Effectiveness of Waste Vegetable Oil Biodiesel and Soybean Oil Biodiesel as Additive in Water Based Mud System

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***Abstract*—Selection of drilling mud mainly depends on the dual-factors cost and performance. This paper compared the effectiveness of biodiesel produced from waste vegetable oil (cheap) and soybean oil (expensive) as additive in water based mud system at the temperature of 28°C and 180°C in free-salt bentonite mud and calcium contaminated mud. The results showed that soybean oil biodiesel emulsion mud (SBEM) density was higher (8.762 1b/gal) compared to waste vegetable oil biodiesel emulsion mud (WBEM) (8.679 1b/gal) in salt-free bentonite muds at 28°C. Comparatively, WBEM density was higher 8.887 1b/gal whilst SBEM was 8.846 1b/gal when the muds were exposed to calcium contaminant. Additionally, after aging at 180°C, WBEMs demonstrated better retained of their plastic viscosities than that of SBEMs at different conditions studied. Furthermore, API filtration loss test results in free-salt bentonite mud indicated that SBEM and WBEN fluid loss volume were (1.6 cm^3- 10.3 cm^3)/7.5 min and (1.5 cm^3-1.9 cm^3)/ 7.5 min respectively at the temperature of 28°C and 180°C. However, SBEM fluid loss volume was (2.6 cm^3-17.3 cm^3)/ 7.5 min compared to WBEM (1.85 cm^3-2.25 cm^3)/7.5 min in calcium contaminated mud. Through out these results, the formulated WBEM demonstrated superior performance than that of SBEM in geothermal and saline condition.**

***Index Terms*— Waste vegetable oil biodiesel emulsion mud, Soybean oil biodiesel emulsion mud, Plastic viscosity, API filtration loss, Calcium contaminated mud.**

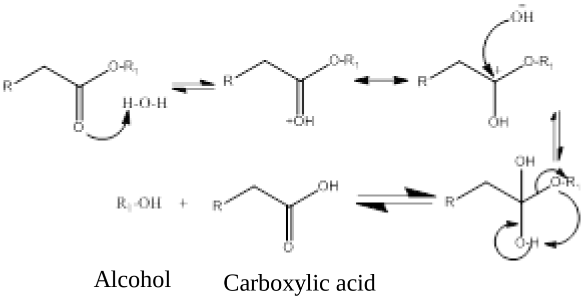
I. INTRODUCTION

WITHIN these last centuries, biodiesels (esters) amassed great attention by oil and gas companies in their different drilling activities. This in response to the tightly environmental regulations imposed by countries worldwide because of the use of diesel oil based mud which highly environmentally-unfriendly feature is among the major concerns of world communities [1],[2],[3]. Produced from renewable sources, biodiesels have very low level of toxicity, they content moisture leading to reduce oil viscosity and it is also used to improve stability [4],[5]. Generally, biodiesel is produced by the reaction of a free fatty acid with a low molecular weight alcohol (methanol, ethanol, or propanol) to form free alkyl (methyl, ethyl, or propyl) ester. Although they are environmentally-innocuous, their applications in the wellbore with a bottom-hole of 300°C or less are restricted, because of susceptible degradation [6].

As a consequence of high heat treatment, thermal degradation occurred, specifically leading to hydrolytic degradation of esters compound [7]

The degradation of ester in drilling fluid generally occurred in three different forms (R and R1 are alkyl group).

