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Lignocellulosic-Based Rheological Modifier for High Temperature Oilfield Drilling Operations

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Abstract: **-** In this study, a rheological modifier for water-based drilling mud is prepared by exploiting the Kraft pulping residual of oil palm empty fruit bunch (OPEFB) fibers. From an experimental point of view, readily combination between water-based drilling mud and Lignin Graft Copolymer (LGC) provided an optimum rheological performance and gelling effect for the water-based drilling mud. This new water-based drilling mud additive demonstrated competitive characteristics to other existing commercial additives. The rheological performances of LGC are studied and the findings show that LGC gives good gelling, viscosity building, and pH controlling abilities at low concentration of 0.5% w/w. It is also illustrates excellent thermal stability at high temperature up to 200°C.

Keywords: **-** *Rheological modifier; Drilling mud; OPEFB fibers; Lignin Graft Copolymer; Thermal stability*.

I. INTRODUCTION

The selection of proper drilling mud during the rotary drilling process is vital for the success of any drilling operation. In fact, most of drilling problems are a direct or indirect consequence of improper mud selection. Within this context, there are many types of drilling mud used in the petroleum industry. Generally all of these types are classified into three main categories: (1) air and foam-based mud (ABM); there are drilling conditions under which a liquid drilling fluid is not the most desirable circulating medium. In such a case, air or foam is used as drilling mud to accommodate these special conditions. Moreover, this is the most advantageous and effective type of drilling mud in consolidated rock formations, (2) oil-based mud (OBM); this drilling mud is made up of oil as the continuous phase. Diesel oil is widely used to provide the oil phase. In addition, this type of drilling mud is more expensive, as it requires stringent pollution control measurement and is also difficult to dispose, and (3) water-based mud (WBM); this type is the mud in which water is the continuous phase. This is the most common drilling mud used in oil drilling and it consists mainly of water, clay, and specialized chemical additives. Besides that, this type is mixed friendly with water and allows drilling mud additives to perform efficiently. Beyond that; it is inexpensive and presented less environmental problems compared to oil-based mud [1]. Owing to that fact, the type of drilling mud used in this study is a water-based mud.

Nevertheless and during the course of drilling an oil or gas well, the drilling mud without any additives is unable to provide satisfactory rheological properties required for optimum performance in well drilling [2]. Thus, a number of additives are used to alter the mud properties to fulfill all of the requirements of drilling mud. In addition, different types of additives, either chemicals or polymers, are used in designing a drilling mud to meet some functional requirements, such as appropriate mud rheology, density, mud activity, fluid loss control, etc [3]. It is noteworthy to mention that when drilling in deep wells for oil, gas, or geothermal reservoirs; high temperatures are usually encountered which adversely influence the performance of drilling muds [4]. Also, a major difficulty in formulating high-temperature drilling muds is that mud is negatively affected by elevated temperatures, first gelling excessively and then becoming inert at extreme temperatures [3]. For that reason, there is always a need for drilling mud additives which can stabilize drilling mud suspensions at high temperatures. This need can be fulfilled by developing new additives (polymers) that have better resistance to the high temperature drilling operations. Accordingly, both naturally occurring and synthetic polymers have been widely used. Among them, chemically modified biopolymer is probably one of the most extensively studied due to its low cost, lack of toxicity, and biodegradability characteristics [5]. In the same way, this study is designed to produce chemically modified lignin by means of graft copolymerization technique. Such technique could offer new type of drilling mud additives, i.e. thermally stable rheological modifier.

Traditionally, lignin has been viewed as a waste material or a low value by-product of pulping and paper industry with its utilization predominantly limited to its use as a fuel to fire the pulping boilers [6]. Almost all lignins extracted from lignocellulosic materials from the pulp and paper industry are burnt to generate energy and considered as an excellent fuel, since lignin yields more energy when burnt than cellulose. Nevertheless, the possible development in the lignin industrial utilization is limited to very low growth because until now only a small amount (2%) of lignin is commercially used [7]. This includes the manufacturing of wide range of products. In fact, due to the lack of appropriate industrial processes, lignin is considered as a mostly non-commercialized product.

On the other hand, lignins have many specifications (chemical and biophysical properties) which can advantageously be exploited to develop new and environmentally friendly products. In this regard, lignins are non toxic, potentially of high value, inexpensive, and available in large amounts. They possess highly reactive locations that can be surprisingly modified through a selection of chemical, physical and/or enzymatic reactions, which give them a great potential for their exploitation as industrial raw materials [8]. In agreement with that, this study is an effort to investigate the potentiality of using modified lignin as a drilling mud additive in oilfield drilling operations especially in high temperature and high pressure conditions.

II. EXPERIMENTAL STUDY

2.1 Materials

The raw material used in this study was oil palm empty fruit bunch (OPEFB) long fiber supplied by Sabutek (M) Sdn. Bhd, a Malaysian company that specializes in the recycling of OPEFB.

The catalyst p-toluenesulfonic acid (PTS) was used as received from Merck (Merck, Germany). Acrylic acid (AA) with 99% purity was purchased from Aldrich® (Sigma-Aldrich, USA). AA was purified under vacuum distillation process to remove phenolic inhibitors, stored in the refrigerator, and brought to room temperature before being used. The commercial viscosifying and gelling agents, High Viscosity Sodium Carboxy Methyl Cellulose (CMC-HV), Guar Gum (GG), and Xanthane Gum (XG) were supplied by Kota Mineral Chemical (M) Sdn. Bhd, Sim Company and Aldrich® (Sigma-Aldrich, USA).

