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TIN-TANNIN-LIGNOSULFONATE COMPLEX: AN IMPROVED LIGNOSULFONATE-BASED DRILLING FLUID THINNER

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Abstract. An improved drilling fluid thinner, tin-tannin-lignosulfonate (TTLS) complex; was formulated by imposing slight modifications to a commercially available thinner, lignosulfonate. The reactions involved include reaction of a lignosulfonate acid with tannin at 105°C in the presence of formaldehyde to initiate the cross-linking reaction. The mixture was further chelating with stannous ions. The modifications reactions were verified by an infrared (IR) spectroscopy analysis and its performances as a polymeric thinning agent for aqueous bentonite mud were evaluated. The rheological performances of the modified thinner were then compared with lignosulfonate. The modified thinner shows better thinning performance at higher temperature and indicates more tolerance to salt contamination compared to lignosulfonate.

Key words: lignosulfonate; drilling fluid/mud; thinner; stannous ion; tannin; rheological performances

Abstrak. Satu penipis lumpur gerudi yang diperbaiki iaitu kompleks stanum-tanin-lignosulfonat, telah dihasilkan dengan melakukan pengubahsuaian terhadap penipis komersil iaitu lignosulfonat. Tindak balas yang terlibat termasuk tindak balas rangkai silang antara asid lignosulfonat dengan tanin pada suhu 105°C dengan kehadiran formaldehid yang berfungsi sebagai pemula tindak balas tersebut. Campuran tersebut selanjutnya dikelatkan dengan ion stanum. Tindak balas pengubahsuaian tersebut ditentusahkan menerusi analisis spektroskopi inframerah (IR) dan prestasinya sebagai agen penipis berpolimer bagi lumpur bentonit akueus dinilai. Prestasi reologi penipis terubahsuai tersebut kemudiannya dibandingkan dengan lignosulfonat. Keputusan menunjukkan bahawa penipis terubahsuai mempunyai prestasi penipisan yang lebih baik berbanding lignosulfonat pada suhu tinggi dan juga ketahanan yang lebih tinggi terhadap pencemaran garam.

Kata kunci: lignosulfonat; bendalir/lumpur gerudi; penipis; ion stanum; tannin; prestasi reologi

1.0 INTRODUCTION

In drilling process, thinner plays an important role in controlling rheological properties of a drilling fluid. There are varieties of polymeric thinning agents one could choose from in order to reduce the viscosity of drilling mud. One of the most commonly used thinning agents in hydrocarbon drilling industry is lignosulfonate.

Lignosulfonate is very versatile and utilized in mud to act as a deflocculant agent. The lignosulfonate molecules adsorb on the clay surfaces (bentonite) and prevent the platelets from linking by eliminating electrochemical attractive forces between clay

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particles. Besides, lignosulfonate is valuable for stabilizing oil-in-water emulsions which give the drilling mud improved properties in control of water loss, reduction of torque on the drill stem, increase of bit life and general improvement of bore-hole conditions [1]. Adding lignosulfonate into drilling fluid system can reduce the viscosity of the mud and therefore will reduce the amount of energy needed to rotate the drill stem and the drill bit. As an example of their effectiveness as a thinner, lignosulfonate with sodium hydroxide are the best treatment for salt contamination, which come from formation and cementing [2].

Nowadays, lignosulfonate had been modified into varieties of forms in order to improve its performance as a thinner such as calcium-lignosulfonate, chrome-lignosulfonate and ferrochrome-lignosulfonate, just to name a few. The usage of these products especially chrome-lignosulfonate and ferrochrome-lignosulfonate, invites a major environmental concern due to highly toxic of hexavalent-chrome present. The situation becomes serious when down hole lost circulation problem occurs where these toxic chemicals could enter the formation and contaminate ground water supply. In addition, the usage of these materials in offshore drilling will cause severe damage to the marine environment [3].

The main objective of this study is to improve the performance of lignosulfonate as a thinning agent and at the same time to maintain its property as a chrome-free water-based drilling fluid thinner. This paper presents a modified lignosulfonate known as tin-tannin-lignosulfonate (TTLS) as an alternative for a widely used ferrochrome-lignosulfonate in drilling industry. This modified lignosulfonate-based thinner was prepared by cross-linking lignosulfonate acid with tannin in the presence of formaldehyde and further chelating with stannous ions. Tin was chosen in this study because it is less toxic compared to chromium while tannin is important to promote cross-linking process. The qualitative data for various functional groups and linkage types in TTLS was examined and studied using infrared (IR) spectroscopic technique. Besides, the rheological performances of this improved lignosulfonate-based thinner were compared with lignosulfonate.

