

## Preparation of Lignin Graft Copolymer as a Fluid Loss Additive for Water-based Mud

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**Abstract:** *During offshore oil and gas exploration, drilling at high temperature and pressure in a geological formation is usually the cause of damage to water-based mud. In this paper, a water-soluble lignin graft copolymer (LGC) was grafted via condensation polymerisation using soda lignin recovered from oil palm empty fruit bunch (OPEFB) fibre and itaconic acid. This LGC was applied in a water-based drilling mud formulation as a fluid loss control additive. Lignin graft copolymer was characterised using Fourier Transform Infrared (FTIR) spectroscopy and Differential Scanning Calorimetry (DSC) techniques. In tests of mud properties, the filtration performances of LGC and a commercial fluid loss additive (Ressinex II) were compared. Using an additive dosage determination test, we found the optimum dosage of LGC and Ressinex II to be 0.7%. The fluid loss properties measured after thermal aging showed that LGC can be used as a fluid loss additive for drilling operations at temperatures up to 190°C. The rheological performances of LGC and commercial fluid filtration additives were also compared. Compared to the commercial additives, LGC provides more tolerance to salt contamination at room temperature and at high temperatures.*

**Keywords:** Oil palm empty fruit bunches, graft copolymer, soda lignin, itaconic acid, condensation polymerisation, fluid loss reducer

### 1. INTRODUCTION

Today, water-based drilling fluid is widely used in most drilling operations. Technologies have been developed to increase the performance of water-based drilling mud, especially in offshore exploration. These technologies have been developed because of stringent environment regulations implemented in the 1980s to regulate the use of oil-based drilling fluids with high thermal stability in hostile drilling operations. Long periods of drilling at high temperature (more than 150°C) and pressure are common circumstances encountered by drilling engineers. Such conditions are highly detrimental to the flow properties and filtration loss control of water-based drilling fluid, due to the hydrolysis, depolymerisation or degradation of the additives and the flocculation or irreversible transformation of the clay.

Briefly, filtration loss happens in the well under both dynamic and static conditions. Filtration loss occurs when the liquid phase of the drilling fluid flows into the permeable formation because the borehole pressure is higher than the formation pressure, which can cause drilling problems such as water leaks, excessive torque and drag, differential pressure sticking, borehole instability and formation damage. This phenomenon causes difficulties and incurs extra costs for the drilling operation. To solve this problem, fluid loss control additives are usually added to the drilling fluid during the drilling process.

Currently, various types of fluid loss additives are available in the market. Such additives can be natural products, modified natural products or fully synthetic chemicals. Suitable filtration control agents are added in the drilling process to reduce the filtrate volume and filter cake thickness of the drilling mud. The selection of the additive is generally based on the technical and environmental factors of the well bores.<sup>1</sup> Unfortunately, most of these types of additives are not resistant to high temperature and pressure conditions.

In contrast, approximately 90 million tonnes of renewable biomass (trunks, frond, shells, palm press fibres and empty fruit bunches) are produced in the oil palm industry every year. However, this biomass is considered waste and is not fully utilised.<sup>2</sup> Oil palm empty fruit bunch (OPEFB) fibre is a form of renewable biomass that is non-toxic, abundant and cheap, and it has high lignocellulosic content. Therefore, the lignin recovered from OPEFB has high potential as a raw material for value-added products.<sup>3</sup>

Lignin recovered from OPEFB is also a natural polymer with high thermal stability and chemical resistance due to its chemical structure. Considering all of the information from previous studies of lignin modification,<sup>4-6</sup> we propose an alternative method for preparing a new polymeric product using soda lignin recovered from OPEFB fibres.

The objective of this investigation is to develop a better water-based fluid loss drilling additive that is greener and more stable under high temperature and pressure conditions. Lignin graft copolymer (LGC) was prepared by grafting itaconic acid onto soda lignin recovered from OPEFB via condensation polymerisation. Lignin graft copolymer was characterised using instrumental analyses such as Infra-Red spectroscopy (IR) and Differential Scanning Calorimetry (DSC). The rheological properties and fluid loss of LGC were analysed using standard procedures of the American Petroleum Institute (API).

## **2. EXPERIMENTAL**

### **2.1 Isolation and Purification of Soda Lignin**

A lab-scale 20 L stainless steel rotary digester was used to cook OPEFB long fibres. The pulping process was performed using methods modified from Sun.<sup>9</sup> The OPEFB long fibre was mixed in a ratio of 1:10 (W/V) with cooking liquor and soaked in water for 2 days to remove non-fibrous materials. Then, the fibre was air dried. Cooking liquor was prepared by dissolving sodium hydroxide into the appropriate amount of distilled water.