2.2 Methods

2.2.1 Isolation of Kraft Lignin (KL)

This technique includes different laboratory procedures. In addition, these procedures have been applied subsequently in order to produce pure KL. Apart from these, they consist of three experimental processes as explained in the following subsections.

2.2.1.1 Kraft pulping of OPEFB

The Kraft pulping process involves digesting of OPEFB fibers at elevated temperature and pressure in cooking liquor, which is an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). The cooking liquor chemically dissolves the lignin that binds the cellulose fibers together.

Prior to the pulping process, 1000 g of OPEFB fibers was soaked in water for two days to remove non-fibrous materials. In the pulping process, the soaked OPEFB fibers were mixed with 41.8 g of Na_2S, 128.7 g of NaOH, and 5.6 L of distilled water in a 20 L stainless steel rotary digester. After which, the mixture was heated from approximately 70°C to a maximum cooking temperature 170°C, followed by 3 hr cooking period. Once the cooking period was completed, the contents of the digester were transferred to a container and washed in the pulp washer, where the spent cooking liquor (black liquor) was separated from the pulp.

2.2.1.2 Extraction of KL

The extraction of KL from the black liquor was accomplished by employing an acidification method. In this direction, the high alkali pH black liquor which was collected after the completion of the pulping process was then acidified using sulphuric acid in order to recover KL as precipitate. In particular, 800 mL of black liquor in 1000 mL beaker was acidified with 20% v/v sulphuric acid until pH 2; thereby a precipitation of KL was formed. The precipitate was filtered and washed with pH 2 water, which was prepared using the same acid in the previous step. KL was then dried in a vacuum oven at 45°C for 72 hr. In order to avoid the moisture in the KL particles, it was grinded to a powder form and dried again in a vacuum oven at 45°C for 72 hr.

2.2.1.3 Purification of K L

In general, lignins are rarely isolated as pure materials, and are always associated with carbohydrate linkages (cellulose and hemicellulose) to varying extent depending on their isolation procedure [9].

The purification of KL was conducted by extracting KL in the soxhlet apparatus for 6 hr with n-pentane to remove lipophilic, non-lignin matters such as wax and lipids [10]. The precipitate was filtered and washed twice with pH 2 water to remove the excess n-pentane and non-lignin phenolic compounds which may still remain after the pulping process. The purified KL was then dried further in the vacuum oven at 45°C for another 48 hr.

2.2.2 Preparation of Lignin Graft Copolymer (LGC)

A grafting reaction was achieved in small test tubes equipped with magnetic stirrers. In details, about 0.75 g of PTS was introduced into test tube with appropriate amounts of Kraft lignin (KL) and acrylic acid (AA). The tube was deoxygenated by flushing it with nitrogen gas for 10 min, sealed with aluminum foil and then placed in a water bath at 80^{o}C for 18 hr with vigorous stirring. After a specific reaction time, the tube was immersed in an ice bath at 0^{o}C for one hour with incessant stirring. The result was a highly turbid black liquid that was decanted into 0.1 M zinc sulfate aqueous solution at a ratio of 1:10 v/v with agitation and was allowed to stand at room temperature overnight. After this period, unreacted KL was precipitated and removed by filtration. The light brown liquid was evaporated to remove the aqueous solution and unreacted AA. The lignin graft copolymer (LGC) was obtained as light brown fine particles. These particles were collected and dried in an oven at 100^{o}C for 72 hr to remove moisture from the LGC [11].

2.2.3 Application of LGC

In this study, LGC, which is a chemically modified biopolymer, was used as a drilling mud additive, i.e. viscosity building (viscosifying) agent, gelling agent, and pH controlling agent. In addition, LGC was subjected to the simulated hydrocarbon drilling conditions in order to evaluate its ability as a drilling mud additive.

2.2.3.1 Preparation of water-based mud

In the present study, in all the experiments related to mud property tests, the basic water-based mud was prepared by adding 80 g of bentonite and 4 g of sodium carbonate into 1000 mL of water that was previously heated in a large beaker at 80°C. The ingredients of water-based mud were mixed with pre-heated water gradually with vigorous stirring using mixer which was set at high speed of 2000 revolution per minute. This process was conducted for half an hour, after which, the beaker was sealed with aluminum foil and allowed to stand for 24 hours at room temperature [12-18].

2.2.3.2 Effect LGC as a rheological modifier

The rheological properties of the water-based mud samples in this study were measured using a direct-indicating rheometer (Fann Rheometer model 286). The Fann rheometer constants had been adjusted so that the apparent viscosity, plastic viscosity, and yield point could be obtained using readings from rotor sleeve speeds of 300 rpm and 600 rpm. Rotor speeds of 300 or 600 were obtained by setting the position of the speed control lever. Measurements were read directly from the deflection scale. Accordingly, these parameters could be calculated using the following formulae from API Recommended Practice of Standard Procedure for Field Testing Drilling Fluids [19-20].

$$\text{Apparent viscosity } (\mu_a) = \theta_{600} / 2 \text{ (cp)}$$
$$\text{Plastic viscosity } (\mu_p) = \theta_{600} - \theta_{300} \text{ (cp)}$$
$$\text{Yield point } (\tau_y) = 0.511(\theta_{300} - \mu_p) \text{ (lb/100 ft}^2\text{)}$$

Additionally, gel strength (θ) measurements were read directly from the deflection scale. When making gel strength measurements, force was applied manually by turning the gel knob and observing the maximum reading on the deflection scale before the gel broke. In order to estimate the effect of different aging temperatures on the drilling mud rheological parameters, the API drilling mud aging experiments were carried out using a Fann Roller Oven Series 2500 and a 500 mL Fann stainless steel aging cell.

