

Feasibility Study of Tannin-Lignosulfonate Drilling Fluid System for Drilling Geothermal Prospect

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ABSTRACT

Deflocculant is added into drilling fluid to disperse the flocculated clay that may lead to the loss of rheological properties at a higher temperature. Drilling into a well at the temperature above 150 °C, drilling fluid components or additives is susceptible to degrade, thus it affects the performance of drilling fluid. This study aims to evaluate the potential of tannin-lignosulfonate as a deflocculant in drilling fluid for drilling a geothermal well. Tannin-lignosulfonate was synthesized by a crosslinking of four different weight ratios of *Acacia spp.* tannin and lignosulfonate. The functional group of synthesized tannin-lignosulfonate was confirmed using Fourier transform infrared (FTIR) spectrum over a range of 4000 and 400 cm⁻¹ wave number. Subsequently, the decomposition rate assessment by thermogravimetric analysis (TGA) provided an evidence of thermal stability tannin-lignosulfonate. Gel strength of tannin-lignosulfonate drilling fluid was measured using Fann-viscometer at room temperature for 7 different drilling fluids sample. The thermal stability of tannin-lignosulfonate was identified at 294 °C and remains more than 60% of weight at that temperature. It was found that the 10 seconds and 10 minutes gel strengths were reduced with the addition of deflocculant in each sample.

1. INTRODUCTION

Drilling fluid plays important roles in the whole drilling program and serves several purposes in circulation system. Among those are (1) cooling and lubricating the drilling strings while it is circulating, (2) transporting the cuttings that created at the bottom of the hole and release them at the surface, (3) controlling the formation pressure while maintaining the wellbore stability, (4) sealing the permeable formations across the wellbore, and (5) assisting the logging operations. In drilling operations, the basic properties of drilling fluids are usually defined by the well program and monitored includes rheology, density, fluid loss, solid content, and chemical properties. To avoid any drilling problems such as a blowout, stuck pipe and few more, engineers are always searching for a good performance of drilling fluid systems that is fit for the purpose.

Dealing with standard temperature and pressure condition, the properties of drilling fluid are much easier to handle. While in a hostile drilling condition like high temperature environment, the selection of drilling fluid is more crucial alongside with the lithology that is one of the factors to be considered. As shown in Figure 1, the range of pressure and temperature for oil and gas development were clustered into 4 different groups (Naganawa, 2015). The high temperature environment often said to be at the temperature more than 150 °C. In geothermal drilling, the down hole temperature can reach up to 250 °C – 350 °C at the depth of 1000 to 2000 m. At this temperature conditions, the selection of drilling fluid becomes more stringent due thermal stability of drilling fluid system as well as materials used in the system. High temperatures can cause chemical alterations of various drilling fluid components. Thus, it is affecting the filtration and viscosity as well as increase the tendency of gelation (Fabbri and Vidali, 1970). In addition to that, clay activities are greatly affected with high tendency to flocculate and gel.

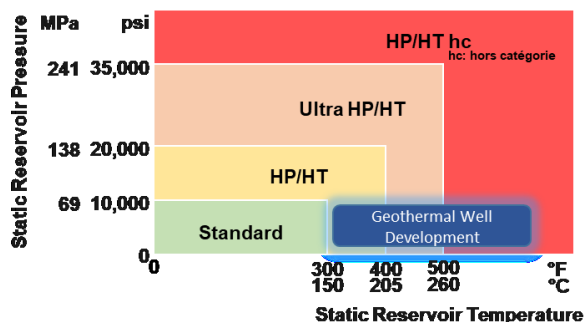


Figure 1: Static reservoir pressure and temperature classification for oil and gas development and geothermal resources development

