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## Lignin Graft Copolymer as Mud Thinner for Deep Well Drilling Operation

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**Abstract:** Lignin extracted from black liquor of oil palm Empty Fruit Bunch (EFB) was refluxed with acrylic acid at 30°C in the presence of nitrogen atmosphere to form lignin acrylic acid (lignin AA). Methanol was used as a reaction medium in this experiment. At the end of the copolymerization process, a small amount of hydroquinone 1% was added to inhibit polymerization process. The formation of graft copolymer was proven by the attachment of acrylic acid side chain to the lignin, which was demonstrated by Differential Scanning Calorimetry (DSC) and infrared (IR) spectroscopy analyses. Rheological performances of lignin AA as a drilling mud thinner were compared with a commercial thinner (lignosulfonate). Results found that the newly formulated thinner (lignin AA) shows better thinning performance at high temperature (190°C) with the optimum dosage of 0.3% of total mud volume for water based mud system compared to lignosulfonate. Furthermore, the lignin AA also shows better performance as a fluid loss reducer agent against a commercial fluid loss reducer agent, Ressimex II towards salt contamination.

**Key words:** Empty fruit bunches, lignin, drilling mud thinner, rheological performance

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### INTRODUCTION

The increasing amount of waste from oil palm industry is another environmental concern in Malaysia that necessitates the need for better waste management. There are 2.5 million hectares of oil palm estates and over 300 palm oil processing plants all over the country (<http://www.sabutek.com.my>). The demand for oil palm is back on the rise regardless of the competition from other vegetable oils. This could be due to the low cholesterol content in the palm oil as well as its richness in vitamin E. Nevertheless, palm oil processing plants are facing with challenges to eliminate the Empty Fruit Bunch (EFB) from their compounds.

Fibrous derivatives from EFB, however, represent a renewable source of non-wood lignocellulosic materials which has created considerable research interest, especially in the pulping and composite industry (Khoo and Lee, 1991; Lubis *et al.*, 1994; Wan Daud *et al.*, 1998). The process of producing cellulosic pulp from oil palm trunk fiber and other non-wood fibers requires delignification with sodium hydroxide under pressure (Sun and Tomkinson, 2001). This liberates the cellulosic fiber and produces a large quantity of black liquor which is discharged into waters without effective treatments (Alonso *et al.*, 1993).

Soda lignin extracted from the oil palm lignocellulosic waste especially the EFB has been successfully transformed into drilling mud thinners i.e., FTLs and FTL which had been discussed elsewhere (Mohamad Ibrahim *et al.*, 2003a). The rheological performance of these thinners especially the FTL is comparable with commercial thinner available in the market. Besides acting as thinner in drilling operation, FTL can be a good fluid reducer agent as well for water-based mud system.

Formulation of drilling mud is one of the most important aspects in drilling engineering. This is because as drilling progresses, the mud would become more viscous that subsequently reduces the optimum speed of the drill bits. Therefore, the right formulation of drilling mud is needed to ease drilling operation. This is achieved by using additives that act as an agent to disperse colloidal suspensions responsible for mud viscosity. The problem with the current drilling mud system is that some of the additives are toxic, such as FeCr-lignosulfonate. The scenario is more worrying if there is any leakage during drilling operation that may cause the toxic drilling mud to migrate and contaminate drinking water zone.

The present study is to address the problem of thermal decomposition of lignin based mud additives above 121°C (Meister *et al.*, 1985). In order to increase its

thermal stability, the lignin has been copolymerized with acrylic acid to produce lignin acrylic acid or better known as lignin AA.

## MATERIALS AND METHODS

The raw material used in this study was oil palm empty bunch (EFB) long fiber supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia, a local company specializing in recycling oil palm lignocellulosic wastes. This study was conducted from July 2004 until January 2005 at School of Chemical Sciences, Universiti Sains Malaysia.

The EFB fiber was pulped in a 20 L stainless steel rotary digester unit together with 25% NaOH (cooking liquor) for three hours at a maximum cooking temperature of 170°C. The mixture of cooking liquor to the EFB fiber was in the ratio of 10:1. Prior to the pulping process, the fiber was soaked in water for two days to remove dirt.