2.0 PREPARATION OF TTLS

Lignosulfonate (LS) and bentonite clay used in this study were supplied by Kota Mineral (Malaysia) Sdn. Bhd., a service company which specializing in the supply of chemicals for drilling fluids for the upstream oil and gas industry. The rest of the chemicals including sulfuric acid, formaldehyde, tin (II) sulfate and dried tannin were purchased from local chemical agents and the chemicals grade used was an analytical grade.

In this study, each batch of TTLS sample was prepared by adding 75 g of LS into desired amount of 10% volume per volume of hydrochloric acid. The mixture was continuously stirred. The pH of the mixture was adjusted to 4 by adding sodium hydroxide before filtering it to obtain lignosulfonate acid, which was a clear brown solution. To 800 ml of lignosulfonate acid, add 30 g of tannin in the presence of 4 ml of formaldehyde at 105°C for 2 hours. The mixture was further chelated with the required amount of tin (II) sulfate (8.05 g) for 30 minute at the same temperature. The reacted mixture was then allowed to air dried before dried under vacuum at 65°C for 3 hours. The prepared TTLS was a fine dark brown powder.

3.0 MUD PROPERTY TESTS

Four sets of experiments were performed in this study. These mud property tests were performed according to American Petroleum Institute (API) specifications [4, 5, 6]. Each batch of base mud used in each experiment was prepared by adding 80 g bentonite together with 4 g of sodium carbonate into 1000 mL water before aging it for more than 24 hours [6].

Experiment I was designed to measure the basic mud rheological parameters such as apparent viscosity (μ_a), plastic viscosity (μ_p) and yield point (τ_y) at different pH values. These basic parameters are crucial to mud engineers working in the fields in the senses that correct treatment can be specified should any problem arises and to perform hydraulics calculations. Hydraulics calculations are performed in order to evaluate circulating pressures and friction losses of the mud while drilling. These parameters were determined as follows [2].

$$\mu_a = \mu_{600}/2 \tag{1}$$

$$\mu_p = \theta_{600} - \theta_{300} \tag{2}$$

$$\tau_y = 0.511(\theta_{300} - \mu_p) \tag{3}$$

θ_{300} and θ_{600} are viscometer readings at 300 and 600 revolutions per minute, respectively.

Experiment II was specially designed to evaluate the performance of the additives against different levels of salt contamination. This is important because common contaminant encountered in drilling is salt (NaCl), which sometimes are also found in make-up water. When make-up water is very salty, bentonite will neither hydrate nor disperse [7]. The bentonite particles will then tend to flocculate which will result in increase in yield point and apparent viscosity values. As in the first experiment, the basic mud rheological parameters such as μ_a, μ_p and θ_y at different salinity were recorded in this experiment.

Experiment III was performed to evaluate the thinning performance at different aging temperature for 30 minutes. This experiment was designed to observe the influence of temperature towards the performance of each thinner. This is because drilling processes normally will take place at high temperature, which is usually greater than 60°C. At higher temperature, the electrochemical charge of hydrate dispersion bentonite become unstable and tends to flocculate or thickening. Besides, the flocculating is also due to the evaporation of initial make-up water at high temperature.

Finally, the effect of different dosages of each thinner used under strong agitation (90°C) was studied in Experiment IV. This experiment try to highlight the importance of using correct dosage of treatment for optimization of thinner performance as well as to save unnecessary cost. Besides, the use of excessive or insufficient dosage may also bring out negative impact to the mud properties.

