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DEVELOPMENT OF WATER-BASED DRILLING MUD BY USING LIGNIN FROM NATURAL RESOURCES AS THINNING AGENT

(Pembangunan Cecair Penggerudi Berasaskan Air Menggunakan Lignin Sebagai Agen Penipisan)

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Abstract

Drilling in a geological formation at high temperatures and pressures during offshore oil and gas exploration is often the cause of water-based mud damage. This study extracts lignin from coconut husk, oil palm fibre, and sawdust through the organosolv process. This lignin was a thinning agent in a water-based drilling mud formulation. The lignin was characterised by using Fourier Transform Infrared (FTIR) spectroscopy. The IR spectra of both lignin and lignosulfonic acid sodium salt showed bands at 3695.52 cm^{-1} and 2972.38 cm^{-1}, indicating hydroxyl groups in phenolic and aliphatic structures, the stretching of C-H bonds in aromatic methoxyl groups and methyl and methylene groups of side chains, respectively. When analysing mud properties, lignin's rheological and fluid loss properties were compared to lignosulfonic acid sodium salt, a commercial thinning agent. The dosage determination tests indicated that 0.6% was the optimum choice of lignin and lignosulfonic acid sodium salt. After thermal ageing, the rheological properties and fluid loss characteristics showed that lignin might be utilised as a thinning agent for drilling operations at temperatures as high as 90°C.

Keywords: lignin, lignosulfonic acid sodium salt, thinning agent, formic acid, organosolv process

Abstrak

Penggerudian dalam formasi geologi pada suhu dan tekanan tinggi semasa penerokaan minyak dan gas luar pesisir sering menjadi punca yang merosakkan cecair penggerudi berasaskan air. Dalam kajian ini, lignin daripada sabut kelapa, gentian kelapa sawit, dan habuk papan diekstrak melalui proses organosolv. Lignin ini digunakan sebagai agen penipisan dalam rumusan cecair penggerudian berasaskan air. Lignin dikenalpasti menggunakan spektroskopi inframerah transformasi Fourier (FTIR). Spektrum IR kedua-dua sampel lignin dan asid lignosulfonat menunjukkan jalur pada 3695.52 cm^{-1} dan 2972.38 cm^{-1}, menunjukkan kumpulan hidroksil dalam struktur fenolik dan alifatik, regangan ikatan C-H dalam kumpulan metoksil aromatik dan kumpulan metil dan metilena rantai sampingan, masing-masing. Apabila menganalisis sifat cecair penggerudi, sifat reologi lignin dan sifat kehilangan bendalir dibandingkan dengan asid lignosulfonat, yang merupakan agen penipisan komersial. Ujian penentuan dos menunjukkan bahawa 0.6% adalah pilihan optimum garam natrium lignin dan asid lignosulfonat. Selepas penuaan terma, sifat reologi dan ciri kehilangan bendalir menunjukkan bahawa lignin mungkin digunakan sebagai agen penipisan untuk operasi penggerudian pada suhu setinggi 90°C.

Kata kunci: lignin, asid lignosulfonat, agen penipisan, asid formic, proses organosolv

Introduction

Drilling fluid is an essential component of drilling operations, used to aid in creating a stable and gauged borehole to the desired depth with minimal damage to surrounding formations. Water-based drilling fluids (WBM) are becoming more popular with increasing environmental and economic concerns, particularly in high-
temperature, high-pressure (HTHP) environments. Dispersed WBM is one of the most widely used and cost-effective drilling fluids. However, drilling at high temperatures and pressures can cause filtration loss and damage the flow properties of drilling fluids.

Therefore, thinning agents are often added to drilling fluids to reduce viscosity and prevent gelation and thickening. High-viscosity fluids tend to increase filtration loss and can damage flow caused by low efficiency in flowing through rock formations in oil reservoirs. By reducing viscosity, thinning agents will help drill fluids flow more easily through these formations, thus reducing filtration loss and minimizing damage to the flow channels [1]. Drilling fluids used in HTHP environments tend to undergo gelation or thickening, which can further reduce flow and filtration loss. Thinning agents can prevent this gelation process by interacting with the fluid molecular structure, keeping it more fluidized. By maintaining the drilling fluids in these conditions, thinning agents can help to prevent the formation of gels and subsequent thickening of the drilling fluids, thus ensuring a smoother flow through the reservoir and reducing filtration loss [2]. Currently, most commercial thinning agents use chrome lignosulfonate, the most common thinner in water-based muds. Lignosulfonate is a natural polymer found in wood and plant materials. However, it was chemically modified to enhance its thinning properties. Adding chromium ions produces chrome lignosulfonate, which can be toxic to aquatic organisms and ecosystems if released into the environment [3].