During the pulping process, the pH of black liquor was measured as 12.45 and its density was determined to be 0.987 g mL<sup>-1</sup>. The soda lignin was precipitated from the concentrated black liquor by acidifying it to pH 2 using 20% sulfuric acid. The precipitate was filtered and washed with pH 2 water, which was prepared using the same acid as in the earlier step. The soda lignin was then dried in an oven at 55°C for 24 h prior to further analysis.

The commercial thinner, lignosulfonate and bentonite clay used in this study were supplied by Kota Mineral (Malaysia) Sdn. Bhd. The rest of the chemicals including 2-propenamide (acrylamide), ferrous ammonium sulphate, benzoyl peroxide, methanol and acetone were purchased from local chemical agents and the chemicals used were of analytical grade.

The reaction solution was prepared by mixing 0.5 g lignin, 0.02 g ferrous ammonium sulphate and 50 mL of methanol in a three-neck flask until complete dissolution. The mixture was saturated with nitrogen for 10 min before 0.02 g of benzoyl peroxide was added into the mixture. After being saturated with nitrogen for 20 min, 2.5 g of acrylic acid was added to the mixture, which was further saturated with nitrogen for another 10 min. This reaction process continued for about two hours before it was terminated using 0.5 mL of 1% of hydroquinone as a retardant. The prepared lignin acrylic acid graft copolymer (lignin AA) consisted of a fine dark brown powder.

## MUD PROPERTIES TEST

Three sets of experiments were performed in this study. These mud property tests were performed

according to the American Petroleum Institute (API) specifications (Wan Daud *et al.*, 1998; Sun and Tomkinson, 2001; Alonso *et al.*, 1993). Each of base muds used in each experiment was prepared by adding 80 g of bentonite and 4 g of sodium carbonate into 1000 mL of water before aging it for more than 24 h (Wan Daud *et al.*, 1998; American Petroleum Institute, 1997).

For each of the experiment, a Fann model 286 viscometer was used at two rotating rates of 300 rpm ( $\theta_{300}$ ) and 600 rpm ( $\theta_{600}$ ), respectively. Then apparent viscosity ( $\mu_a$ ), plastic viscosity ( $\mu_p$ ) and yield point ( $\tau_y$ ) were calculated as follows (Bourgoyne *et al.*, 1991):

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

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

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

In experiment I, the effect of different dosages of each thinner used at room temperature and under strong agitation (90°C) were studied. Three dosage levels of lignin AA were tested in different percentages which were 0.3, 0.5 and 0.7%. This experiment tried to highlight the importance of using correct dosage treatment for the optimum performance of thinner as well as to save unnecessary cost. Besides, the used of excessive or insufficient dosage might bring negative impact to the mud properties (Mohamad Ibrahim *et al.*, 2003b).

For experiments II and III, the base mud samples were added either with 0.3% of lignin AA or 0.3% LS (commercial thinner). 0.3% was chosen since lignin AA acts optimically as a thinner at this level (based on experiment I results). Experiment II was performed to evaluate the thinning performance at different aging temperatures for 16 h. This experiment was designed to observe the influence of temperature towards the performance of each thinner. This is because drilling process 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.

Experiment III was designed to evaluate the performance of the additives against salt contamination before and after the mud samples were heated in a Fann roller oven series 2500 at 160°C for 16 h. These conditions were used to simulate the actual drilling process. This experiment is important because common contamination encountered in drilling is salt (NaCl), which sometimes is also found in make-up water. When make-up water is very salty, bentonite will neither hydrate nor disperse

(Van Olphen, 1963). As a result, the undispersed or the unhydrated bentonite particles will tend to flocculate which will result in an increase in yield points and apparent viscosity values.

Complementary to experiment II and III, the API filtrate volume data was presented in order to evaluate the performance of the additives as a fluid loss reducer. The Fann filter press model series 300 was used to measure the API filtrate volume. Filtered volume is the amount of fluid that can be delivered through a permeable filter medium after it has been subjected to a set of differential pressure for a specified period of time.

**RESULTS AND DISCUSSION**

Graft polymerization is the process of adding a polymeric side chain to an existing polymer (lignin) to produce a two-part molecule. The two parts of the molecule are of different chemical composition or structure. In this case, the graft polymer formed, trivially named lignin acrylic acid copolymer, lignin AA (Meister *et al.*, 1985).

