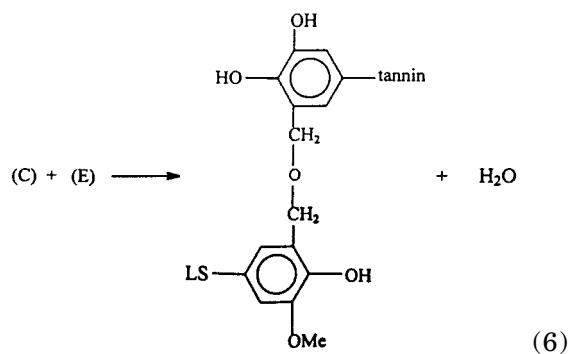
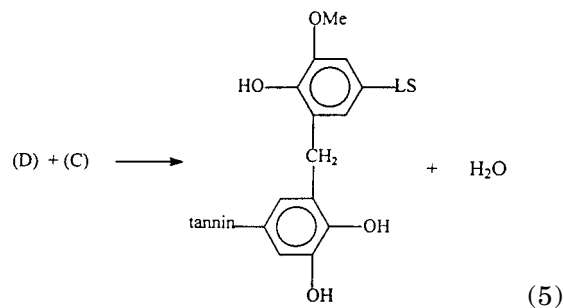
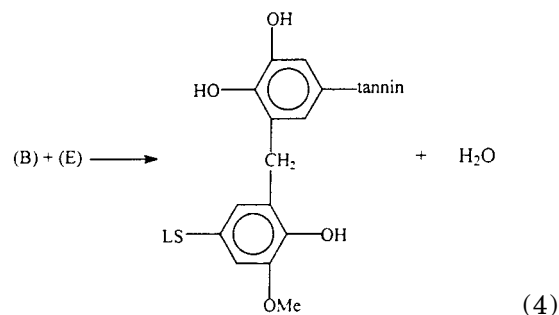
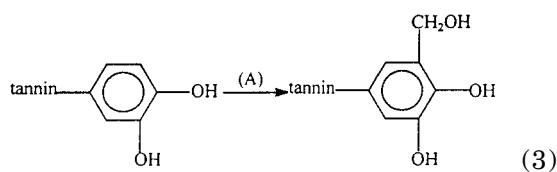
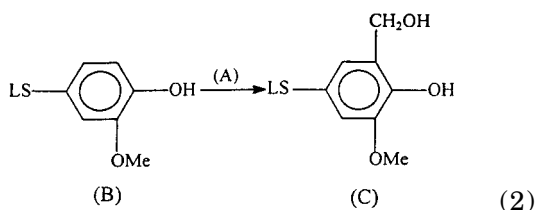
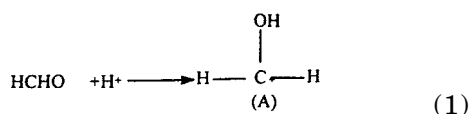


Figure 1 Infrared spectra of LS, tannin, TLS, and FTLS.

ethers, and 1601 and 1500 cm^{-1} for aromatic rings. The IR spectrum of tannin shows a broad absorption band in the region of $\sim 4000\text{--}3000$ cm^{-1} , in addition to intense bands at 1725, 1265, 1610, and 1509 cm^{-1} , characteristic of stretching vibrations of hydroxyl groups, carbonyl groups, aromatic ethers, and aromatic rings, respectively. In contrast to the spectra of LS and tannin, the IR spectrum of TLS shows not only the characteristic bands of LS and tannin, but also noticeable bands at 1380 cm^{-1} for methylene bridges and 830 cm^{-1} for dimethylene ether bridges. The methylene and dimethylene ether bridges may be formed through the following reactions.



For FTLS, its spectrum shows similar main spectral features to TLS, but some bands appear at shifted positions of 3376, 1710, and 1010 cm^{-1} and different intensities. These indicate that TLS was chelated with ferrous ions.