Water-based drilling fluid is one of the main drilling fluid types used in geothermal drilling. In water-based drilling fluid, bentonite is used to aid the transportation of cuttings by providing a good viscosity and gel strength. However, at the temperature above than 121 °C or 250 °F, flocculation of bentonite suspension started to increase, which can lead to severe problem (Caenn, Darley, & Gray, 2017). Flocculation happens when the clay particles bind together to form a flocculated clay and at the same time, it creates an open network that cause the filtration loss (Altun et al., 2015). The extreme gelation of drilling fluid is possible to cause problems in logging operation. Deflocculant or thinning agent often added into drilling fluid system to bring back the rheological properties to the normal condition (Zhang and Yin, 1999). However, the degradation of those additives limits the functionality. Even though those additives are able to defloc the flocculated bentonite, it faced a serious degradation issue at elevated temperature whereby most additives started to degrade at a temperature of more than 107 °C (225 °F).

At the initial stage of drilling, most of the solid particles in the drilling fluid come from the weighting agents that are used in formulating drilling fluid. As the drilling progress, excessive solid particles from the drilled solid produce a higher viscosity drilling fluid. When drilling hits a high temperature zone, the drilling fluid gets thicker hence solid particles are prone to sag and settle at the bottom part of the wellbore. Clay particles that initially added to the drilling fluid started to agglomerate and cause excessive of viscosity and gelation. Attraction between negative face charges and the positive edge charges will contribute to the flocculation thus the clay particles will stick together and creating a thick drilling fluid with high viscosity. When deflocculant is added into drilling fluid, the edge of clay particle as shown in Figure 2 will attracted to the different charges of the additive. Deflocculant will anchor and absorb at the surface of clay particles. The negatively charge additives will neutralize the positive charges of the edge particles thus repulsive charges will then create a distance from each other to avoid association between particles. Lignosulfonate is among the commonly used deflocculants in the industry. While chrome-lignosulfonate was invented to be used as deflocculant and work best in the high temperature conditions (Darley et al., 1988). Though it is capable to solve the problem, the existence of chromium ion in drilling fluid system raised the environmental concern.

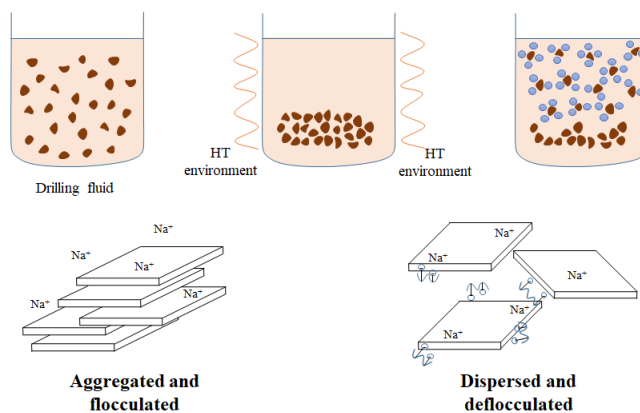


Figure 2: Mechanism of dispersion and deflocculation

Several findings in the past development of adhesives show that the thermal stability of lignosulfonate is improved by addition of tannin (Chupin et al., 2015) as shown in Figure 3. The crosslinking of tannin with sodium lignosulfonate shows an improvement to the thermal stability of adhesive. Thus, in this study tannin-lignosulfonate is proposed to be an environmentally friendly deflocculant with a prediction to have a good thermal stability. Tannin and lignin are known as the most abundant compounds extracted from biomass. Tannin is a polyphenolic compound that is natural, non-toxic and biodegradable and can be found in various parts of vascular plants. Lignosulfonate on the other hand is a byproduct from paper pulping process. Tannin and lignosulfonate are cross-linked to obtain tannin-lignosulfonate for the use as a high-temperature drilling fluid deflocculant. Wide availability of tannin and lignosulfonate is also an advantage from a manufacturing cost viewpoint.