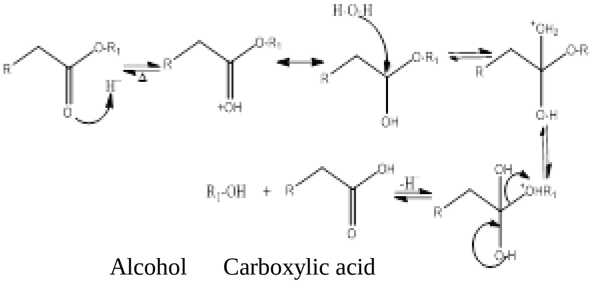
1.1. Uncatalyzed reaction



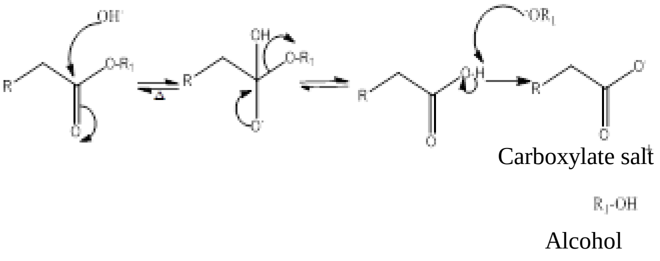
Hydrolytic degradation under uncatalyzed reaction

1.2. Hydrolytic degradation under acid/basic condition.

The rate of hydrolytic degradation reaction is higher compared to uncatalyze reaction since ester is exposed to high temperature under acidic/basic aqueous conditions.



Hydrolytic degradation under acidic condition



Hydrolytic degradation under alkaline condition

Under alkaline condition the deprotonated carboxylic acid is represented in carboxylate form, rendering the reaction to be irreversible. Hydrolytic degradation of ester produced alcohols and carboxylate salts or carboxylic acid which cause detrimental effect on the mud performance such as: large increase in the filtration volume leading to thick filter cake. These situation will then result in excessive drag, high-pressure surges, differential-pressure sticking, and reduction in production-zone permeability, and increases in shale sloughing [8],[9],[10],[11]. However, much global researches are presently on-going and are focused on the investigation of suitable working conditions in the field in spite of its less adaptivity when exposed to severe wellbore conditions.

[12] selected methyl laureate ester and isopropyl laureate ester base on the high stability under alkaline condition. Their potentiality to reduce filtration loss was investigated in ester based invert emulsion fluids. They found that isopropyl laureate ester was demonstrating greater performance as a fluid loss reducer than that of methyl laureate ester due to its ability to form a thin filter cake.

[13] developed more environmentally friendly high performance synthetic oil-based drilling mud with ester and a blend of ester and paraffin and a blend of ester and mineral oil as the main oil components.

[6] developed polymeric carbodiimide as an additive in ester based drilling fluid in order to inhibit the ester hydrolysis. He found that the hydrolysis inhibition was more than 90% in the whole mud, hence it can be used in more thermally-demanding wellbore.

[14] in his research discovered that waste vegetable oil biodiesel was demonstrating superior stability with the temperature rise compared to soybean oil biodiesel, he concluded that this observation could be attributed to the presence of antioxidants

This work focused on evaluation of the effectiveness of waste vegetable oil biodiesel as a potential substitute of biodiesel produced from edible feedstocks, used as additive in water based mud system. This in order to enhance mud performance at low price.

1.3. Drilling mud system(DMS)

Drilling mud is a mixture of complex components used by driller to achieve several functions such as: maintain wellbore stability, control formation pressure, remove, suspend drill cuttings from the well, seal permeable formation, minimize formation damage

1.3.1. Water based drilling mud (WBM)

Water itself can be considered as a drilling fluid. However, to provide better circulation while drilling activities, the fluid needs to exhibit some level of viscosity which is generated by incorporating clay, and several polymers. These additives enhance mud viscosity, improve upon the suspending capacity of the drill cuttings and also able to form a thin low permeability filter cake resulting to prevent fluid permeating into the reservoir pore space.

1.3.2. Oil-based emulsion drilling mud (OBEM)

Oil-based emulsion drilling mud can also be considered as a category of water based drilling mud, by the only difference that oil is added with the aid of emulsifiers to stabilize the emulsion in order to improve mud rheological properties.

II. EXPERIMENTAL SECTION

2.1. Pre-treatment of the waste vegetable oil.

The Waste Vegetable Oil (WVO) supplied by Wuhan Mejie Feiyou Chuli Company Limited (Wuhan, China) was first dried and hot-filtered. The initial acid value of the oil was determined according to China standard method [15] and was found to be 83.07 mg KOH/g oil using equation (1)

$$acid\ \text{value} = \frac{56.1[\text{base}]\text{V}}{\text{w}} \qquad (1)$$

where V is volume of base, [base] is concentration of base, w is mass of oil sample.