Therefore, in this study, lignin from coconut husk (LCH), lignin oil palm biomass fibre (LOPBF) and lignin sawdust (LS) will be prepared as a thinning agent for water-based drilling muds using the organosolv method, with formic acid as the solvent for extraction. The materials used are non-toxic, abundant, and inexpensive renewable biomass with high lignocellulosic content. Lignin from coconut husk, oil palm biomass fibre and sawdust have the potential as a thinning agent for water-based drilling muds due to its high thermal stability and chemical resistance, as well as its ability to prevent damage to aquatic and terrestrial environments.

This study aims to develop lignin from coconut husk, oil palm biomass fibre and sawdust as a more environmentally friendly alternative to chrome lignosulfonate as a thinning agent for water-based drilling muds. The rheological properties of lignin were analyzed and characterized using FTIR.

Materials and Methods

Raw materials

This experiment's primary materials are sawdust, coconut husk and oil palm biomass fibers (OPBF). It is also known as renewable resources. Raw materials were collected from millworks and a local mill near University Malaysia Pahang Al-Sultan Abdullah and were received in ambient-dry conditions. The raw materials were inserted into the oven at 100°C for 24 hours to minimize the moisture content. Next, the raw materials were mechanically prepared using a blander and were sieved using 250-micrometre sieves. The organosolv medium uses formic acid as a solvent [4]. All chemical substances, such as formic acid, bentonite, and sodium carbonate, were purchased from Sigma-Aldrich (UK).

Organosolv process

The pulping process is the first step of the extraction process. At a solid to-solvent of 1:10, formic acid will be added to the raw materials in the flask and let to boil on a hot plate for 3 hours. 400ml of formic acid was added to the 40g raw material and was heated and stirred for 400 rpm at 105°C for 3 hours. After 3 hours, the flask and its contents can cool to room temperature. The content is then filtered through a Filter Press [4]. The

black liquid is obtained during the filtration procedure, and the remaining liquid may be classed as solution hemicellulose, and cellulose will not be utilized.

Evaporation process

The black liquor was evaporated using a Rotary Evaporator at 80°C and 90 rpm to separate the acid from the raw lignin-containing hemicellulose. The process continued until the black liquor was 60% dry [5]. 100 ml distilled water was then added to the balance of the liquor, and the raw lignin was manually stirred to rinse before going to the filtration process again.

Isolation of lignin

This step was used to isolate the lignin. The residue that got after the filtration was put in an oven at 100°C, atmospheric pressure, for 24 hours. The lignin was successfully obtained.

FTIR analysis

The infrared bands and absorbance were investigated using a Perkin Elmer 2000 FTIR spectrometer. Samples were scanned in the range of 4000 to 1000 cm^{-1} at a resolution of 4% using the KBr pellet technique [3].

Mud preparation

Five sets of lignin composition were used in mud formulation, as tabulated in Table 1. In addition to lignin, bentonite, sodium carbonate, and distilled water were incorporated in the mud and weighed precisely using a balancer. The mixing was done at 3000 rpm for 15 minutes.

Table 1. Composition of Mud

Materials	MUD 1	MUD 2	MUD 3	MUD 4	MUD 5
Lignin (g)	0	0.55	0.82	1.37	1.6
Lignin (w/w%)	0	0.2	0.3	0.5	0.6
Bentonite (g)	20	20	20	20	20
Sodium Carbonate (g)	1	1	1	1	1
Distilled Water (ml)	250	250	250	250	250