Many researches have been done to understand the rheology and the factor that affect the rheological properties at elevated temperature, but still there is no consensus on the mechanism of viscosity enhancement is achieved (Kelessidis, 2017). Thus, in this study an environmental friendly tannin-lignosulfonate is proposed as an additive to enhance the performance of drilling fluid in high temperature. This paper discloses the method of synthesizing the tannin-lignosulfonate. The characterization of synthesized deflocculant was carried out using FTIR to verify the chemical compound in the materials followed by analysis of thermal stability by using FTIR. The performance of tannin-lignosulfonate and industrial range deflocculant in water-based drilling fluid system were compared in the rheological analysis.

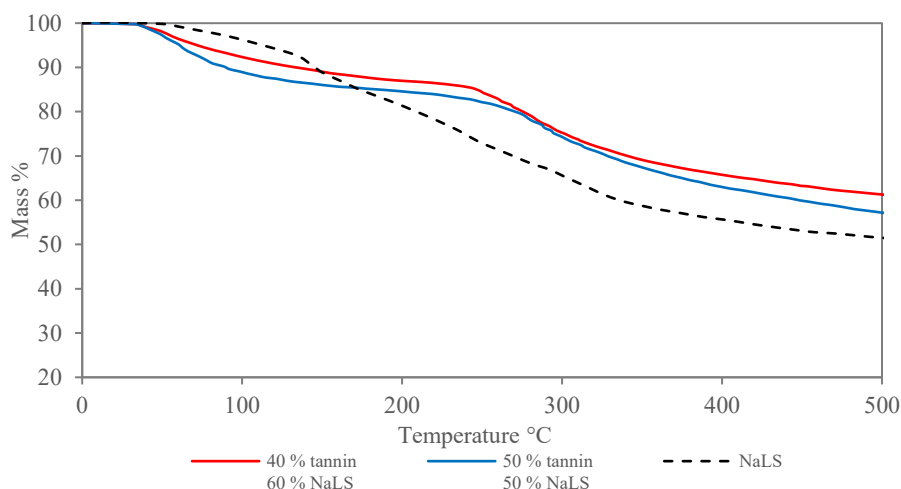


Figure 3: TG analysis of tannin-lignosulfonate adhesive

2. MATERIALS AND TANNIN-LIGNOSULFONATE PREPARATION

2.1 Materials

Tannin used in this study was extracted from Australian species of *Acacia sp.* and was purchased from Kawamura & Co. Ltd. (Japan). The commercial calcium lignosulfonate (CaLS) was purchased from Kono New Material Development Co. (Japan). The analytical grade of other chemicals, formaldehyde and sulfuric acid (H_2SO_4) including sodium hydroxide (NaOH) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were all purchased from Kanto Chemical Co. Inc. (Japan).

2.2 Synthesizing of tannin-lignosulfonate

Calcium lignosulfonate (CaLS) was dissolved in hydrochloric acid solution for decalcification process. The amount of CaLS added into the solution is depending on the weight ratio of CaLS and tannin. The mixture was frequently stirred and sodium hydroxide was added to adjust the pH of the solution between 3 to 4. Then, calcium sulfate was removed from the solution through filtration to obtain the lignosulfonic acid. On the hot plate with the temperature $105^\circ C$, 4ml of formaldehyde was added to the solution to initiate the crosslinked process. Tannin was added according weight ratio for each sample. Then, solution was continuously stirred for 2 hours. Later, ferrous sulfate heptahydrate was chelated with the solution for 30 minutes at the same temperature. Finally, the tannin-lignosulfonate (TLS) solution was dried under vacuum oven at temperature $60^\circ C$.

3. CHARACTERIZATION

The functional groups of each sample were characterized by using a Fourier transform-infrared (FTIR), JASCO FT/IR 6100. The spectra were obtained in a wavelength of $400 - 4,000\text{ cm}^{-1}$. The thermogravimetric analysis (TGA) was used to measure the thermal stability and decomposition rate of the sample over wide range of heating condition from $20 - 500^\circ C$ with constant heating rate at $10^\circ C/min$ and nitrogen flow rate at 100 mL/min . The TGA used to perform this experiment was Hitachi Hitech TG/DTA 7200.