In this study, two sets of experiments were performed according to the American Petroleum Institute standard procedures [12-13]. In the first experiment, the basic drilling mud samples were treated with different concentrations of LGC in order to optimize its efficiency as a drilling mud viscosifier and gelling agent. Furthermore, two values of temperature were chosen to study the performance of LGC at room temperature and high temperature. In details, LGC were added with different concentrations of 0.3, 0.5, and 0.7% w/w into the basic mud samples, after which, the rheological parameters were measured before and after heating and vigorous agitation at 25°C and 90°C for half an hour. The second experiment was designed to evaluate the performance of LGC as a drilling mud viscosifier and gelling agent at high temperature (200°C). Moreover, the viscosity building and gelling abilities of LGC were tested and compared to the commercial viscosity building and gelling agents that are available in the market, such as sodium carboxy methyl cellulose (CMC), guar gum (GG), and xanthane gum (XG). In this experiment, the basic drilling mud samples were treated with either 0.5% w/w of LGC, CMC, GG, or XG simultaneously with vigorous stirring in order to homogenize the mud samples with the additives. This concentration (0.5%) was chosen since LGC acts optimally as a viscosity building and gelling agent at this level (based on the first experiment result). The rheological parameters were measured before and after the heating and aging process at 200°C for 16 hr.

2.3 Characterizations

2.3.1 Differential Scanning Calorimetry (DSC) analysis

In this study, glass transition temperature (T_g) values of KL and LGC were estimated using Perkin Elmer model Pyres 1 DSC. Approximately 10 mg of sample was heated from -50°C to 180°C at the heating rate of 20 °C/min in a nitrogen atmosphere at the flow rate of 30 mL/min.

2.3.2 Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectroscopy was used as an analytical technique for the estimation of the functional groups presented in lignin [21].

In this study, FTIR spectroscopy was able to differentiate the chemical bonds in the molecular structure of KL and LGC. The ungrafted KL and LGC samples were analyzed using KBr pellet technique. In this technique, the KBr thin pellet was prepared by grinding 1% of sample into potassium bromide (KBr). It was then scanned by the Perkin Elmer system 2000 FT-IR spectrometer in the range from 4000 cm^{-1} – 400 cm^{-1}.

III. RESULTS AND DISCUSSION

3.1 Extraction of KL

During the Kraft pulping process, the lignin that dissolved from the raw material (OPEFB) is separated in the form of a liquor, rich in phenolic compounds, that represents the process effluent [22]. This effluent is dark brown or black in color; hence is called black liquor. The black liquor contains, in addition to the main fraction, lignin, sugars from degraded hemicellulose and cellulose, hereafter grouped as hemicellulose and salts [23].

Conventionally, lignin can be separated from other black liquor components using acid precipitation method. In addition, the acid precipitation method is the most common method to recover the lignin from the black liquor [24]. From an experimental point of view, the reduction in the pH of this liquor which is proportioned by the sulphuric acid addition caused the precipitation of the solubilized lignin, such that the lower the pH the higher the recovered lignin mass [25]. In this study, Kraft lignin (KL) was extracted from the black liquor by means of minimizing its alkali pH (11.52) to acidic pH (2) using acid precipitation method via diluted (20%) sulphuric acid (H_2SO_4); thereby KL was precipitated as a brown powder.

3.2 KL graft copolymerization reaction

The main chemical functional groups in KL are the hydroxyl, methoxyl, carbonyl, and carboxylic groups [26]. These functional groups present prospective positions on lignin structure to associate with other monomers and induce the graft copolymerization reaction. Therefore, acrylic acid may possibly polymerize with KL and the reaction takes place by the formation of the ester bond which linked AA with KL. A possible reaction mechanism of grafting the AA chain onto the KL structure might comprise two reaction steps, as shown in Figure 3.1. The suggested mechanism involved in the attachment of polyacrylic acid (PAA) chain onto the KL backbone via polycondensation process produced LGC and eliminated water. An ester bond was formed by the interaction, i.e. the esterification between hydroxyl group in KL and carbonyl group of AA homopolymer chain. Furthermore, the ester bridge linked PAA as a pendant chain onto the KL main chain {Figure 3.1(a)}. The PAA homopolymer chain was formed using a PTS inducement of AA monomers, as shown in Figure 3.1(b).