Black liquor obtained from the pulping process was then filtered. Soda liquor was recovered via acidification of black liquor using 20% V/V sulphuric acid until the black liquor solution reached pH 2. The precipitate was filtered and washed using pH 2 distilled water. The soda lignin was collected and dried in a vacuum oven at 60°C for 24 h before further analysis.

### **2.2 Graft Copolymerisation**

A condensation copolymerisation method was used in this study. Reactions were performed in three-neck round bottom flasks equipped with reflux condensers and nitrogen inlets, with magnetic stirring.<sup>7,8</sup> The appropriate amounts of soda lignin and itaconic acid were weighed out and dissolved in 1,4-dioxane in ratios of 1:8 (W/V) and 1:5 (W/V). P-toluene sulfonic acid (PTS) was added to the solution to a concentration of 10% by mass. This mixture was added into the apparatus and flushed with nitrogen gas for 5 min. The reaction was conducted in an oil bath at 80°C for 18 h with vigorous stirring. When the reaction was complete, the apparatus was immersed in an iced water bath at 0°C for half an hour with constant stirring. Then, unreacted lignin was precipitated by decanting the mixture into a vigorously stirred pure water solution. The precipitate was filtered, and the filtrate was collected. The filtrate was continuously vaporised to remove the solvent, and the sample was vacuum dried at 60°C until a constant weight was obtained. The lignin graft copolymer was collected in the form of dark brown fine particles.

### **2.3 Fourier Transform Infrared (FTIR) Analysis**

A Perkin Elmer 2000 FTIR spectrometer was used to investigate the infrared bands and absorbance. All of the samples were analysed using the KBr pellet technique and scanned in the range of 4000 to 400  $\text{cm}^{-1}$  at a resolution of 4%.<sup>7-10</sup>

## 2.4 Differential Scanning Calorimetry (DSC) Analysis

The glass transition temperatures ( $T_g$ ) of the soda lignin and lignin graft copolymer were compared and evaluated using the Perkin Elmer Pyres 1 DSC. Approximately 10 mg of each sample was heated from  $-50^\circ\text{C}$  to  $180^\circ\text{C}$  at a rate of  $20^\circ\text{C}$  per min in a nitrogen atmosphere at a flow rate of 30 mL per min.<sup>8</sup>

## 2.5 Mud Property Test

In this study, three set of experiments were designed and evaluated mud according to the API specifications.<sup>11,12</sup> Each batch of water-based drilling mud was prepared by stirring 80.0 g of bentonite and 4.0 g of sodium carbonate in 1000 mL of distilled water before aging it for 24 h.<sup>12</sup>

Filtrate loss volume is the amount of fluid that can be delivered through a permeable filter medium after it has been subjected to a differential pressure for a specified period of time. The filtrate loss volume ( $V_{30}$ ) was determined using a Fann Filter Press model series 300 (LTLP). The rheological parameters of the mud were analysed using a Fann model 286 viscometer, with measurements of mud viscosity occurring at two rotating rates of 300 rpm ( $\theta_{300}$ ) and 600 rpm ( $\theta_{600}$ ). Apparent viscosity ( $\mu_a$ ), plastic viscosity ( $\mu_p$ ) and yield point ( $\Gamma_y$ ) were calculated using the following equations:

$$\mu_a = \theta_{600}/2 \quad (1)$$

$$\mu_p = \theta_{600} - \theta_{300} \quad (2)$$

$$\Gamma_y = 0.511\theta_{300} - \mu_p \quad (3)$$

$\theta_{300}$  and  $\theta_{600}$  are the viscometer shear stress readings at 300 and 600 rpm, respectively.<sup>13</sup> The effects of aging temperature on water-based mud rheological and filtration loss properties were determined using a Fann model roller oven series 2500 and a 500 mL Fann stainless steel aging cell.

Three different types of experiments were performed and are referred to herein as Experiment I, II and III. A commercial filtration loss additive, Ressinex II, was used for comparison with LGC. In Experiment I, the effects of different doses of lignin graft copolymer in water-based mud were analysed at room temperature and under strong agitation ( $90^\circ\text{C}$ ). Doses of 0.3%, 0.5% and 0.7% W/W mud were used.

The effects of aging temperature on water-based mud containing additive were analysed in Experiment II. The mud samples were heated in the Fann model roller oven series 2500 at 190°C for 16 h. These experimental conditions are representative of an actual high-temperature drilling process.