4. DRILLING FLUID RHEOLOGY

In this study, tannin-lignosulfonate based drilling fluid was prepared by having water as base fluid, bentonite, barite and other additives such as sodium hydroxide (caustic soda) and sodium carbonate (soda ash). Bentonite, barite and 3 different deflocculants were purchased from Telnite Co. Ltd. Caustic soda and soda ash were purchased from Wako Pure Chemical Industries Ltd. Drilling fluid systems were design to compare the performance of synthesized tannin-lignosulfonate in drilling fluid with the industrial range deflocculants. All drilling fluid components were mixed by using Hamilton Beach FANN single mixer. Each drilling fluid system was designed to have 9-12 lb/gal of weight with the pH range 9.5 to 11.0. The rheological properties of drilling fluids were measured by Fann-35SA viscometer according to API RP 13-B1 Recommended Practice for Field Testing Water-based Drilling Fluid and API RP 13-I Recommended Practice for Laboratory Testing of Drilling Fluid (American Petroleum Institute, 2009a; American Petroleum Institute, 2009b).

5. RESULT AND DISCUSSION

5 samples of tannin-lignosulfonate with 4 weight ratios were prepared for the purposed of characterization. A total of 10 samples were studied their functional group using FTIR which include 5 synthesized samples, 2 pure calcium lignosulfonate and tannin and the 3 industrial grade deflocculants. 1 sample of tannin-lignosulfonate was studied using TGA to analyze the thermal stability. As for rheological evaluation, all 4 synthesized tannin-lignosulfonates and 3 industrial grade deflocculant samples were used in preparing the drilling fluid samples to compare the gelation effect in the presence of deflocculant.

5.1 FTIR spectroscopy

The functional groups of synthesized tannin-lignosulfonate were confirmed through characterization using FTIR. Table 1 shows the summary of FTIR spectrum for all samples. A broad absorption band between 3500 and 3300 cm^{-1} was observed due to the presence of phenolic compound. Tannin shows a peak of 3308 cm^{-1} which is the normal peak of a phenolic compound in tannin (Lisperguer, Saravia, and Vergara 2016). Meanwhile, calcium lignosulfonate has a slightly higher absorption band at 3436 cm^{-1} as shown in Table 1 and Figure 5. A similar result of phenolic compound observed for calcium lignosulfonate characterized by Wang, Yang, and Zou (2015). The phenolic FTIR spectrum for all synthesized tannin-lignosulfonate was found in between the two-absorption band. The absorption around 2940 cm^{-1} reflected the stretching vibration of C-H bond. The aromatic rings were observed at the peak around 1600, 1500 and 1400 cm^{-1} for all samples. Various peaks from 1000 to 1300 cm^{-1} were identified as the stretching band of C-O. It can be confirmed that all synthesized tannin-lignosulfonate samples in Figure 4 are having a similar range of adsorption band with industrial grade deflocculant in figure 6.

Table 1 FTIR summary table

Functional group	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)	Wave number (cm-1)
	Sample A TLS	Sample B TLS	Sample C TLS	Sample D TLS	Sample E LS	Sample F Tannin	Sample G TLS	Sample H IGD A	Sample I IGD B	Sample J IGD C
O-H (stretch)	3437	3429	3437	3430	3437	3308	3413	3412	3402	3369
C-H (stretch)	2943	2932	2940	2936	2939	2936	2935	2947	2939	2932
Aromatic ring	1634	1632	1623	1621	1604	1613	1617	1567	1613	1583
	1514	1510	1512	1508	1511	1508	1513	1455	1511	1384
	1453	1455	1455	1455	1459	1453	1454	1409	1453	
C-O (C-O-C stretch)	1125	1110	1111	1126	1209	1236	1131	1170	1160	1111
	1047	1044	1041	1039	1043	1070	1038	1119	1091	1034
C-H (out-of-plane bend)	614	614	614	615	653	662	616	625	612	534