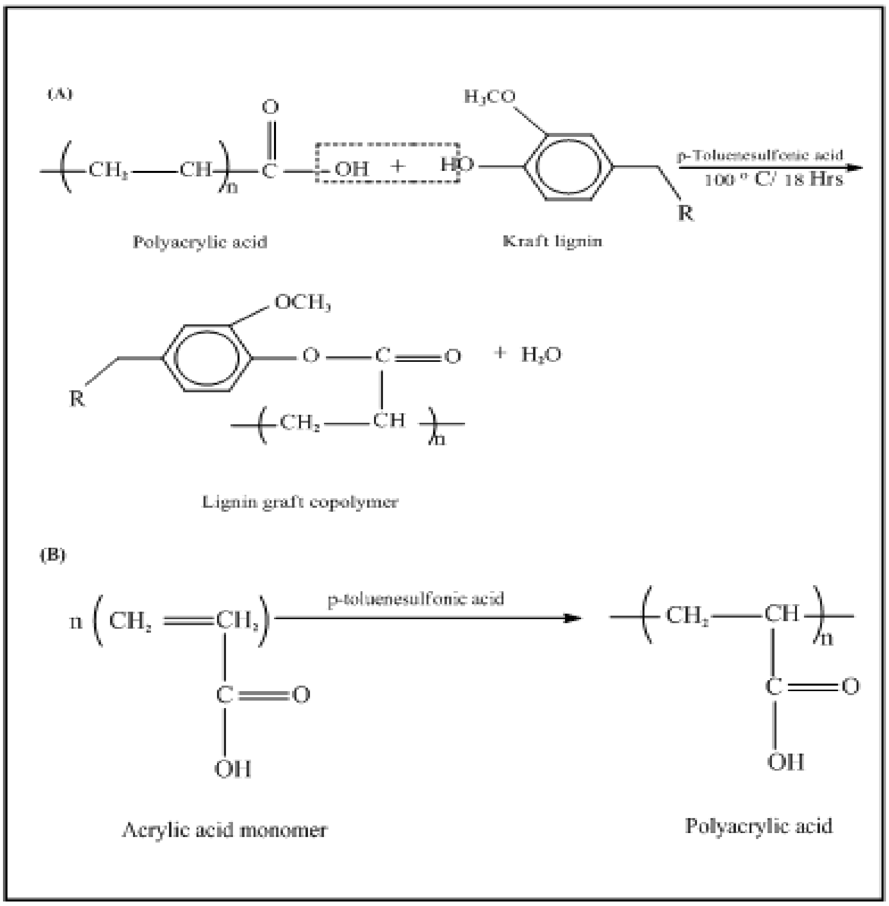


Figure 3.1 Suggested reaction mechanism of grafting AA chain onto KL main chain

3.3 Thermal properties of KL and LGC

The thermal properties of ungrafted KL and LGC were studied using the DSC analysis. The KL is an amorphous compound with T_g at 58.03^{o}C, as illustrated by DSC thermogram in Figure 3.2. The amourphousity of the KL may be due to the complication in its structure which somewhat impedes the occurrence of an arrangement in its composition. Therefore, no melting temperature T_m or crystallization temperature T_c has been recorded in the DSC thermogram.

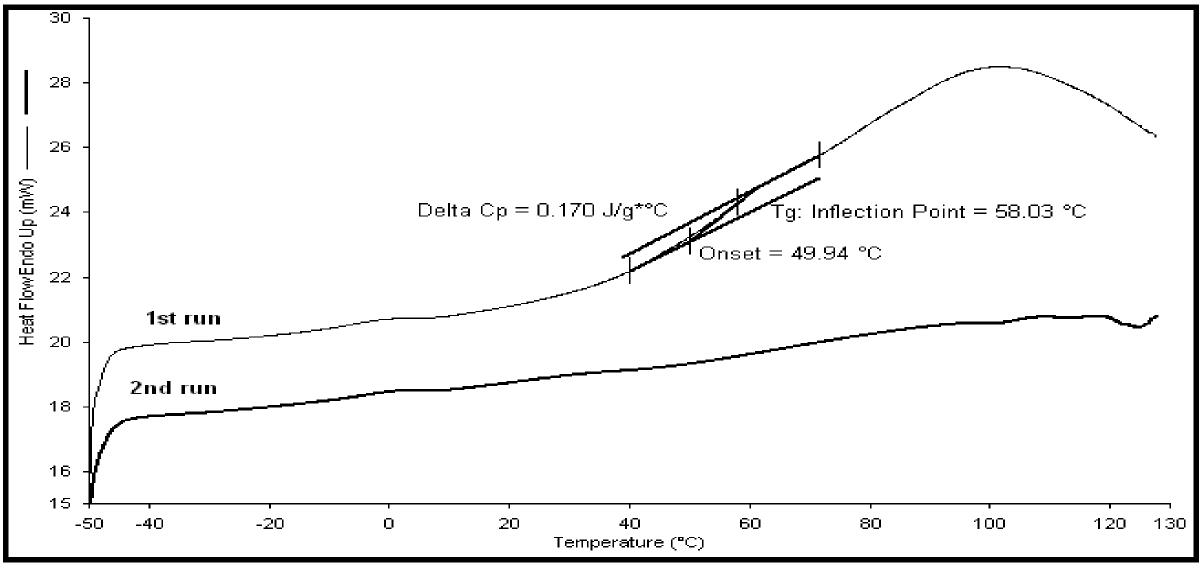
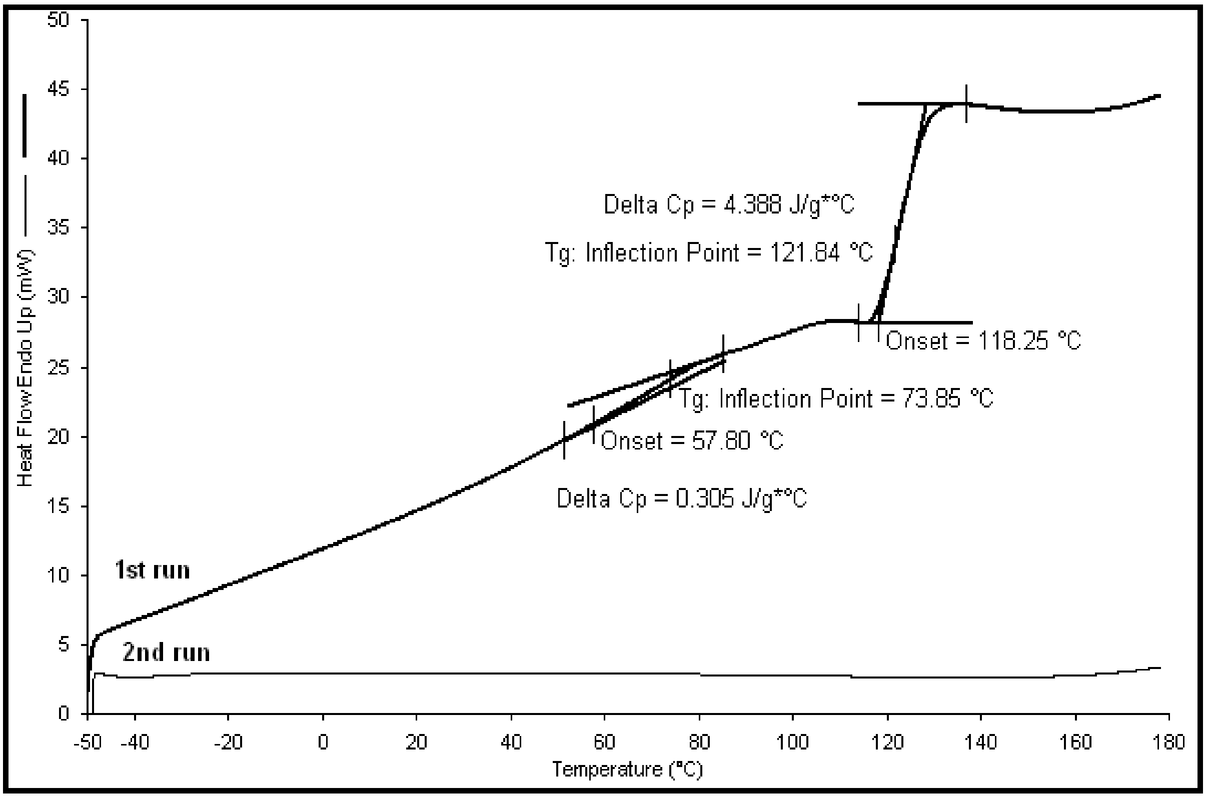