Figure 1 depicts the infrared (IR) spectra of lignin AA and lignin samples. The IR spectrum of lignin shows absorption at 3412  $\text{cm}^{-1}$  for phenolic or hydroxyl group. The absorption at 1609  $\text{cm}^{-1}$  is attributed to the aromatic ring and the absorption at 1462  $\text{cm}^{-1}$  is assigned to either CH stretching of methyl or methylene group. Lignin AA shows different bands from lignin which are 1718  $\text{cm}^{-1}$  for carbonyl group ( $\text{C} = \text{O}$ ), 1516  $\text{cm}^{-1}$  for aromatic  $\text{C} = \text{C}$  stretch, 1214 and 1113  $\text{cm}^{-1}$  which cannot be seen in lignin spectrum. The shift of bands and the existence of new peaks suggested that chemical reactions were taken place.

Figure 2 and 3 show the DSC thermogram for lignin and lignin AA, respectively. Lignin as an amorphous compound does not have any melting point peak as shown in Fig. 2. The formation of macromolecule after copolymerization process caused a steric hindrance which demonstrated by the present of very high melting point at 238°C for lignin AA as clearly shown in Fig. 3.

Result of experiment I are tabulated in Table 1 where it shows the optimum dosage of lignin AA is 0.3%, which gave the lowest yield point compared to other dosage at

Table 1: Basic mud rheological under different lignin AA dosages

Mud formulation	T (°C)	$\mu_s$ (mPa.S)	$\mu_p$ (mPa.S)	$\tau_v$ (Pa)
Base mud + 0.3% Lignin AA	27	22.15	14.60	7.72
Base mud + 0.5% Lignin AA		24.84	14.84	10.21
Base mud + 0.7% Lignin AA		26.50	16.00	10.73
Base mud + 0.3% Lignin AA	90	14.10	5.50	8.79
Base mud + 0.5% Lignin AA		18.67	5.83	13.12
Base mud + 0.7% Lignin AA		19.52	5.60	16.27