2.2. Production of waste vegetable oil biodiesel (WVOB) and soybean oil biodiesel (SBOB)

The production was carried out in a three-necked flask equipped with a reflux condenser, placed in a water bath.

- WVOB was produced using three steps.

Acid-catalyzed esterification reaction was first used to reduce oil acid level. Ethanol (35%vol) and hydrochloric acid (1.1vol%) were respectively used as reagent and catalyst at 65oC for 5 hours. This was reduced the acid value to 3.36 mgKOH/g. Ethanolic de-acidification was then used to further reduce the acid value of the product to 0.56 mgKOH/g (< 2 mgKOH/g) required to enhance the yield of the transesterification reaction. Lastly, Based-catalyzed transesterification reaction was performed by using potassium hydroxide (1.5wt%) prior dissolved in a de-ionized water (10wt%) and ethanol (35wt%) at $70^{o}C$ for 6 hours as described in [16]

- SBOB was produced using base-catalyst

Transesterification process as shown in Fig.1 at the similar condition used to produce WVOB. The SBOB and WVOB were washed with warm de-ionized water and dried.

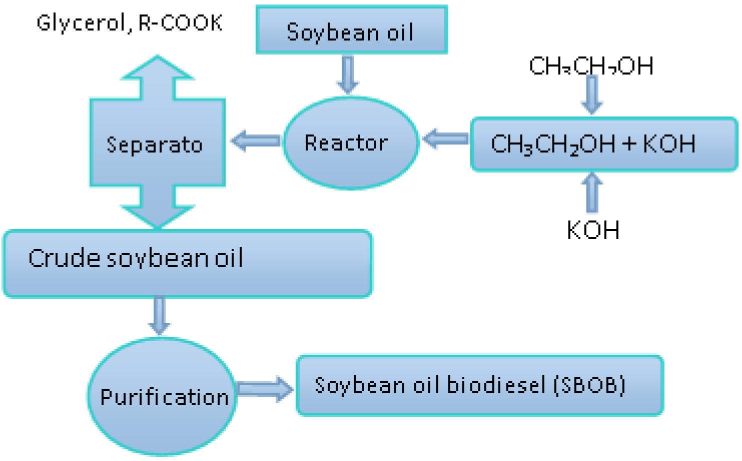


Fig. 1. Schematic batch of soybean oil biodiesel production

2.3. Evaluations of the oil properties

The produced WVOB and SBOB used in this comparative study were characterized by determining some basic physico-chemical properties.

2.3.1. Acid Value

The acid values of the samples were determined same as the pre-treatment stage according to China standard method [15].

2.3.2. The viscosity

The viscosity was estimated using Brookfield DV-III Ultra programmable rheometer (Brookfield Engineering Lab, Middleboro, USA) equipped with a temperature controller at 40^{o}C as described in [17].

2.3.3. Moisture content

Moisture content of the biodiesel was estimated by the weight loss method after drying the sample at 103^{o}C for 12 hours as detailed in Association of Official Analytical Chemists methods [18].

2.3.4. Density

The density was determined using JA5003N digital precision electronic analytical balance at 15^{o}C according to [19].

2.3.5. Flash point

The flash point was also estimated using Pensky-Martens closed cup method [20]

2.4. Drilling mud formulation and property evaluation

In the three formulations, base mud consisting of 380 ml de-ionized water, 3g sodium carbonate and 16g (and 15g for WBM) bentonite clay was first prepared using electrical mechanical stirrer and allowed to age for one day at 28^{o}C. Other ingredients were then added in bits with uniform mixing using high speed mixer to form the (WBEM), (SBEM) and Water Based Mud (WBM) according to Table 1. After aging, the muds were cooled at 28^{o}C and stirred for 5 min in a mixing cup with a high speed mixer, then different tests were then conducted according to [21]. Rheological properties of the different muds were measured using ZNN-D6 six speed rotating viscometer. API Filtration loss was measured using ZNS-A filter press test by applying nitrogen gas of 0.7 Mpa. The thermal stability of the muds was investigated using roller-oven to age for 16 hours at temperatures of 180^{o}C. The Baroid Mud Balance was used to determine the muds densities. All the instruments used in these tests were supplied by Qingdao Haitongda Specialized instrument Factory.