4.0 RESULTS AND DISCUSSIONS

Figure 1 depicts the infrared (IR) spectra of LS, tannin and TTLS samples. The IR spectrum of LS shows absorption at 3422 cm^{-1} for phenolic or hydroxyl groups. The absorptions at 1159, 1124 and 615 cm^{-1} in the spectrum has been attributed to sulfonic acid whereas, the aromatic ring can be seen at 1647 cm^{-1}. The spectrum of tannin is also showing high intensity for phenolic or hydroxyl groups at 3375 cm^{-1}. The intense bands at 1322, 1707 and 1613 cm^{-1} indicate the stretching vibrations of aromatic ethers and benzene group respectively [8]. In contrast to the LS and tannin spectra, the TTLS spectrum shows similar main characteristic bands of both LS and tannin in addition to sulfonate asymmetry stretching at 1351 cm^{-1} and ethylene bridges at 1454 cm^{-1} [9]. The cross-link may be formed during the reaction between lignosulfonate and tannin [6]. The shifted band and intensity for phenolic or hydroxyl groups (3434 cm^{-1}) indicate that tannin-lignosulfonate was chelated with stannous ions.

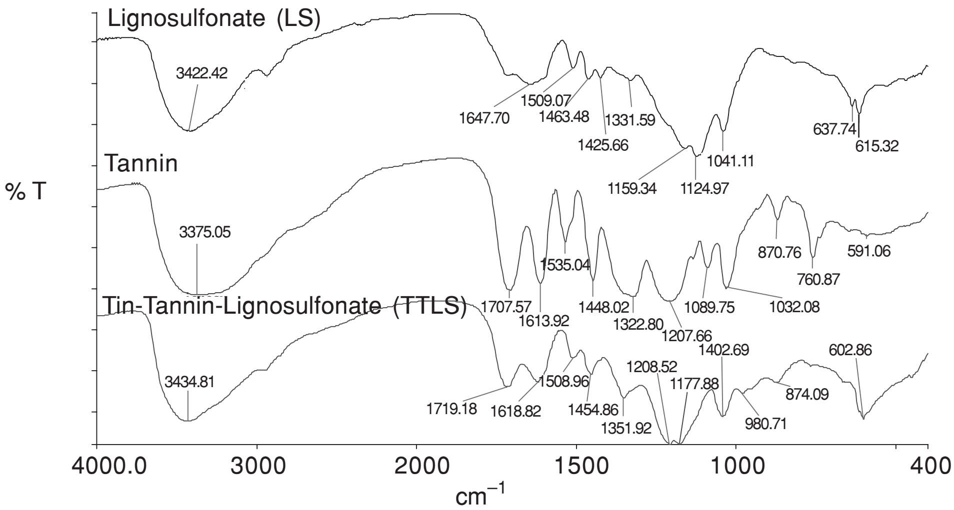

Figure 1 Infrared spectra of LS, tannin and TTLS

While drilling, pH lowers than 7.0 (pH of pure water) should be avoided because it will accelerate corrosion of pi peline and equi pments. A pH of greater than 7.0 should be maintained throughout the drilling process because in alkaline condition, chemical thinners are more effective, corrosion is reduced and gel strength and yield point are slightly reduced [10]. That is why acidic conditions were not considered in this study (Experiment I). Table 1 (refer to appendix) shows the rheological performances of TTLS against LS as drilling mud thinner at various pH values. Sodium hydroxide (NaOH) solution was added to the mud in order to adjust their pH values.

Table 1 Basic mud rheological properties at various pH values for three different types of mud

Types of Mud	**pH**	**μ_a (mPa.S)**	**μ_p (mPa.S)**	**τ_y (Pa)**
Base Mud	10.66	23.0	9.0	14.31
Base Mud + 0.3% LS	10.40	16.5	12.0	4.60
	11.53	12.0	9.0	3.07
	12.25	8.8	6.5	2.30
	12.60	30.5	4.0	27.08
Base Mud + 0.3% TTLS	9.84	17.0	11.0	6.13
	11.49	10.1	6.8	3.45
	12.35	7.5	5.2	2.30
	12.60	10.2	5.0	5.37
	12.70	23.5	4.0	19.93

In general, the thinning abilities of TTLS and LS vary with pH of the mud. In the pH range of 9.8 up to 12.4, the mud treated either with TTLS or LS has lower μ_a, μ_p and θ_y values. TTLS, however, performed a better job as a thinner compared to LS in terms of μ_a, μ_p and $\theta_{y.}$ These results were in line with the general rule of mud preparation where if there are no unusual holes problems, the mud should be kept as thin as possible [10]. At the same time, a moderate yield point is preferred over a negligible yield point because better lifting capacity is achieved at lower solids concentrations. Beyond this pH value (12.4), both TTLS and LS, however, exhibit bad thinning abilities. This is because the present of access OH^- ions in the system will cause the electrochemical charges in the mud become unstable. This phenomenon causes the bentonite platelet to flocculate.