All test data were measured at 27±1°C

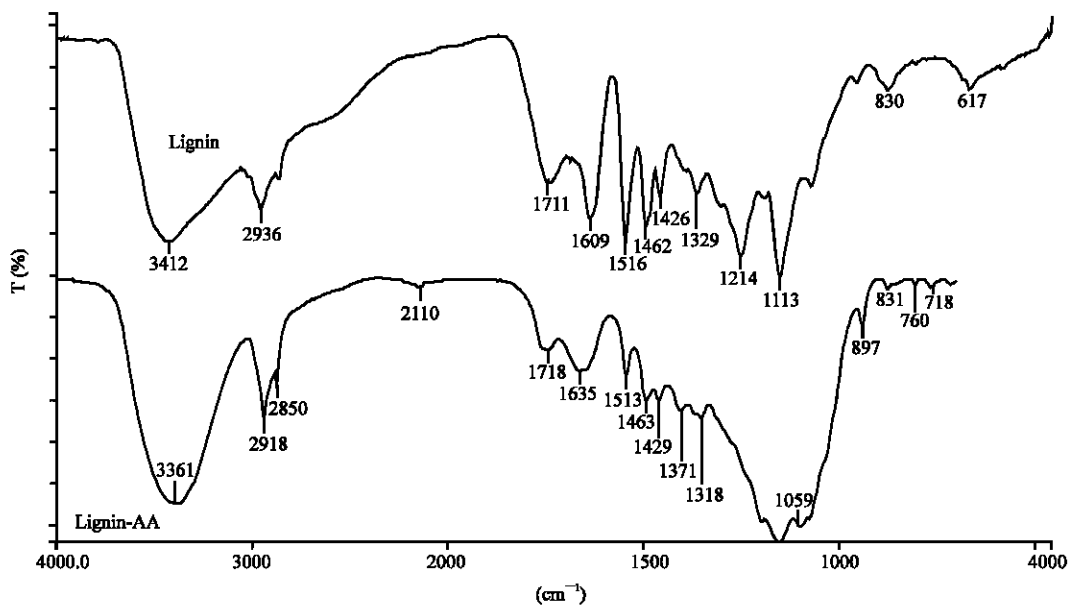


Fig. 1: IR spectra of lignin and lignin AA

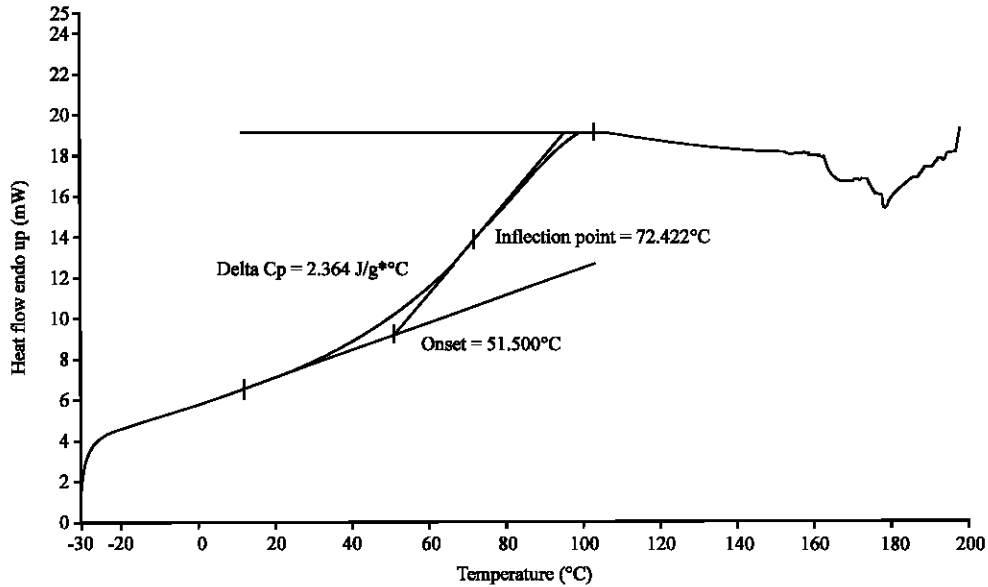


Fig. 2: DSC thermogram for lignin

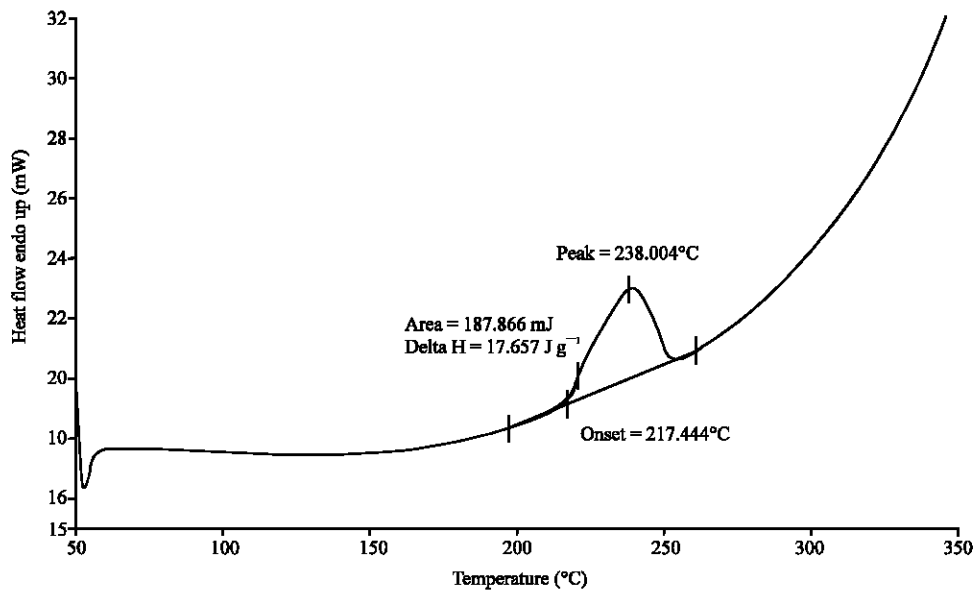


Fig. 3: DSC thermogram for lignin AA

both temperatures of 27 and 90°C. The two values of temperatures were used to confirm the performance of lignin AA would be consistent at either room temperature or at high temperature. Yield point represents the degree of electrostatic interaction between clay platelets. The higher this value, the higher the friction between drill string and mud. Usually, moderate yield point is preferred over negligible one because better lifting capacity is achieved at lower solids concentration and will increase the drilling rates.