Sample A - 75% Calcium Lignosulfonate (CaLS):25% tannin	Sample B - 65% Calcium Lignosulfonate (CaLS):35% tannin
Sample C - 55% Calcium Lignosulfonate (CaLS):45% tannin	Sample D - 45% Calcium Lignosulfonate (CaLS):55% tannin
Sample E - Calcium Lignosulfonate	Sample F – Tannin
Sample G - 55% Calcium Lignosulfonate (CaLS):45% tannin without Ferrous ions	Sample H – Industrial grade deflocculant A
Sample I – Industrial grade deflocculant B	Sample J – Industrial grade deflocculant C

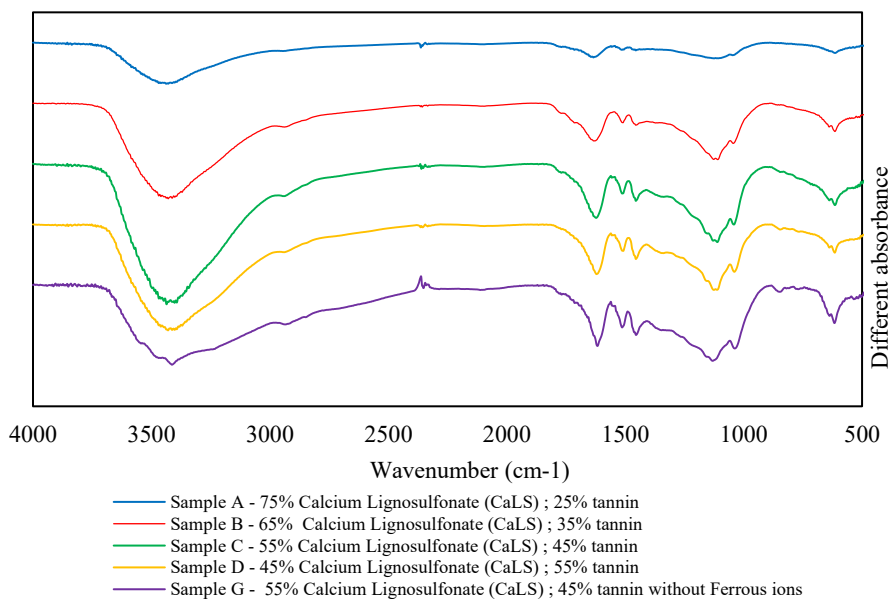


Figure 4: FTIR spectra of tannin-lignosulfonate

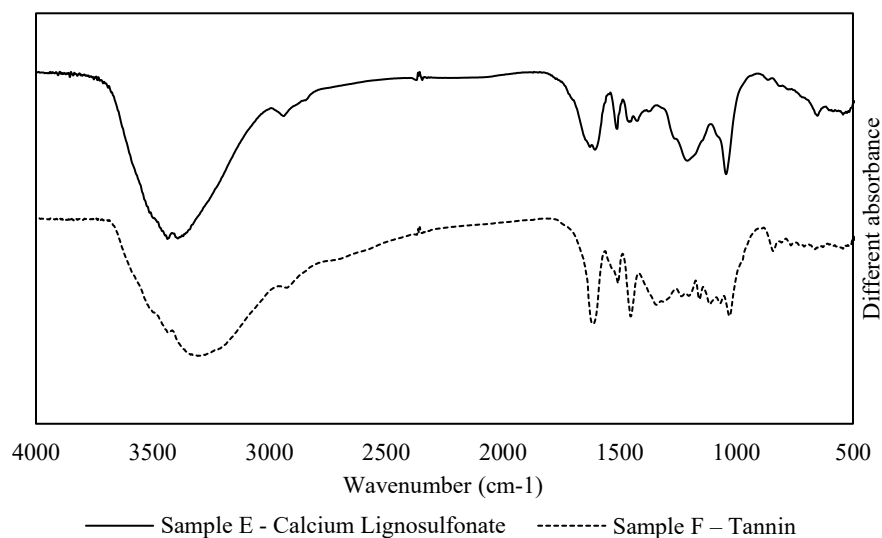


Figure 5: FTIR spectra of tannin and calcium lignosulfonate

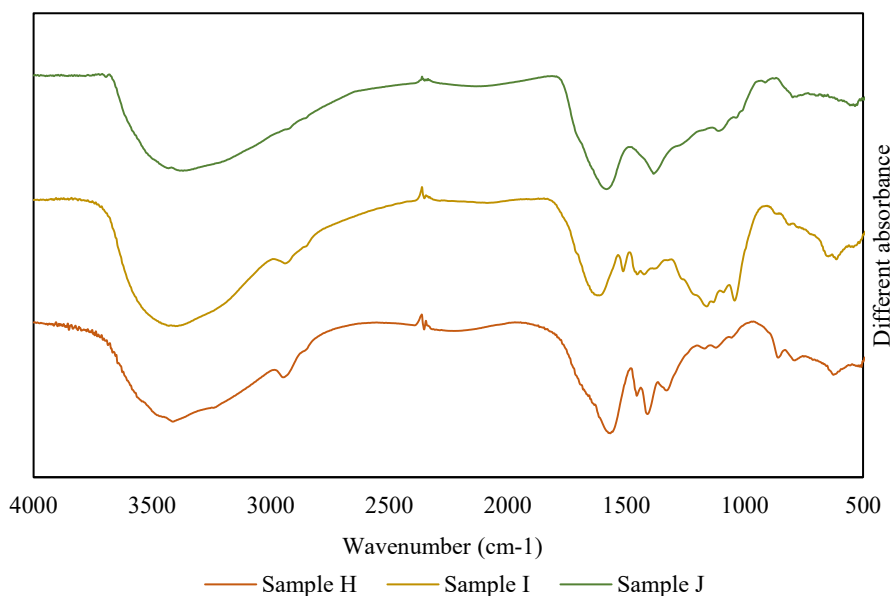


Figure 6: FTIR spectra of industrial deflocculants

5.2 Thermal properties of tannin-lignosulfonate

The thermal stability and decomposition behaviour were evaluated through TGA analysis. Sample C was chosen for thermal stability assessment based on observation by Chupin et al. on the increasing of tannin ratio. The thermal stability reached the optimum value at the same temperature with 55% of tannin ratio (Chupin et al., 2015). Figure 7 presents the decomposition curves of tannin-lignosulfonate (TLS C). Based on this result, tannin-lignosulfonate showed a good thermal stability up to 294°C. Tannin-lignosulfonate are also able to hold more than 60% of weight after being heat up 500°C as shown this figure. This result proved that tannin-lignosulfonate is resistant at higher temperature more than 250 °C, thus, made it possible being a good candidate of deflocculant in drilling fluid for drilling higher temperature conditions.