Figure 3.2 DSC thermogram of KL

After the grafting reaction had been achieved, it was observed that the resulting LGC also occurred in an amorphous phase, verifying that the grafting reaction had not strongly adapted the complexity of KL starting material. LGC has two T_g values at 73.85°C and 121.84°C respectively, as shown in the DSC thermogram in Figure 3.3. This illustrates the incompatibility in the LGC structure. The possible explanation of occurrence of these two T_g values is based on the free volume concept, which attributed a low T_g value to the large free volume in the graft copolymer chain while the highest T_g value refers to the chain with less free volume [27].

As free volume increases, the T_g temperature tends to decrease [28]. The above-mentioned explanation investigated the correlation between free volume property and LGC chemical structure that was suggested in Figure 3.1. Therefore, the lower T_g value corresponds to AA homopolymer branched chain which is a hydrocarbon chain without bulky groups that gives PAA molecules enough space to move. This means, the mobility of PAA molecules tends to be more flexible, which may increase the free volume and decrease the T_g. On the contrary, the phenyl groups in KL may increase the bulkiness in KL main chain and decrease its molecules mobility as well as its chain flexibility; thus, the free volume decreases and high T_g value obtained. Furthermore, the grafting reaction has enhanced the thermal properties of KL, whereas the two T_g temperatures of LGC are both more than the T_g temperature of KL.



DSC thermogram of LGC

3.4 FTIR spectroscopy

Figure 3.4 illustrates the FTIR spectra of KL and LGC. The KL spectrum shows absorption at 3415.52 cm^{-1} assigned to (OH) broaden band of either hydrogen bonded or hydroxyl group in the phenolic and aliphatic compounds. The absorption peak at 2935.29 cm^{-1} was due to (C-H) stretch band of methyl group [29]. The vibration at 1712.69 cm^{-1} exhibited (C=O) stretch band of carbonyl group [30]. The stretching of (C=C) and (C-C) bands in the aromatic range were recorded at 1616.20 cm^{-1} and 1462.98 cm^{-1} respectively [31]. The peak at 1143.11 cm^{-1} could be attributed to (C-O) bond in ethers.

In the LGC spectrum, the presence of peak at 3419.04 cm^{-1} was assigned to (OH) stretch bonds of hydroxyl group [32]. The frequency at 2920.86 cm^{-1} was due to the stretching of (C-H) band of methyl group in lignin [33]. Peaks at 2489.21 cm^{-1} and 1919.17 cm^{-1} were considered aromatic overtones. The absorption at 1723.07 cm^{-1} was due to (C=O) the stretch band in α and β-unsaturated esters which verified the placement of ester bonds between aromatic rings in the KL structure and unsaturated polymeric chain of PAA and supported the expected grafting reaction mechanism in Figure 3.1. The characteristic ester group in the spectrum substantiated that the LGC was formed by ester bonding between the KL and PAA. 1601.55 cm^{-1} and 1497.10 cm^{-1} wave numbers were distinguished as (C-C) stretching bonds in aromatic rings in lignin components [34]. Further evidence to the occurrence of the ester groups among LGC structure was provided by the absorption at 1189.59 cm^{-1} which was assigned as an expanding (C-O) bond in the ester groups.