Mud property test

This experiment completed four main sets of tests: viscosity, fluid loss, density, and pH. Three equations will be used to compute apparent viscosity, μ_a (a), plastic viscosity, μ_p (p), and yield point, Γ_y (y) that is:

$$\mu_a = \theta 600/2 \quad (1)$$

$$\mu_p = \theta 600 - \theta 300 \quad (2)$$

$$\Gamma_y = 0.511(\theta 300 - \mu_p) \quad (3)$$

The filtrate loss (FL) volume is the amount of fluid that can pass through a porous filter medium after it has been exposed to a differential pressure for a set period. The mud's rheological features were investigated using a Fann model 286 viscometer, with mud viscosity measurements at two different rotation rates of 300 rpm (θ300) and 600 rpm (θ600). The viscometer's shear stress readings at 300 and 600 rpm are θ300 and θ600, respectively. Using a Fann model roller oven series 2500 and 500 mL Fann stainless steel ageing cell at 90°C for 24 hours, the ageing temperature (T) effects on water-based mud rheological and filtration loss qualities were studied [6]. The summary of the mud property test is tabulated in Table 2.

Table 2. Mud Property Test

Mud Property Test	Focus on Test	Machinery
Viscosity	1. Investigate the effects of various dosages of lignin in WBM at room temperature and under vigorous agitation (90°C).	Fann Model Viscometer
Fluid Loss	2. Mud doses of 0%, 0.2%, 0.3%, 0.5%, and 0.6% w/w were utilized.	Fann Model Filter Press
Density		Fann Model Mud Balance
pH		pH Meter

Results and Discussion

An FTIR analysis was performed to confirm the presence of lignin following the organosolv process. Figure 1 illustrates the spectra of LOPBF, LS, LCH, and LASS. In the infrared spectra of lignin OPBF, the alcohol is identified by a broad band with wavelengths ranging from 3695.53 cm^{-1} to 3663.42 cm^{-1}. Bands 2972 cm^{-1} and 2843.55 cm^{-1} reflect the stretching of C-H bonds in alkane groups. The stretching N=C=S was shown at bands 2077.72 cm^{-1}. The stretching of conjugated aldehyde yields a narrow broadband at 1691.72 cm^{-1}. Medium bands at 1512.51 cm^{-1} demonstrate the presence of nitro chemicals. The alcohol component is identified once again at 1345.74 cm^{-1} to 1331.20 cm^{-1}. The lignin OPBF structure grew robust, producing aromatic amines at 1268.33 cm^{-1} bands. C-H deformations create the band at 1164.06 cm^{-1} to C-O stretching. Finally, bands ranging from 1054.55 cm^{-1} to 1032.58 cm^{-1} show C-O bond stretching in the primary alcohol group.

A wide band at 3695.55 cm^{-1} to 3680.17 cm^{-1} in the LS spectrum may be attributed to the alcohol group. Alkane bands range from 2980.63 cm^{-1} to 2843.55 cm^{-1} at C-H stretching. The stretching of an isothiocyanate functional group results in a prominent band at 2077.84 cm^{-1}, indicating the strength of N=C=S stretching. A stretching O-H characterises the phenol functional group at bands at 1345.76 cm^{-1}. The medium peak indicates the C-O stretching vibration in the LS major alcohol group at 1054.67 cm^{-1}. The relative strength of absorption bands 1032.61 cm^{-1} is given to an out-of-plane S=O bond, which identifies as a sulfoxide functional group.

The alcohol group is represented by the broad, sharp bands in the LCH spectra ranging from 3695.47 cm^{-1} to 3662.92 cm^{-1}. The bands at 2972.39 cm^{-1} to 2843.57 cm^{-1} show an alkane functional group. A stretching C=C also happens at a wavelength of 1658.10 cm^{-1}. These peaks represent the alkene functional group of disubstituted (cis). N-O stretching occurs at 1535.79 cm^{-1} and O-H bending at 1391.87 cm^{-1}, indicative of the alcohol functional group. The structure of LCH at bands 1136.47 cm^{-1} displays a strong C-O stretching bond at the tertiary alcohol functional group. At band 1032.62 cm^{-1}, the structure exhibits C-O stretching and corresponds to an out-of-plane S=O functional group at band 1012.29 cm^{-1}.