Evaluation as Drilling Mud Thinner

Where shale instability is not a critical issue, the most commonly used aqueous drilling fluids are dispersed or high solids mud formulated with bentonite clay, a low cost additive. Bentonite is employed at a concentration from ~ 2 to 8 wt % in these drilling muds to impart Bingham-type rheology to the fluids. However, in high salinity conditions or at elevated temperatures, bentonite dispersions tend to thicken or gel. Thus, polymer thinning agent must be added to control the dispersion properties and reduce the viscosity and the gel strength.^{6,10}

Table I Properties of Test Mud Under Different pH Values

Formulation of Mud	pH	η_a (mPa s)	η_b (mPa s)	τ_0 (Pa)
Base Mud	9.7	38.5	15.0	22.56
Base Mud + 0.5% FCLS	6.6	23.0	18.0	4.80
	7.2	14.0	10.0	3.84
	8.6	9.0	6.0	2.88
	9.5	6.0	4.0	1.92
	11.8	7.5	5.0	2.40
	13.0	11.0	8.0	2.88
Base Mud + 0.5% FTLS	6.5	22.0	17.5	4.32
	7.5	12.5	9.0	3.36
	8.7	9.0	6.5	2.88
	9.5	8.5	7.0	1.44
	11.9	7.0	5.5	1.44
	13.0	8.0	6.0	1.92

All test data were measured at $30 \pm 1^\circ\text{C}$.

To estimate the effectiveness of FTLS as drilling thinner under various conditions, a series of mud tests were made in this study. The commercial thinner, FCLS, was used as a contrast. The aspects investigated included the effects of the pH of mud, the dosage of thinner, the aging temperature, and the salinity on the properties of the mud treated with FTLS and FCLS, respectively. From the test results shown in Tables I to IV, the following are found.

(1) The thinning abilities of FTLS and FCLS vary with the pH of mud, but they have a near pH range of 8.6–11.9, at which the mud treated with FTLS or FCLS has lower η_a , η_b , and τ_0 (Table I).

(2) The amounts of FTLS and FCLS affect their thinning properties. The dosage of 0.5% is optimum for either FTLS or FCLS, at which the best thinning effects are obtained. At the same dosage of 0.5%, however, the η_a , η_b , τ_0 , θ_1 , and θ_{10} of the mud treated with FTLS before and after hot rolling at 150°C for 16 h are lower than the corresponding parameter values of the mud treated with FCLS, indicating that FTLS has better thinning properties under this condition (Table II).

(3) TCLS has good thinning ability at lower temperatures up to 120°C , but beyond that point its thinning ability becomes obviously weak. In contrast with FCLS, FTLS can offer better resistance to elevated temperatures. At a temperature of 150°C , for example, the η_a , η_b , τ_0 , θ_1 , θ_{10} , and API filtrate volume of the mud treated with FTLS remain low (Table III).

(4) Aqueous bentonite mud tends to thicken when NaCl is introduced, producing high η_a , η_b , τ_0 , and API filtrate volume. Compared with FCLS, FTLS has a matched thinning ability for aqueous salt/bentonite mud, showing good tolerance to added NaCl (Table IV).

Investigation of Thinning Mechanism

Bentonite clay consists of superimposed layers composed of two Si—O tetrahedral sheets framing an Al—O—OH octahedral sheet.¹⁹ In aqueous dispersions, water can penetrate into the interlayer space and cause swelling of the bentonite. This process results in a dispersion of colloidal, plate-shaped particles bearing two clearly differentiated interfaces: the faces with many negative electric charges and the edges with about 5% of the total surface area.^{6,19} According to Brown-

Table II Properties of Test Mud Under Different Thinner Dosages (before and after hot rolling at 150°C for 16 h)

Formulation of Mud	η_a (mPa s)		η_b (mPa s)		τ_0 (Pa)		θ_1 (Pa)		θ_{10} (Pa)	
	Before	After	Before	After	Before	After	Before	After	Before	After
Base Mud + 0.3% FTLS	8.0	10.0	6.0	7.0	1.92	3.12	1.92	1.92	6.24	4.32
+0.5% FTLS	4.5	5.5	4.0	5.0	0.48	0.48	0	0	0	1.44
+0.7% FTLS	4.0	6.0	3.5	5.0	0.48	0.96	0	1.44	0.96	3.36
+0.9% FTLS	4.0	7.5	3.5	6.0	0.96	1.44	0.48	1.44	2.88	7.68
Base Mud + 0.3% FCLS	6.0	18.0	4.0	11.0	1.92	6.72	0.96	4.32	2.40	8.16
+0.5% FCLS	7.0	9.5	4.5	7.0	2.40	2.40	0.96	0.96	4.32	2.40
+0.7% FCLS	8.5	7.0	6.0	5.0	2.64	1.92	1.92	1.92	4.80	4.08
+0.9% FCLS	11.0	6.5	8.0	5.0	3.36	1.68	3.36	0.48	7.68	6.48
Base Mud	38.5	—	15.0	—	22.56	—	28.80	—	35.04	—

All test data were measured at $30 \pm 1^\circ\text{C}$.