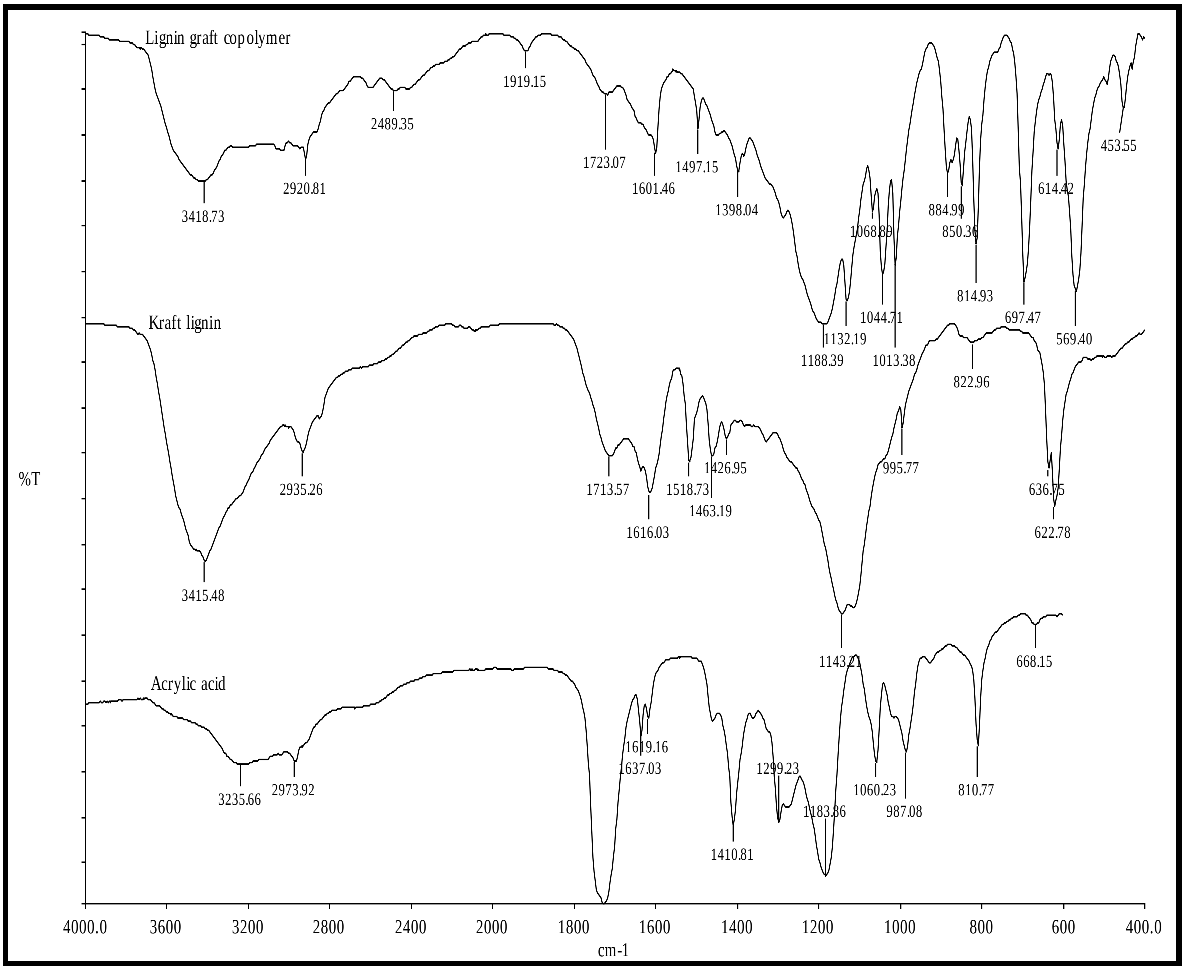


Figure 3.4 FTIR spectra of LGC, KL, and AA

3.5 Effect of LGC on drilling mud properties

The study was conducted to explore the use of this water-soluble LGC as a potential drilling mud multi-functional additive.

3.5.1 LGC Rheological effect

The mud rheological tests were performed according to the American Petroleum Institute (API) standard specifications by means of a direct-indicating viscometer with other equipment which specifically designed to simulate the hydrocarbon drilling well conditions.

Table 3.1 shows the rheological experimental data of water-based mud and different concentrations of LGC-based mud under different aging temperatures. In this regard, the rheological properties of water-based drilling mud without any additives (i.e. as the basic mud sample) was tested before and after the aging process at two temperatures; ambient temperature of 25°C (room temperature) and high temperature of 90°C. These two values of temperature were chosen in order to investigate the effect of temperature on the rheological behavior of the drilling mud. Regarding to that, the rheological parameters such as apparent viscosity, plastic viscosity, and gel strength of water-based mud were increased as the aging temperature elevated to 90°C. These phenomena could be related to the decrease of the mud pH value, which simultaneously decreased with the increase in the aging temperature. The pH of the mud was slightly decreased after experiencing high temperature rolling process. In conformity with the elevated temperature, the decrease of the pH value facilitates the occurrence of the interlayer dehydration reaction [35]. In addition, the dehydration at high temperature may release a small amount of water present between the layers. Thus, the loss of water causes the aggregation of the mud interlayers or plates. As a consequence, this aggregation generated the increase of drilling mud viscosity and gel strength due to the corresponding increase of the aging temperature.