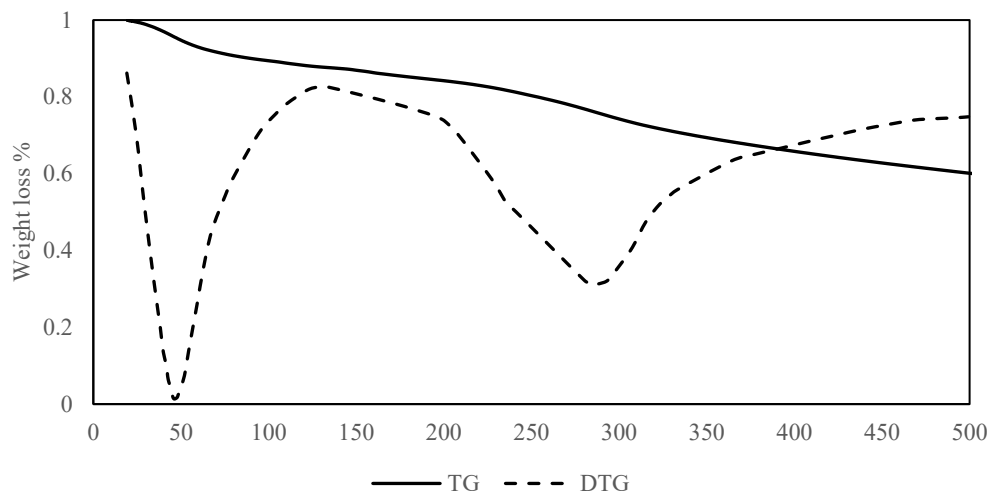


Figure 7: Decomposition curves of tannin-lignosulfonate

5.3 Rheological properties

In rheological properties evaluation, gel strength was assessed to observe the performance of deflocculant in reducing the gelation. 10 seconds and 10 minutes of gel strength was recorded as shown in Figure 8. A thick and viscous drilling fluid was formulated to imitate an excessive gelation condition. The physical of drilling fluid was changed drastically after adding deflocculant which is becoming less viscous. IGD A, IGD B and IGD C were representing the industrial grade of deflocculant. IGD A performed best in reducing the gel strength with low concentration of deflocculant. The performance of synthesized tannin-lignosulfonate TLS A, TLS B, TLS C and TLS D is comparable with IGD B and IGD C. The gelation was reduced with 0.5 g and 1.0 g of deflocculant.