Table III Properties of Test Mud Under Different Aging Temperatures for 16 h

Formulation of Mud	Temperature (°C)	η_a (mPa s)	η_b (mPa s)	τ_0 (Pa)	θ_1 (Pa)	θ_{10} (Pa)	API Filtrate Volume (mL)
Base Mud	60	5.5	4.5	0.96	0	0.48	13.0
Base Mud + 0.5% FTLS	80	5.5	4.5	0.96	0.48	2.88	15.1
	100	4.5	3.5	0.96	0	0.96	16.2
	120	4.5	4.0	0.48	0	0	21.4
	150	5.5	5.0	0.48	0	1.44	21.7
	170	11.5	11.0	0.48	0	1.92	23.6
Base Mud	60	5.0	4.0	0.96	1.92	6.72	15.9
Base Mud + 0.5% FCLS	80	6.5	5.5	0.96	0.96	9.60	14.8
	100	5.0	5.5	1.44	0.48	4.80	17.6
	120	5.0	3.0	1.92	0.48	1.44	21.3
	150	9.5	7.0	2.40	0.96	2.40	25.9
	170	13.5	12.5	0.96	0.48	1.44	27.6

All test data were measured at $30 \pm 1^\circ\text{C}$.

ing,²⁰ the viscosity and gel strength characteristics in bentonite mud are achieved by clay particle–clay particle interaction. In other words, clay particles in the water phase are attracted to each other under certain conditions and build up a structure that produces viscosity and gel strength. Many polymeric thinners are considered to be adsorbed on clay particles to reduce or inhibit the attractions between clay particles by electrostatic stabilization.^{7,21,22}

Figure 2 gives the adsorption isotherms of LS, TLS, and FTLS, respectively. For LS, only a low level of adsorption is seen. In contrast, relatively higher amounts of TLS is adsorbed, showing that

the adsorption capacity of LS can be improved by its crosslinking modification with the tannin containing many phenolic groups. And compared with the adsorption of TLS, the quantity of FTLS adsorbed has an obvious increase, indicating that the introduction of ferrous ions is very favorable to the adsorption.

From the data shown in Table V, the zeta potential of the bentonite is known to be negative (-43 mV), confirming that there are many negatively charged surfaces on the bentonite platelets due to the isomorphic substitution, and to be little affected by the adsorption of LS and TLS. It appears that the adsorption of LS and TLS on the

Table IV Properties of Test Mud Under Different Salinity (before and after hot rolling at 150°C for 16 h)

Formulation of Mud	η_a (mPa s)		η_b (mPa s)		τ_0 (Pa)		API Filtrate Volume (mL)	
	Before	After	Before	After	Before	After	Before	After
Base Mud + 0.7% NaCl	77.0	36.4	9.5	6.5	45.12	24.58	26.2	35.3
Base Mud + 0.7% NaCl + 0.5% FTLS	31.0	26.3	12.5	9.0	13.92	9.60	22.5	26.7
Base Mud + 0.7% NaCl + 0.5% FCLS	29.7	37.4	6.0	8.5	18.72	23.04	24.5	30.6
Base Mud + 1.2% NaCl	91.0	41.2	11.5	8.0	68.64	36.48	24.1	38.5
Base Mud + 1.2% NaCl + 0.5% FTLS	40.7	28.4	10.5	7.5	15.60	12.00	23.9	25.8
Base Mud + 1.2% NaCl + 0.5% FCLS	39.2	39.0	8.5	11.0	21.12	27.84	22.5	26.7

All test data were measured at $30 \pm 1^\circ\text{C}$.