The alcohol functional group is identified in the LASS infrared spectrum by a broad band with wavelengths ranging from 3695.52 cm^{-1} to 3680.218 cm^{-1}. Bands 2972.38 cm^{-1} and 2843.55 cm^{-1} demonstrate the stretching of C-H bonds in alkane groups. An influential band at 2077.84 cm^{-1} is due to the stretching of an isothiocyanate functional group, indicating the strength of N=C=S stretching. A stretching C=C distinguishes the conjugate of the alkane functional group at bands at 1641.08 cm^{-1}. LASS structure at bands 1345.91 cm^{-1}, revealing alcohol functional group with medium O-H stretching. The structure of LASS becomes strong between 1136.33 cm^{-1} and 1032.56 cm^{-1}, where the structure shows C-O stretching, indicating a tertiary alcohol functional group, and corresponds to an out-of-plane S=O stretching, indicating a sulfoxide functional group.

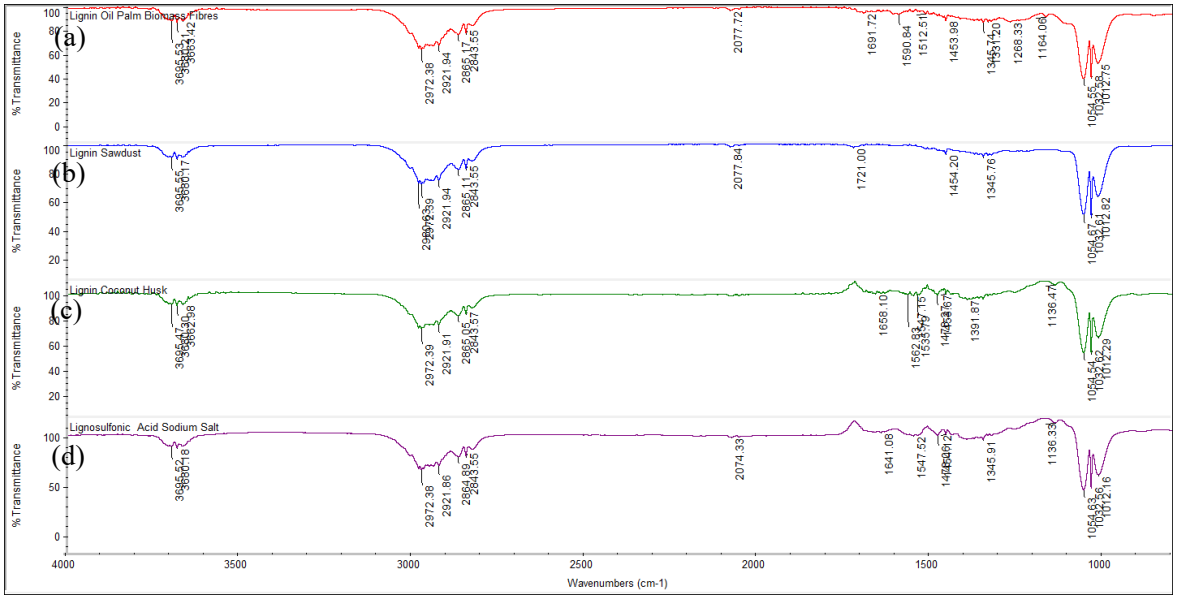

Figure 1. FTIR spectra of (a) lignin oil palm biomass fibre (LOPBF); (b) lignin sawdust (LS); (c) lignin coconut husk (LCH); (d) lignosulfonic acid sodium salt (LASS)

Base mud rheological properties

The goal of the present study was to investigate the feasibility of using lignin from oil palm biomass fibre (LOPBF), sawdust (LS) and coconut husk (LCH) as thinning agents in WBM. An attempt was made to compare the rheological properties of WBM containing LOPBF, LS and LCH with those of commercial thinning agents known as lignosulfonate acid sodium salt (LASS). Results of the experiment are tabulated in Figure 2(a)-(f), where the optimum composition of lignin in this experiment is 0.6 w/w %. Referring to Figure 2(a), as the composition of lignin in a WBM increased, the apparent viscosity decreased. This is due to the polymer chains in lignin interacting, making the mud less viscous [7]. In addition, lignin can create aggregates, which aids in lowering mud viscosity. These aggregates may develop due to the interaction of lignin with other mud components such as clay minerals or salt. The aggregates can alter the rheological characteristics of the mud, making it less viscous [8].