TABLE 1: CONSTITUENCY OF DIFFERENT MUD FORMULATION

Mud Formulation	WBEM	SBEM	WBM	Mixing time (min)
Water, ml	380	380	380	/
WVOB, ml	24	/	/	5
SBEM, ml	/	24	/	5
Bentonite, g	16	16	15	10
Emulsifier, ml	12	12	/	5
Na_2CO_3, g	3	3	3	10
SMP-3, g	12	12	12	5
SNPH, g	12	12	12	5
CMC, g	2	2	2	10
Barite, g	40	40	40	10

2.5. Investigation of the rheological properties of the mud samples.

Rheological properties were investigated in free-salt bentonite muds and calcium contaminated muds at the temperatures of 28^{o}C and 180^{o}C. The different properties tested were: Mud density (at 28^{o}C), plastic viscosity, thixotropy, yield point, API filtration loss.

III. MATH

3.1. Properties of the produce biodiesel samples.

The results of the basic physico-chemical properties of the waste vegetable oil biodiesel (WVOB) and soybean oil biodiesel (SBOB) are shown in Table 2.

TABLE.2: BASIC PHYSICO-CHEMICAL PROPERTIES OF BIODIESELS PRODUCED

Parameters	WVOB	SBOB	US/China Standard
Viscosity (cP)	4	4.2	1.9-6
Density (g/cm^3)	0.86	0.91	0.86-0.9
Water content (W%)	0.04	0.035	< 0.05 max
Flash point (^{o}C)	185	175	> 170 min
Acid Value (mgKOH/g)	0.44	0.25	< 0.5 max

3.2. Effect of the salt on the mud density

In this study, water was first used as a calibrating fluid, the muds densities were then measured at 28^{o}C. Stability of the drilling mud density is essential for proper control of formation pressure. As presented in Table 3 compared to WBEM, SBEM has higher density in free-salt contamination, this could be attributed to the high density of SBOB as shown in Table 2. When exposed to $CaCl_2$ contaminant, WBEM shows an increase in density of 2%, whilst SBEM and WBM were roughly 1% and 8% respectively. This was indicating the highest stability of SBEM against Calcium contamination compared to WBEM and WBM.

TABLE 3: MUDS DENSITIES

Type of muds	WBEM, 1b/gal	SBEM, 1b/gal	WBM,1b/gal
Without salt	8.679	8.762	8.971
Mud + 0.25%$CaCl_2$	8.887	8.846	9.764

3.3. Effect of the aging on the mud properties

Muds samples without salt contamination

TABLE 4: RHEOLOGICAL PROPERTIES OF THE DIFFERENT MUDS TESTED

Parameters	WBEM		SBEM		WBM	
	BHA	**AHA**	**BHA**	**AHA**	**BHA**	**AHA**
600 rpm	73	62	73	68	63	70
300 rpm	48	42	46	51.5	41	54
200 rpm	35	33	36	42	32	45
100 rpm	21	25	22	32	20	35
6 rpm	4	12	4.5	14	5	17
3 rpm	3	11	3.5	12	4	15
PV, cP	25	20	27	17.5	22	16
YP (1b/100ft^2)	23	22	19	23.5	19	38
G 10" (1b/100ft^2)	3	12	3	10	4	19
G 10' (1b/100ft^2)	11	14	16	13	15	20
API Filtrate (ml/ 7.5 min)	1.5	1.9	1.6	10.3	1.65	19