Table V Zeta Potential of Test Suspensions

Composition of Suspensions	Zeta Potential (mV)
Bentonite	-43
Bentonite + LS	-45
Bentonite + TLS	-49
Bentonite + FTLS	-21

bentonite occurs mainly on its edges because of the strong repulsion between the negatively charged bentonite faces and anionic LS or TLS, resulting in lower adsorption capacity (Fig. 2) and slight changes in the zeta potential of the bentonite (Table V). In the case of the adsorption of FTLS, however, the distinct shift of the zeta potential toward less negative values is observed. It seems that FTLS follows a less selective adsorption and is probably adsorbed on both the faces and the edges of the bentonite, resulting in greater adsorption amounts (Fig. 2). The adsorption of FTLS onto the faces of the bentonite particles may ascribe to the bridging of chelated divalent cations (Fe^{2+}) between the polymer and the surface, which determines the shifts of the zeta potential toward less negative values. As a result, FTLS reduces the interactions between bentonite particles by electrostatic stabilization or a steric barrier more effectively than LS or TLS and thereby allows the aggregated bentonite particles more freedom of movement (Fig. 3), leading low mud viscosity and gel strength.

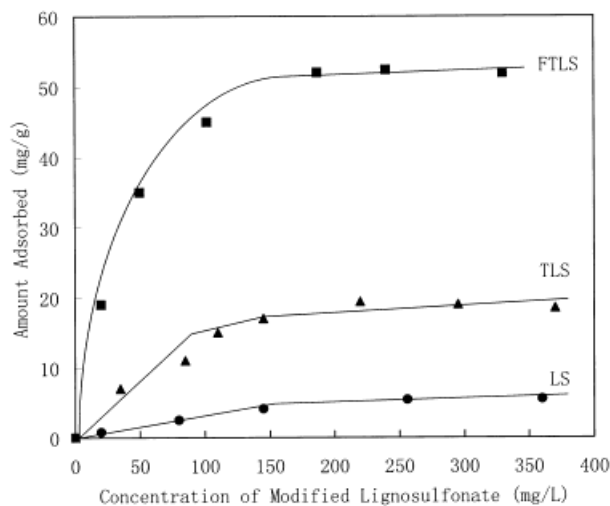
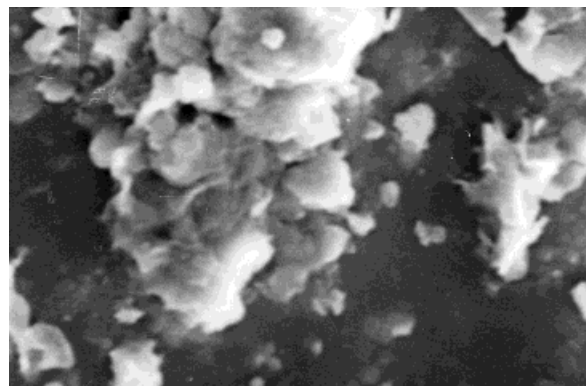
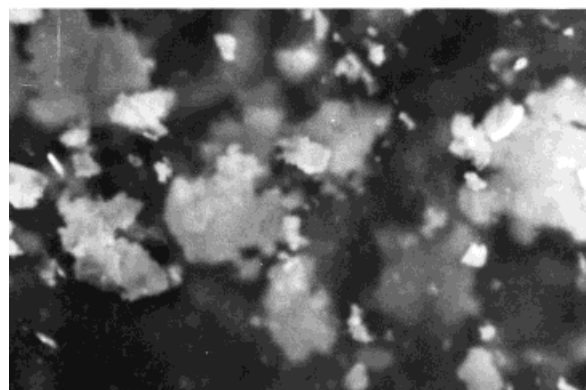


Figure 2 Adsorption isotherms of LS, TLS, and FTLS on bentonite from aqueous 0.5% NaCl solutions (pH 9.0, 30°C).



untreated



treated

Figure 3 SEM photos of the bentonite slurries untreated and treated by FTLS ($\times 2000$).

CONCLUSIONS

A new chrome-free lignosulfonate thinner, called FTLS, for aqueous bentonite muds in oilfields could be prepared by crosslinking LS with naturally occurring tannin extract in the presence of formaldehyde and further chelating with ferrous ions. IR analyses have verified the modification reactions. The data for drilling mud tests have demonstrated that FTLS has better thinning property and resistance to elevated temperature as well as matched tolerance to high salinity when compared with widely used FeCr-lignosulfonate thinner, showing a potential use as new lignosulfonate-based drilling thinner with envi-

ronmental acceptability. Combined modifications of LS by the crosslinking and chelation greatly improve its adsorption onto the bentonite. Unlike LS, FTLS can adsorb on negatively charged faces of bentonite platelets as well as on its positively charged edges. This becomes an advantage when applied to the thinning of aqueous bentonite mud.

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