Experiment III was performed to evaluate the effect of salinity on the performance of lignin graft copolymer. Information about these effects is important, because salt (NaCl) contamination occurs often in well bores and is common in mud. The salt concentrations tested ranged from 0.7% and 1.2% W/W mud.

### 3. RESULTS AND DISCUSSION

#### 3.1 FTIR Spectra

Figure 1 shows the spectra of soda lignin, itaconic acid and lignin graft copolymer. In the infrared spectra of soda lignin, a broad band with wavelength 3410  $\text{cm}^{-1}$  indicates the hydroxyl group. Bands of 2936  $\text{cm}^{-1}$  and 2842  $\text{cm}^{-1}$  represent the stretching of C-H bonds in the methyl and methylene groups. A small broad band at 1710  $\text{cm}^{-1}$  is due to conjugated carbonyl stretching. The presence of aromatic rings is indicated by medium bands at 1606  $\text{cm}^{-1}$  and 1511  $\text{cm}^{-1}$  that represent aromatic skeletal vibration. The band at 1462  $\text{cm}^{-1}$  is caused by C-H deformations.

The broad band at 3112  $\text{cm}^{-1}$  in the itaconic acid spectrum represents a hydroxyl group in an acid, and the small broad peak at 1710  $\text{cm}^{-1}$  indicates a carbonyl group in a carboxylic acid. A stretch peak also occurs at a wavelength of 1307  $\text{cm}^{-1}$ . These peaks indicate the carboxylic functional group of itaconic acid. A band at 1433  $\text{cm}^{-1}$  is characteristic of  $\text{CH}_2$  bending. Bands at 626  $\text{cm}^{-1}$ , 917  $\text{cm}^{-1}$  and 988  $\text{cm}^{-1}$  correspond to an out-of-plane C=C functional group.

In the spectrum of LGC, a broad band at 3116  $\text{cm}^{-1}$  may be attributed to the hydroxyl group of itaconic acid. Peaks at 2622  $\text{cm}^{-1}$  and 1972  $\text{cm}^{-1}$  are considered to be aromatic overtones. A significant sharp band at 1701  $\text{cm}^{-1}$  is attributed to the stretching of an ester functional group, which indicates that itaconic acid was grafted onto soda lignin, as illustrated in the figure. A stretch and sharp peak at 1309  $\text{cm}^{-1}$  is characteristic of the  $\text{CH}_3$  functional group of itaconic acid. The sharp peak at 1216  $\text{cm}^{-1}$  indicates the C-O stretching vibration in the ester group of LGC. The relative intensity of the absorption of bands 912  $\text{cm}^{-1}$  (assigned to an out-of-plane C=C bond) and 626  $\text{cm}^{-1}$  (assigned to an out-of-plane C=C bond) increased significantly after the grafting reaction.

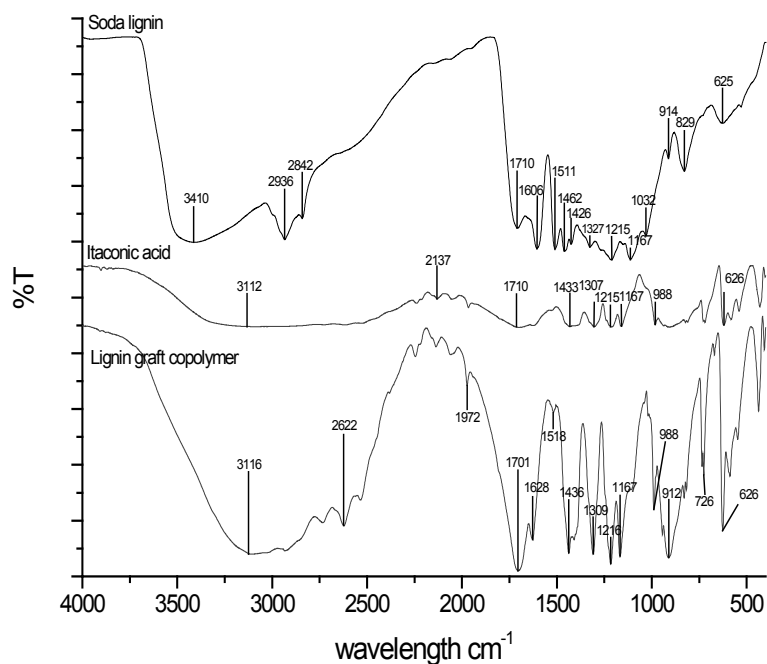


Figure 1: Infrared spectra of soda lignin, itaconic acid and LGC.