BHA: Before Hot Aging, AHA : After Hot Aging

Mud samples + 0.25% $CaCl_2$ incorporated

TABLE5: RHEOLOGICAL PROPERTIES OF THE DIFFERENT MUDS TESTED

Parameters	WBEM		SBEM		WBM	
	BHA	**AHA**	**BHA**	**AHA**	**BHA**	**AHA**
600 rpm	74	65	67	54	59	70
300 rpm	46	45	41	43	40	60
200 rpm	35	37	32	32	31	38
100 rpm	21	27.5	19	24	20.5	30
6 rpm	4	13	3.5	16	5.5	20
3 rpm	3	12	3	14	5	19
PV, cP	28	20	26	11	19	10
YP (1b/100ft^2)	18	25	15	32	21	50
G 10" (1b/100ft^2)	3	8.50	3.5	7	4.5	18
G 10' (1b/100ft^2)	14	14	17	10	11	20
API Filtrate (ml/7.5min)	1.85	2.25	2.6	17.3	3.5	28

BHA: Before Hot Aging, AHA : After Hot Aging

Plastic Viscosity (PV) can be defined as the resistance of the fluid to flow. Its stability is crucial to ensure proper circulation of the drilling fluid in the reservoir. As shown in Fig. 2 compared to SBEM, WBEM has a lower plastic viscosity at 28°C without contamination. This was attributed to the high viscosity of SBOB. After heat treatment at 180°C WBM and SBEM plastic viscosity both reduced to 17.5 cP (35%) and 16 cP (27%) respectively ,whilst WVEM demonstrated better retention of its plastic viscosity by reducing to 20 cP (20%). Contaminant simulation with $CaCl_2$, WBM and SBEM drastically dropped from 19cP to 10cP (47%) and 26 cP to 11 cP (57%) respectively at the temperature of 28°C and 180°C. WBEM was also affected but not as much as WBM and SBEM.

Due to the emulsification that took place,WVOB which probably contains antioxidants, through the absorption of oil upon the colloid system of the mud, under heat treatment, clay platelets dehydration was reduced as well as attractive forces which leads to aggregation, flocculation and the interaction between clay charged particles and ionic molecules of CMC(carboxymethyl Cellulose) through hydrogen bonding of water molecules was enhanced, resulting in better retention of WBEM plastic viscosity, whilst SBOB undergone severe hydrolytic degradation compared to WBEM and thermal degradation of CMC leading to plastic viscosity losses. Simultaneously, the insolubility of CMC increased, resulting to reduce polymer expansion due to the interaction of its ionic molecules with calcium ions as well as compression of clay particle double layer which enhanced the flocculation, hence the plastic viscosities collapse in SBEM and WBM.

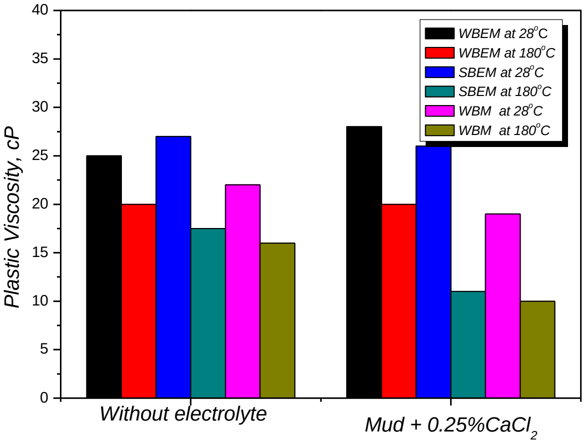


Fig.2. Plastic viscosity of the muds before and after hot rolling

Yield Point (YP) can be quantified as the stress necessary to move the fluid. Excessive yield point can lead to high pressure losses while the mud is circulating, this will cause extracost. Fig. 3 shows that when the muds free of calcium contaminant are heated at 180oC, SBEM and WBM yield value increased by about 19% and 50% respectively, whilst WVEM showed almost constant trend. Exposed to Calcium salt, the yield values were further increasing as followed WVEM 28%, WBM and SBEM 64%, 53% respectively. Although, WVEM yield value increased, it was favourable compared to others. The higher yield values of SBEM and WBM could be attributed to swelling of the clay platelets which further increased in calcium contaminated muds, this led to increase the number of links formed between the particles. However, WBM demonstrated the greatest clay swelling, followed by SBEM and WBEM.