Experiment II was conducted at high temperature of 190°C to simulate the deep well drilling process. Observations to the mud samples were done before and after hot rolling. Lignin AA shows the best  $\mu_s$ ,  $\mu_p$  and  $\tau_y$  values compared to other formulations at high temperature especially after hot rolling as shown in Table 2. Besides, lignin AA also shows good API filtrate volume at high temperature. Thus, it seemed to suggest that lignin AA with its high molecular weight and high decomposition temperature acts nicely in drilling

Table 2: Basic mud rheological properties after aging at high temperature (before and after rolling at 190°C for 16 h)

Mud formulation	$\mu_a$ (mPa.S)		$\mu_p$ (mPa.S)		$\tau_y$ (Pa)		API filtrate (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud	30.00	58.00	16.00	30.00	14.31	33.00	14.00	20.00
Base mud + 0.3% LS	20.00	52.67	14.00	39.00	6.13	13.97	13.50	16.20
Base mud + 0.3% lignin AA	22.15	42.50	14.60	31.00	7.72	11.75	14.20	15.60

All test data were measured at 27±1°C

Table 3: Basic mud rheological properties at different salinity (before and after hot rolling at 160°C)

Mud formulation	$\mu_a$ (mPa.S)		$\mu_p$ (mPa.S)		$\tau_y$ (Pa)		API filtrate (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud + 0.3% NaCl	29.17	70.83	8.66	15.34	20.96	56.71	15.20	23.60
Base mud + 0.7% NaCl + 0.3% LS	30.67	85.83	21.33	18.67	9.54	68.64	12.80	22.60
Base mud + 0.7% NaCl + 0.3% lignin AA	24.50	53.60	10.17	18.52	14.64	35.85	13.40	21.50

All test data were measured at 27±1°C

process where this operation commonly encounters high temperature and high-pressure conditions. Temperature of 190°C represents drilling at about 10,000 m underground.

Results from Experiment III suggested that the newly formulated lignin acrylic acid (lignin AA) exhibited good quality of thinning agent even in the presence of salt contamination especially after hot rolling at 160°C.  $\mu_a$  and  $\tau_y$  values for mud samples treated with lignin AA after hot rolling were the lowest but  $\mu_p$  values showed small improvement. This is due to the effect of reduction in viscosities was smaller compared to the increased in degree of solid concentrations in the mud as more solids (NaCl and lignin AA or LS) being added into the mud. This experiment is important because the common contaminant encountered in drilling is salt (NaCl), which sometimes is also found in make-up water. When make up water is very salty, bentonite will neither hydrate nor disperse (Van Olphen, 1963). The bentonite particles tend to flocculate which will increase the yield point and the apparent viscosity values. More complete results are listed in Table 3.

Experiments II and III show that lignin-based drilling mud thinner (lignin AA) can also act as good fluid reducers. The fluid loss control during drilling process is important to make sure that drilling left-over is efficiently transmitted from the bottom hole to the surface (hole cleaning process). If the mud viscosity is too high due to the fluid lost to the formation, the drilling process will be more difficult due to pipe sticking phenomenon. In other words, the mud sample with small filtrate volume indicates that the mud is capable to hold fluid from losing to the formation. The results of the experiment are to confirm that the formulated thinner, especially lignin AA is not only functioning as a good drilling mud thinner but also at the same time acts as a good fluid reducer.

## CONCLUSION

In general, soda lignin from oil palm empty fruit bunch was successfully copolymerized with acrylic acid to form lignin acrylic acid (lignin AA). The shifted bands and the existence of the new peaks in the IR spectrum for lignin AA indicated that some reactions had occurred. The presence of one  $T_g$  values in the DSC thermogram suggested that the copolymerization reaction may have occurred. Impressive performance of lignin AA against lignosulfonate (LS), a commercial thinner, as water-based drilling mud thinner in the presence of salt contamination strongly suggested that lignin AA has a great potential to be commercialized. Besides good tolerance towards salt contamination, lignin AA also could endure high temperature condition. In the present study, the optimum dosage of thinner was determined at 0.3%. Comparing the performances of lignin AA and LS, the results from this study suggested that the former product has better thinning abilities than the latter product. This newly formulated polymer based additive inevitable thinner could provide a better alternative to deep well hydrocarbon drilling operation as a drilling fluid thinner as well as a fluid loss reduction agent.

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