Nevertheless, lignin graft copolymer was introduced into the basic water-based mud samples at different concentrations (i.e. 0.3, 0.5, and 0.7% w/w) in order to optimize its ability to enhance the rheological properties of the drilling mud. Apart from that, the batches of the drilling mud with different LGC concentrations were subjected to the aging process to explore its thermal stability at low and high temperatures. However, an acceptable thermal stability of the drilling mud additives significantly enhanced the drilling mud transporting properties, e.g. viscosity and gel strength [36]. Within this context, the rheological data reveals that the drilling mud mixed with 0.5% w/w is much thermally stable at high temperature than 0.3%, and 0.7 % w/w LGC-drilling mud. Apart from that, it is also illustrated the optimum concentration of LGC is 0.5% which gives moderate viscosity, gel strength, and yield point compared to others at both temperatures.

Types of Mud	T (^oC)	μ_a (cp)	μ_p (cp)	τ_y (lb/100ft^2)	θ (lb/100ft^2)	pH
Water-based mud	27	28.00	12.00	34.15	48.04	11.91
0.3% w/w LGC + based mud	27	32.50	11.00	45.89	156.67	10.49
0.5% w/w LGC + based mud	27	40.00	14.00	55.50	152.49	9.63
0.7% w/w LGC + based mud	27	45.00	15.00	64.04	139.96	7.45
Water-based mud	90	30.50	15.00	33.08	64.75	11.82
0.3% w/w LGC + based mud	90	41.50	11.00	65.11	189.45	10.15
0.5% w/w LGC + based mud	90	40.50	11.00	62.96	158.76	9.20
0.7% w/w LGC + based mud	90	43.00	11.00	68.31	125.34	7.22

Table 3.1 Rheological experimental data of water-based mud and different concentrations of LGC-based mud with different aging temperatures

It was observed that LGC with low concentrations developed the viscosity and gel strength required for water-based mud. This revealed the viscosity-building and gelling abilities of LGC despite experiencing the temperature changes and the dynamic agitation. Moreover, this phenomenon may attribute to two causes. First, the carboxylate group in the LGC structure {Figure 3.1(a)} provides a negative charge that may absorb effectively onto the positive mud (bentonite) edges via electrostatic attraction force that may develop the rheological properties of the drilling mud. Second, the methoxy group in the LGC structure {Figure 3.1(a)} could be a good proton acceptor during the formation of the hydrogen bond [37]. Within same direction, the hydroxyl group in the LGC structure (LGC FTIR spectrum) eases the progress of the intermolecular hydrogen bonding formation [38]. Consequently, the formation of the hydrogen bond increases the inter-particle attraction forces between the LGC particles and the mud edges which lead to the flocculation in the mud system. Due to the aforementioned results and discussions, LGC has revealed its capability to be a potential rheological controlling agent in terms of viscosifying and gelling the water-based drilling mud.

3.5.2 Effect of LGC concentration on the drilling mud pH

Besides the study of the rheological behavior of the water-based mud with and without LGC addition, the effect of the LGC concentration on the pH of drilling mud samples was also investigated at room temperature and high temperature. In general, it is well known that the pH of the water-based mud is an alkaline pH medium [39]. In agreement with that, the pH of the water-based drilling mud was strong alkali pH value and then it was deviated slightly after the heating and the agitation at 90^oC. On the other hand, the LGC addition has an acidic affect on the water-based mud. As the LGC concentration increases in the drilling mud samples, the pH value decreases. This acidification affect of the LGC could be results from two causes. First, the acidification effect might be due to the use of sulphuric acid during the separation process of the Kraft lignin from the other wood components [40]. The sulphuric acid might have affected the structure of Kraft lignin used in the LGC preparation reaction. The other cause might possibly be corresponding to the branched acrylic monomer in the LGC structure {Figure 3.1(a)}. That might give the acidic character to LGC when it was used as a drilling mud additive. However, the acidic character of the LGC offered advantageously another application to the LGC as a water-based drilling mud additive, i.e. pH controlling agent. Since it is efficiently reduced the pH of the drilling mud without further additives that were normally used in the drilling field. Those additives were employed to control the pH of the drilling mud in order to avoid the corrosivity of the drilling tools. Generally, the corrosion rates are lower at the mildly alkaline pH and higher in the mildly acidic pH range [41]. Within this context, the desired pH value for the drilling operation indicated to be within the range 10 to 8. Regarding to this study, among all LGC concentrations which have been evaluated, only 0.5% w/w of LGC maintained the pH of the water-based mud within the desired pH range.

3.5.3 Effect of high temperature on drilling mud additives

In recent years, there have been a number of challenges for drilling muds to keep pace with the advancing operational drilling mud technologies [42]. Among these challenges is the thermal stability of the drilling mud and the drilling mud additives. In general, the thermal stability of the drilling mud is described as its ability to withstand progressively increasing temperature while flowing downhole and decreasing temperature on flowing back to the surface [41]. The indicator to determine the drilling mud thermal stability is the mud's rheological properties. In relation to this study, the thermal stability of LGC and commercial additives, e.g. CMC, GG, and XG were investigated using the aging process at 200°C for 16 hr. Apart from that, 0.5% w/w of each of them was chosen to be treated with the drilling mud batches. This percentage was chosen since the LGC acted optimally as a drilling mud multi-functional additive at this level.