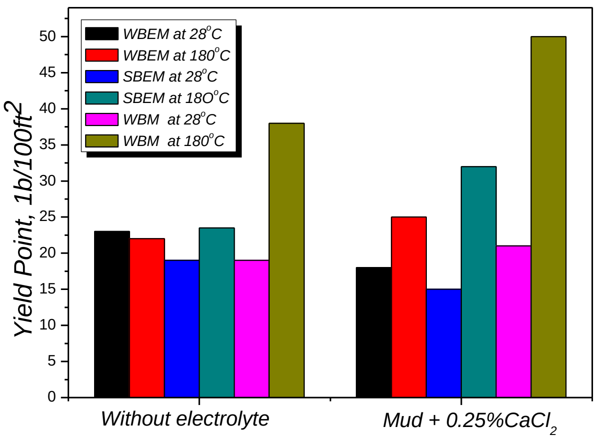


Fig.3. Yield point of the muds before and after hot rolling

The difference between the 10 min gel strength and 10 sec gel strength stand for the thixotropy. It is another important drilling mud property allowing to predict the capacity of the mud to handle cuttings at static period with the time. Higher/lower is the thixotropy, worse will be the efficiency of the mud to clean the hole. As indicated in Fig.4, salt-free WVEM and SBEM demonstrated good capacity in hole cleaning at 180ºC, whilst WBM thixotropy value was lower, hence exhibited a flat gel structure which is an undesirable situation. When the muds were contaminated with Calcium salt, in contrast to the previous situation, WBM and SBEM showed better capacity in terms of handling drill cuttings at high temperature, whilst WVEM thixotropy value was high, hence was developing a progressive gel structure which is also an undesirable phenomenon.

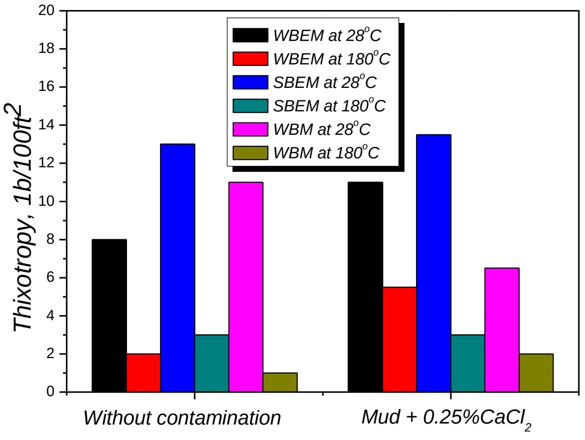


Fig.4. Thixotropy of muds before and after hot rolling

Filtration loss is often the most important property of the drilling fluid and it also characterizes the performance of the mud. Low filtration loss can prevent instability and damage formation. Fig.5 shows the filtration loss of the muds at 28ºC and 180ºC investigated after 7.5 minutes. WBEM produced the lowest filtration loss (1.5cm3-1.8 cm3)/7.5 min compared to SBEM (1.6 cm3-10.3 cm3)/7.5 min and WBM (1.65cm3-19 cm3)/7.5 min when the muds were free of salt. Exposed to calcium contaminant, WBEM was still maintaining the lowest filtration loss, compared to SBEM and WBM before and after aging at 180ºC. The low fluid loss with WBEM could be partly attributed to the absorption of WVOB upon the colloidal properties of the mud system. This stabilized the clay platelets as well as enhanced the synergetic interaction between charged clay platelets, ionic molecules of CMC, SMP-3(Sulfonated Methyl Phenol) and SNPH (Sulfomethyl hunate and phenolic resin) through hydrogen bonding of water by forming a thin low permeability filter cake resulting to reduce