### 3.2 DSC Thermogram

The thermal behaviours of soda lignin and lignin graft copolymer were studied using the DSC technique. This analysis provides information on the enthalpy of transition, phase transition temperatures, degradation temperature and heat capacity. According to previous studies, the glass transition temperature of lignin is influenced by multiple factors, such as the presence of low molecular weight contaminants (water or solvents), the molecular weight of the polymer, thermal history, cross linking and applied pressure. Figure 2 shows the DSC thermogram of soda lignin. The glass transition temperature of soda lignin was recorded in the range of 85°C to 140°C. The glass transition temperature of soda lignin was 71.13°C. The recorded heat capacity was  $2.216 \text{ Jg}^{-1} \text{ C}^{-1}$ , which implies that soda lignin molecular motion is not restricted compared to the  $\Delta C_p$  value of other amorphous polymers. Phenylpropane units in the molecular chain characterised the molecular motion of soda lignin. The DSC thermogram indicates that soda lignin exhibited enthalpy relaxation upon glassification.

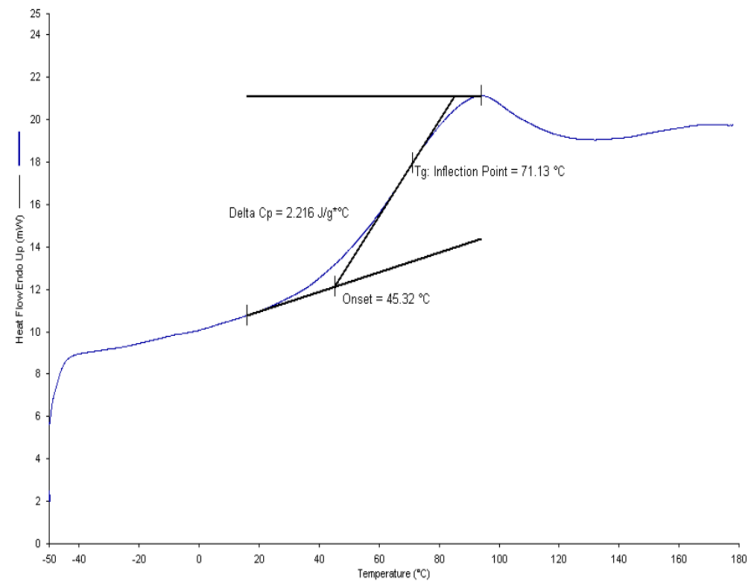


Figure 2: Thermogram of soda lignin.

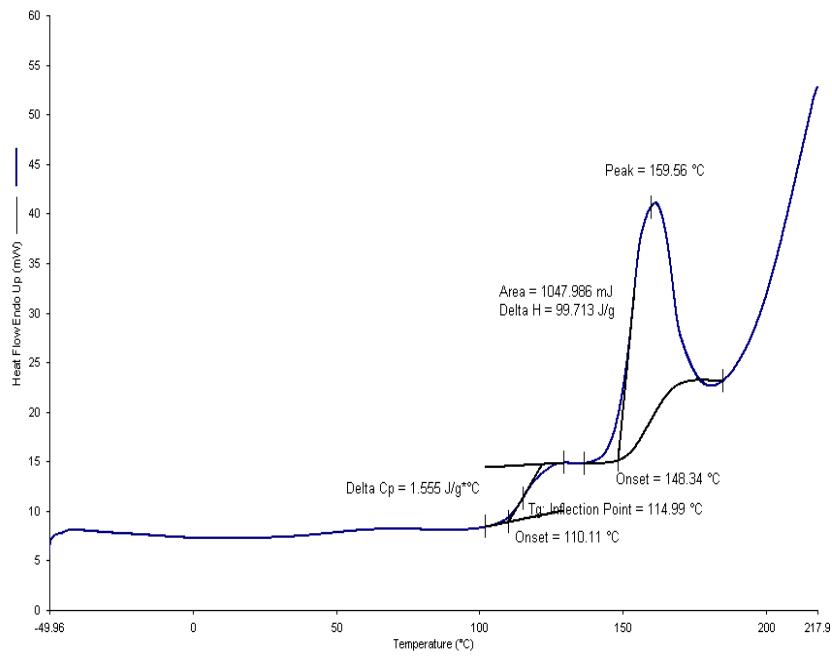


Figure 3: Thermogram of LGC.