Table 3.2 Rheological experimental data of water-based mud with 0.5% w/w of LGC, CMC, GG, and XG before and after the aging process at 200°C for 16 hr

Types of mud	μ_a (cp)		μ_p (cp)		τ_y (lb/100ft^2)	
	Before	After	Before	After	Before	After
0.5% w/w LGC + based mud	38.00	58.50	13.00	37.00	53.37	45.74
0.5% w/w CMC+ based mud	97.50	25.00	19.00	18.00	129.10	14,93
0.5% w/w GG + based mud	105.00	23.50	35.00	18.00	149.36	11.74
0.5% w/w XG + based mud	82.50	21.00	64.00	16.00	58.70	10.67

3.5.3.1 Lignin Graft Copolymer (LGC)

The rheological parameters of LGC were listed in Tables 3.2 and 3.3; these parameters were measured before and after the aging process at 200°C for 16 hr. It was found that the LGC rheological parameters slightly changed after the LGC-drilling mud was exposed to high temperature of 200°C. Accordingly, this change did not affect the miscibility and the consistency of the mud, i.e. inertness was not observed on the drilling mud after the aging process. Interestingly, in spite of the high temperature aging process, the LGC maintained the pH of the drilling mud within the desired drilling pH range. The pH value was slightly deviated after the aging at high temperature. This also reveals the thermal stability of the LGC up to 200 °C. The thermal stability may ascribe to the chemical structure of LGC which comprised different functional groups. These functional groups such as hydroxyl, carboxylate, and methoxy groups may activate the interconnection between the LGC and the mud plates. For that reason, the rheological properties of the drilling mud were developed as explained in the previous section.

3.5.3.2 Carboxy Methyl Cellulose (CMC)

The rheological performance of CMC was investigated under simulated hydrocarbon drilling well conditions, at 200°C with the aging process of 16 hr. The CMC rheological parameters and the pH values were tabulated in Tables 3.2 and 3.3. It was observed that the CMC rheological parameters were drastically decreased after the aging process. Besides and regarding the CMC pH study, the pH value tends to moderate alkali medium after the highly temperature aging process. It was deduced that the CMC illustrated weaker viscosifying and gelling abilities at high temperature 200°C. This could be due to the thermal degradation of the CMC at higher temperature. The poor rheological properties of the CMC at high temperatures are in good agreement with the previous study [43].

3.5.3.3 Guar Gum (GG)

The rheological properties of GG were examined and its rheological parameters were tabulated in Tables 3.2 and 3.3. As shown in these tables, the rheological parameters decreased extensively after the high temperature aging process at 200°C for 16 hr. Accordingly, the pH value deviated from strong alkali medium to weak alkali medium after the exposure to high temperature. The above mentioned results illustrated the insufficiency of the GG as a drilling mud viscosifying and gelling agent at high temperature of 200°C. Besides that, the high temperature drilling simulation was negatively reduced the ability of the GG to control the drilling mud rheological properties. This was resulted from the pronounced effect of the temperature on the degradability of GG. From previous report and this study, high temperature obviously accelerates the GG degradation process [44].

Table 3.3 Gel strength (θ) and pH values of water-based mud with 0.5% w/w of LGC, CMC, GG, and XG before and after the aging process at 200°C for 16 hr

Types of mud	θ (lb/100ft^2)		pH	
	Before	After	Before	After
0.5% w/w LGC + based mud	152.49	154.58	9.65	9.25
0.5% w/w CMC+ based mud	200.54	29.24	11.62	9.30
0.5% w/w GG + based mud	582.83	14.62	11.53	8.73
0.5% w/w XG + based mud	139.96	8.35	11.62	8.64

3.5.3.4 Xanthane Gum (XG)

Likewise other commercial drilling mud additives, the XG rheological parameters severely decreased after the high temperature hydrocarbon drilling simulation at 200°C for 16 hr as observed in Tables 3.2 and 3.3. Furthermore, the pH value was also decreased after the aging process. As a consequence, these results indicated the deficiency of the XG to develop the drilling mud rheological properties at high temperatures. This could be due to the effect of the high temperature on the XG chemical structure. In this regard, the high temperature caused the thermal degradation of XG and therefore influenced its rheological properties [45].

IV. CONCLUSIONS

In this study, the Kraft lignin (KL) was extracted from the Kraft black liquor which is an effluent from the Kraft pulping process of the oil palm empty fruit bunch (OPEFB) fiber. As indicated in the FTIR spectrum, the extracted product has wide diversity of functional groups which chemically considered as active centers. Such functional groups could open newer possibilities to expand the chemically modification process of lignin. Within this sight, this process will enhance the applicability of lignin in many industrial aspects. In this direction, the water soluble LGC was successfully prepared by the means of bulk copolymerization reaction using p-toluenesulfonic acid (PTS) as a catalyst. Apart from that, the reaction mechanism involves an esterification process that facilitates the grafting reaction.

In the application part and unlike other drilling mud additives, the LGC demonstrated an excellence thermal stability regardless the high temperature hydrocarbon drilling well simulation. This becomes an advantage when it is combined with its abilities as a drilling mud viscosifying and gelling agent. Thus, LGC has a remarkable potential to be used as a drilling mud additive.

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