The plastic viscosity of WBM containing LCH shows the lowest value compared to LOPBF, LS and LASS at 0.2, 0.3 and 0.5 w/w/ % of lignin. It is apparent from Figure 2(b) that the plastic viscosity decreases as the lignin composition in WBM increases. The polymer chains in lignin interact with each other in a way that causes the mud to become less viscous [9]. Plastic viscosity is a measure of a fluid's resistance, which is WBM, to flow when it is being sheared or when forces are applied to it. It is an essential property of WBM since it affects the ability of the mud to lubricate and cool the drilling bit and to suspend and transport cuttings to the surface [10]. This is because as the concentration of the polymer increases, the intermolecular forces between the polymer chains become stronger, causing the mud to become more viscous. The higher the concentration of lignin, the lower the value of plastic viscosity. Usually, a lower plastic viscosity is preferred to minimize the potential for formation damage. This type of mud is suitable for drilling soft and porous formations. LOPBF and LS exhibit greater plastic viscosity when compared to LCH and commercial LASS. It is, therefore, ideal for use in harder formations for better hole cleaning.

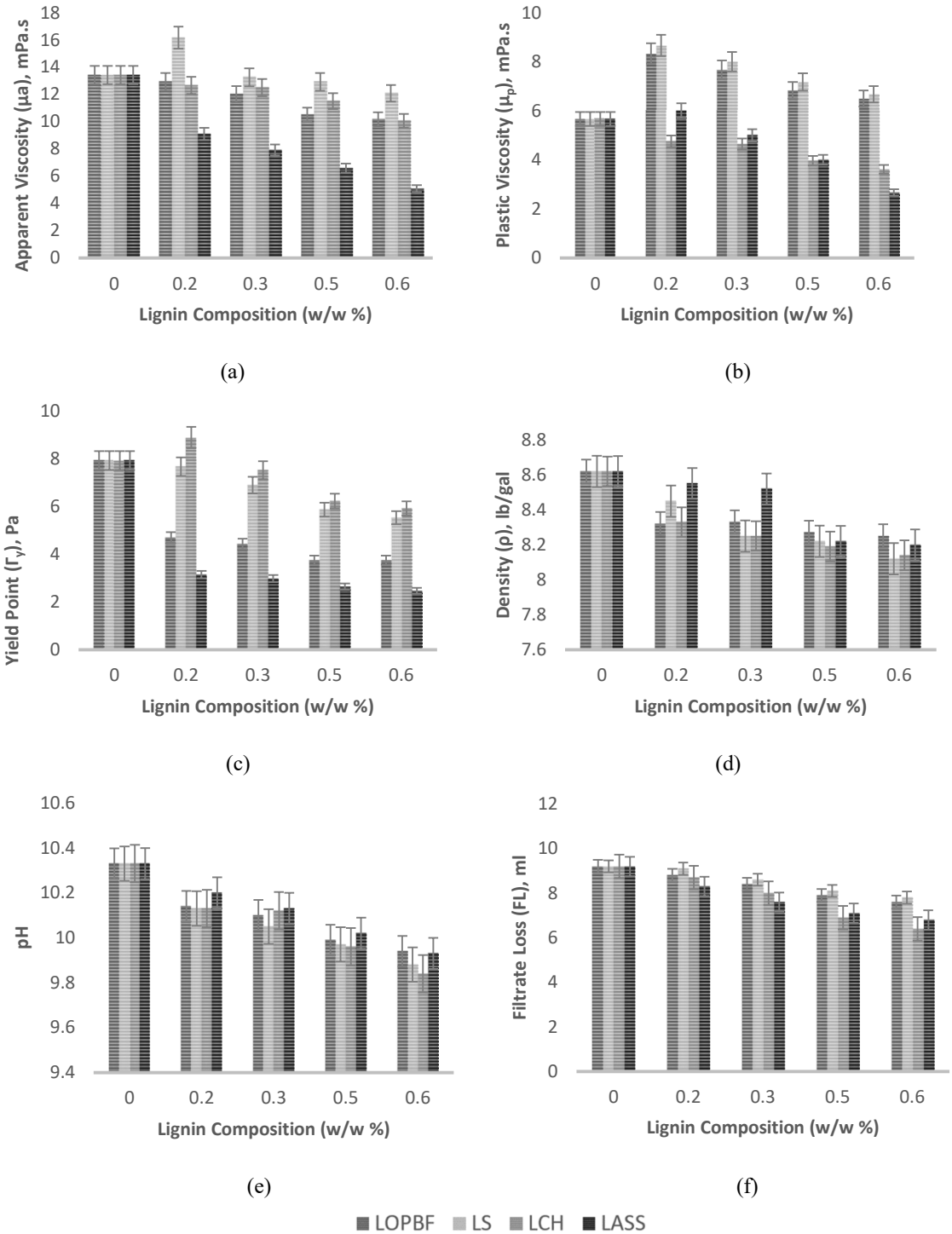

Figure 2. Base mud rheological properties at different lignin composition. The experiment was conducted at 27 °C. (a) apparent viscosity (μ_a); (b) plastic viscosity (μ_p); (c) yield point (Γ_y); (d) density (ρ); (e) pH; (f) filtrate loss (FL)

As the lignin content increased, the fluid's viscosity decreased, resulting in a lower yield point. As tabulated in Figure 2(c), the lowest yield point results from WBM containing LOPBF and LASS at a 0.2 - 0.6 w/w % lignin composition. The development of lignin-water complexes causes the yield point of a WBM to fall as the concentration of lignin increases. These complexes can develop when lignin molecules encounter water molecules in the mud, causing the lignin molecules to become more scattered and less able to resist movement. This lignin molecule dispersion reduces the mud's overall viscosity and lowers the yield point [11].

Overall, the density and pH trend also decreased when lignin composition was increased, as presented in Figures 2(d) and 2(e), respectively. The optimal lignin content is 0.6 w/w %, resulting in the lowest pH of LCH and density of LS. This is due to lignin's acidity, which can reduce the pH of the mud. Some clay minerals may flocculate or cluster together as the mud's acidity rises. As a result of the flocculated clay particles taking up less space, the mud density may drop. Measuring the density and pH of a water-based mud is an essential aspect of mud engineering as it helps to ensure that the mud properties