In Experiment II, the results suggested that the newly formulated thinner exhibits a good quality of thinning agent even in the present of salt contamination. From Table 2, the reductions of at least 30% occur in μ_a and τ_y values at both levels of NaCl concentrations when 0.3% TTLS were added to the mud. μ_p values, however, showed small improvement because the effect of reduction in viscosities was smaller compared

Table 2 Basic mud rheological properties at different salinity

Types of Mud	μ_a (mPa.S)	μ_p (mPa.S)	τ_y (Pa)
Base Mud + 0.7% NaCl	33.2	12.5	26.32
Base Mud + 0.7% NaCl + 0.3% LS	20.0	12.0	8.20
Base Mud + 0.7% NaCl + 0.3% TTLS	22.5	12.0	10.22
Base Mud + 1.2% NaCl	38.5	12.5	26.57
Base Mud + 1.2% NaCl + 0.3% LS	22.1	10.2	12.14
Base Mud + 1.2% NaCl + 0.3% TTLS	25.4	10.5	15.20

to the increased in solids concentrations in the mud as more solids (NaCl and LS or TTLS) being added to the mud. More complete results are presented in Table 2.

From Experiment III, TTLS showed better thinning abilities compared to LS at higher temperature as displayed by the results in Table 3. From Table 3, TTLS preformed poorly at temperature lower than 50°C but showing better thinning abilities compared to LS in terms of μ_a and τ_y at temperature above 70°C. This is because at higher temperature, the presence of metal will improve the absorption of TTLS on the clay surfaces (bentonite) and prevent the platelets from linking. The enhance binding was attributed to the bridging of the multivalent metal ion between the negative-charge faces of the clay particles and the lignosulfonate molecules [11, 12].

Table 3 Basic mud rheological properties at different aging temperature for 30 minutes

Types of Mud	Temperature°C	μ_a (mPa.S)	μ_p (mPa.S)	τ_y (Pa)
Base Mud + 0.3% LS	30	19.0	13	6.13
	50	15.5	11	4.6
	70	19.0	12	7.15
	90	23.0	11	12.26
Base Mud + 0.3% TTLS	30	20.0	13	7.15
	50	17.0	11	6.13
	70	15.5	10	5.62
	90	19.0	12	7.12

Results of Experiment IV were tabulated in Table 4. In Table 4, the optimum dosage of TTLS was 0.3%, which gave the lowest yield point compared to others. Although LS showing the optimum dosage was 0.1%, the thinning ability was poorer

Table 4 Basic mud rheological properties under different thinner dosages (after aging at 90°C for 30 minutes)

Types of Mud	μ_a (mPa.S)	μ_p (mPa.S)	τ_y (Pa)
Base Mud	21.5	6	15.84
Base Mud + 0.1% LS	23.0	10	13.29
+ 0.3% LS	25.0	10	15.33
+ 0.5% LS	36.5	17	19.93
Base Mud + 0.1% TTLS	23.0	10	13.29
+ 0.3% TTLS	23.5	12	11.75
+ 0.5% TTLS	30.0	15	15.33

compared to TTLS in term of τ_y value. Furthermore, the difference between 0.1 and 0.3 was very small anyway.

5.0 CONCLUSIONS

In this study, a chrome-free drilling mud thinner known as tin-tannin-lignosulfonate (TTLS) has been successfully formulated by cross-linking lignosulfonate acid with tannin in presence of formaldehyde and stannous ions. The reactions were discussed and explained by IR spectra.

Impressive performance of the TTLS against LS, a commercial thinner, as a water-based drilling mud thinner, both at different pH values as well as at different salinity levels proved that this product has a great potential to be commercialized. Besides being a good tolerance to salt contamination, this product also shows good tolerance to higher temperature. The optimum dosage of thinner used in the system discussed in this paper was also determined.

The comparisons studies between TTLS and LS simply suggested that the thinning abilities of the later product have improved tremendously. The new stannous complex lignosulfonate inevitably provides a better alternative to hydrocarbon drilling industry as a drilling fluid thinner.

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