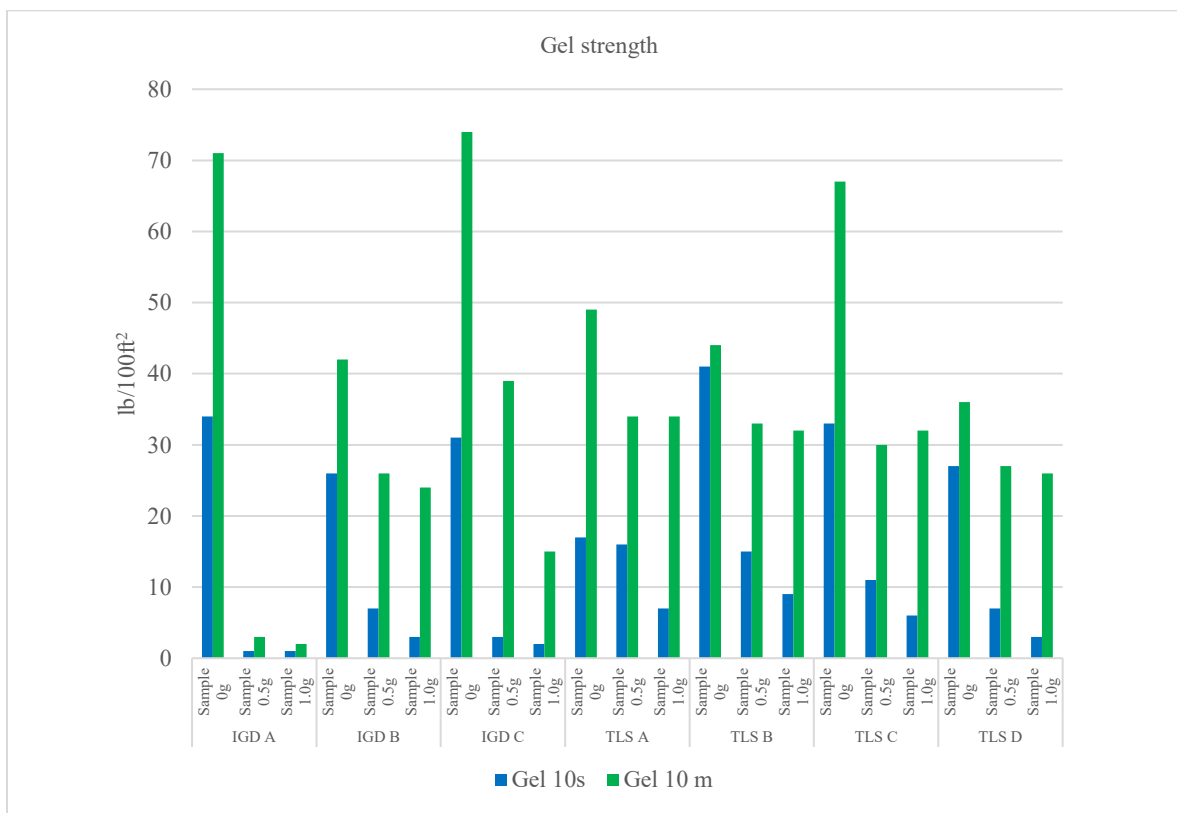


Figure 8: The 10 seconds and 10 minutes gel strength

6. CONCLUSIONS AND RECOMMENDATIONS

1. A biopolymer tannin-lignosulfonate as deflocculant was synthesized and the functional group synthesized tannin-lignosulfonate was confirmed by the FTIR spectrum.
2. Tannin-lignosulfonate has a good thermal stability as it shows high thermal resistance in TG analysis.
3. The performance of tannin-lignosulfonate performance reducing the gelation is comparable with the industrial grade deflocculant but further assessment on other rheological properties need to be carried out.
4. Drilling fluid system need to be aged to imitate the down hole condition which is high temperature.

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REFERENCES

- Altun, Gursat, Ali Etehadı Osgouci, Mustafa Hakan Ozyurtkan, and Umran Serpen. 2015. "Sepiolite Based Muds as an Alternate Drilling Fluid for Hot Environments." *World Geothermal Congress 2015* (April):10.
- American Petroleum Institute. 2009a. *Recommended Practice for Field Testing of Water-Based Drilling Fluids API 13B-1(RP 13B-1)*. 4th ed.
- American Petroleum Institute. 2009b. *Recommended Practice for Laboratory Testing of Drilling Fluids API 13I (RP 13I)*. 4th ed.
- Caenn, Ryen, H. C. H. Darley, and George R. Gray. 2017. "Chapter 1 – Introduction to Drilling Fluids." Pp. 1–34 in *Composition and Properties of Drilling and Completion Fluids*.
- Chupin, Lucie, Bertrand Charrier, Antonio Pizzi, Arturo Perdomo, and Fatima Charrier-El Bouhtoury. 2015. "Study of Thermal Durability Properties of Tannin-Lignosulfonate Adhesives." *Journal of Thermal Analysis and Calorimetry* 119(3):1577–85.
- Darley, H. C. H., George R. Gray, H. C. H. Darley, and George R. Gray. 1988. "CHAPTER 11 – DRILLING FLUID COMPONENTS." Pp. 542–617 in *Composition and Properties of Drilling and Completion Fluids*.
- Fabbri, F. and M. Vidali. 1970. "Drilling Mud in Geothermal Wells." *Geothermics* 2(PART 1):735–41.
- Kelessidis, Vassilios C. 2017. "Yield Stress of Bentonite Dispersions." *Rheology : Open Access* 1(1):1–12.
- Lisperguer, Justo, Yanina Saravia, and Emilio Vergara. 2016. "Structure and Thermal Behavior of Tannins from Acacia Dealbata Bark and Their Reactivity toward Formaldehyde." *Journal of the Chilean Chemical Society* 61(4):3188–90.
- Naganawa, Shigemi. 2015. "Survey on Effective and Feasible Emerging Technologies for EGS Well Drilling." (Lcm):1–6.
- Wang, Fei, Xuping Yang, and Yangxue Zou. 2015. "The Esterification of Sodium Lignosulfonate with Maleic Anhydride in Water Solution." *International Journal of Polymer Analysis and Characterization* 20(1):69–81. Retrieved (<http://dx.doi.org/10.1080/1023666X.2014.961117>).
- Zhang, LI MING and Dai Y. Yin. 1999. "Novel Modified Lignosulfonate as Drilling Mud Thinner without Environmental Concerns." *Journal of Applied Polymer Science* 74(7):1662–68.