are within the desired range for a particular drilling operation. Fluid loss (FL) in a WBM refers to the amount of FL in the formation while drilling. Based on the result in Figure 2(f), the lowest fluid loss value is represented by LCH with a lignin composition of 0.6 w/w %. This is because the lignin can form a thin filter cake on the wall of the wellbore, which acts as a barrier to prevent fluid loss. As the concentration of lignin increases, the filter cake becomes thicker and more effective at avoiding fluid loss [6].

Thermal aging test

In this work, the experiment was designed to simulate a high agitation process at 90°C. This temperature was used to confirm the consistency of rheological properties, including fluid loss, density, and pH of WBM containing LOPBF, LS, and LCH. The filtrate volume and rheological data were recorded before and after the hot-rolling process. The results obtained are tabulated in Figure 3, showing that the apparent viscosity (Figure 3-a), plastic viscosity (Figure 3-b), yield point (Figure 3-c) and filtrate loss (Figure 3-d) of lignin increased swiftly after the thermal rolling process. This finding suggests that LCH has better rheology than other mud formulations at high temperatures (90°C) after a hot-rolling process for 24 hours. This outcome may be due to the lignin's ability to form a stable filter cake at high temperatures. The chemical structure of lignin allows it to be more thermally stable than other fluid loss control additives, such as bentonite. When the mud's temperature increases, the mud's viscosity decreases, making it more challenging to maintain the integrity of the filter cake. LS, however, have higher thermal stability and can keep their viscosity at higher temperatures, allowing them to form a more effective filter cake and reduce fluid loss [10].

The density of WBM also smoothly increases when the lignin undergoes the thermal rolling process. The highest rise is on the optimum 0.2 w/w % concentration of lignin added, which gave LCH the highest increasing density value. This could be due to the chemical and physical properties of LCH. The density rises because the solubility of dissolved salts such as calcium and magnesium can increase dissolved ions in the mud, which can also increase mud density [10, 12]. Temperature can also impact the pH of the mud. The lower is on the optimum 0.6% concentration of lignin added, which gave LS the lowest pH value, which tends to be acidic. At warmer temperatures, the activity of microorganisms in the mud can increase, resulting in the creation of organic acids that can reduce the pH of the mud. Furthermore, heat can produce chemical processes in the mud, such as acid-base reactions and oxidation-reduction reactions, which can modify the pH of the mud.