The thermogram of LGC is shown in Figure 3. A melting point was detected at 159.66°C, as shown by the broad endothermic peak. This finding may correspond to the breaking bonds of homopolymers. A glass transition point was recorded at 114.99°C, which may imply that the polyphenol unit in soda lignin became detached from the copolymer chain.

### 3.3 Mud Properties

The results of Experiment I are shown in Table 1. The results indicate that the optimum dosage of LGC is 0.7%. The dose gave the lowest fluid loss volume (FL) of the three dosages at both 27°C and 90°C. At dosage 0.7%, LGC generated better rheological properties compared to other dosages at both temperatures. These temperature values were used to confirm the consistent rheological and fluid loss performance of LGC at room temperature and under high agitation.

Experiment II was designed as a simulation of a deep-well process at 190°C. The filtrate volume and rheological data before and after the hot-rolling process were recorded, and the results are presented in Table 2. The apparent viscosity, plastic viscosity and yield point of LGC increased swiftly after the thermal rolling process. The fluid loss volume (FL) of LGC after the thermal rolling process had its lowest value compared to the other two formulations. This finding suggests that LGC has better rheological and API filtrate properties compared to other mud formulations at high temperature (190°C) after undergoing a hot-rolling process for 16 h. This outcome may be due to the high molecular weight and low decomposition rate of LGC at high temperature, which indicates that LGC is resistant to a high temperature (190°C) that is representative of drilling at approximately 10,000 m.

Table 1: Base mud rheological properties at different concentrations of LGC.

Mud formulation	T (°C)	$\mu_a$ (mPa S)	$\mu_p$ (mPa S)	$\Gamma_y$ (Pa)	FL (mL)
0.3% w/w LGC + base mud	27	25.00	16.00	9.198	14.00
0.5% w/w LGC + base mud	27	25.00	16.00	9.198	13.60
0.7% w/w LGC + base mud	27	26.50	13.00	13.79	11.00
0.3% w/w LGC + base mud	90	20.00	9.00	11.24	14.40
0.5% w/w LGC + base mud	90	20.50	8.00	12.77	13.60
0.7% w/w LGC + base mud	90	22.00	6.00	16.35	13.00



Table 2: Base mud rheological properties before and after the thermal aging test (before and after rolling at 190°C for 16 h).

Mud formulation	$\mu_a$ (mPa s)		$\mu_p$ (mPa s)		$\tau_y$ (Pa)		FL (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud	24.50	45.00	14.00	34.00	10.73	11.24	14.00	27.00
Base mud + 0.7% Ressinex II	21.00	42.00	14.00	26.00	7.154	16.35	13.00	18.20
Base mud + 0.7% LGC	26.50	36.50	13.00	27.00	13.79	9.709	11.00	17.80

Table 3: Base mud rheological properties at different salinity concentrations (before and after hot rolling at 190°C).

Mud Formulation	$\mu_a$ (mPa s)		$\mu_p$ (mPa s)		$\tau_y$ (Pa)		FL (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud + 0.7% NaCl	29.50	39.00	15.00	3.00	25.04	36.79	15.00	29.00
Base mud + 0.7% Ressinex II + 0.7% NaCl	18.50	47.50	12.00	10.00	6.643	38.32	14.00	26.00
Base mud + 0.7% LGC + 0.7% NaCl	28.00	19.00	9.00	13.00	19.41	6.132	12.80	20.00
Base mud + 1.2% NaCl	35.00	44.00	14.00	11.00	25.25	33.72	18.00	36.00
Base mud + 0.7% Ressinex II + 1.2% NaCl	17.00	66.00	7.00	24.00	10.22	42.92	16.00	35.00
Base mud + 0.7% LGC + 1.2% NaCl	24.00	19.50	9.00	9.00	15.33	10.73	13.50	24.00

The data from Experiment III are presented in Table 3. The mud formulations of LGC had their lowest fluid loss volumes (FL) after the thermal aging tests at 0.7% and 1.2% salinity. The apparent viscosity, plastic viscosity and yield point decreased slightly but showed no significant changes. This outcome may have occurred because of thermal degradation, which reduces the negative charge density of LGC and causes the macromolecular chain to contract at high salinity. In general, however, the LGC mud formulation had better rheological and fluid loss properties, and it was tolerant to salinity exposure at high temperatures.

#### 4. CONCLUSION

In conclusion, LGC has been successfully prepared through condensation polymerisation, and the preparation was characterised using FTIR and DSC instrumental techniques. The comparisons of Ressinex II (a commercial fluid loss reducer) and LGC suggest that LGC has better rheological and fluid loss properties at high temperature and salinity conditions.

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