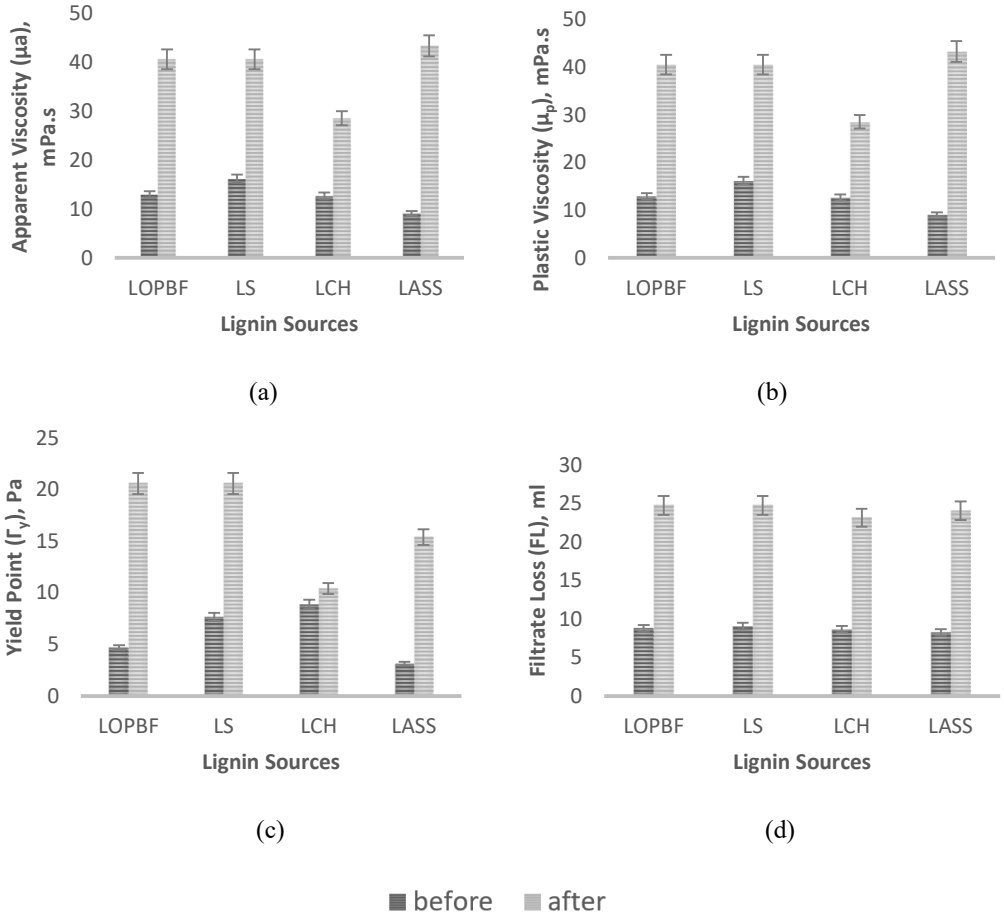

Figure 3. Base mud rheological properties of different lignin sources showing before and after the thermal rolling process at 90 °C. (a) apparent viscosity (μ_a); (b) plastic viscosity (μ_p); (c) yield point (γ_y); (d) filtrate loss (FL)

Conclusion

This study was conducted to observe the effectiveness of LS, LOPBF, and LCH as a thinning agent for water-based drilling mud rheological properties. Formic acid was used as a solvent during the organosolv process to extract lignin from LS, LOPBF, and LCH fibers. Various w/w% of the lignin were examined, including ageing temperature at 90°C and room temperature. Organosolv process was used in this experiment because it is a friendly method for the environment. Research has been done on the six criteria: apparent viscosity, plastic viscosity, yield point, fluid loss, density, and pH. The study showed that as lignin concentration increases, it could effectively function as a thinning agent to lower the viscosity. The viscosity will decline until the concentration of lignin in the mud becomes sufficiently high, causing the WBM to elevate the viscosity instead of reducing it.

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