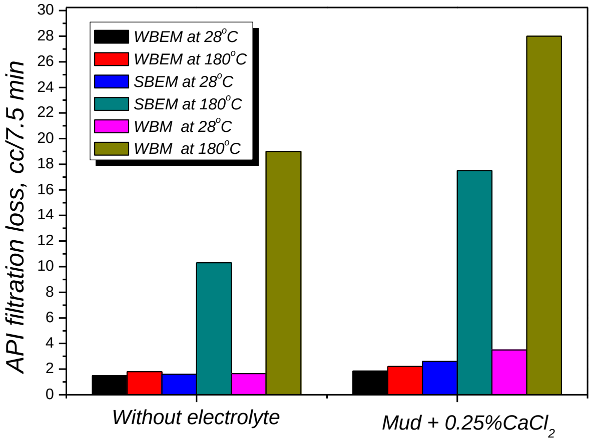


Fig.5: API filtration loss of different muds before and after hot rolling

3.4 Cost comparison of SBOB and WVOB

For a prosperous business, a comprehensive analysis of the potential cost is necessary. A comparative cost study of biodiesel produced from different feedstoks revealed that, the major factor that is taken into consideration is the cost of feedstocks. [22],[23] reported that, almost 70-95% of the total expenses of biodiesel production stand for the acquisition of feedstocks. The actual price of soybean oil is 628.75＄/Metric Ton [24] compared to waste vegetable oil which is 471.97＄/Metric Ton (obtained from the supplier). This definitely reduces the overall cost of WVOB production. Consequently, rendering WBEM cheaper compared to SBEM.

IV. CONCLUSION

This work which aimed at investigating the possible effect of WVBO (Waste vegetable oil biodiesel) and SBOB (Soybean oil biodiesel) in water based mud system as an additive. It was found that WBEM (Waste biodiesel emulsion mud) demonstrated better rheological properties in terms of mud stability at high temperature and presence of contaminant ($CaCl_2$).

WBEM demonstrated better retention of its plastic viscosity compared to SBEM in free-salt bentonite mud at 180°C. When contaminated with $CaCl_2$, both WBEM and SBEM lose their viscosity, but SBEM was severely affected.

Excessive yield value was observed with SBEM at 180°C in free-salt bentonite mud and was further increasing in calcium contamination mud , whilst WBEM yield value demonstrated better trend.

In free-salt bentonite muds, WBEM and SBEM were offering good capacity to handle drill cutting under static condition at 180°C, similar situation was observed with SBEM when the mud was exposed to $CaCl_2$, whilst WBEM was approximating a progressive gel structure.

WBEM produced low filtration loss volume (1.5 cm^3-1.9 cm^3)/ 7.5 min compared to SBEM (1.6 cm^3- 10.3 cm^3)/7.5 min at the temperature of 28°C and 180°C in free-salt bentonite muds. In $CaCl_2$ contaminated muds, SBEM filtration loss increased (2.6 cm^3-17.3 cm^3)/ 7.5 min ,whilst WBEM (1.85 cm^3-2.25 cm^3)/7.5 min. Further investigations should be carried out by adding an appropriate concentration of thinner to reduce WBEM thixotropy when it is exposed to $CaCl_2$ contaminant. Moreover, the understanding of rheological parameters of WBEM when contaminated with drill cuttings should also be considered as well as a possible field trials.

APPENDIX

Appendixes, if needed, appear before the acknowledgment.

ACKNOWLEDGMENT

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NOMENCLATURE

SBOB: Soybean Oil Biodiesel
WVO: Waste Vegetable Oil
WVOB: Waste Vegetable Oil Biodiesel
W%: Moisture content
SMP: Sulfonated Methyl Phenol
SNPH: Sulfomethyl hunate and phenolic resin
CMC: Carboxymethyl Cellulose
WBEM: Waste vegetable oil Biodiesel Emulsion Mud
SBEM: Soybean oil Biodiesel Emulsion Mud
WBM: Water Based Mud
PV: Plastic Viscosity, cP
YP: Yield Point, 1b/100ft^2
$G_{10''}$: Gel Strength at 10 sec (1b/100ft^2)
$G_{10'}$: Gel Strength at 10 min (1b/100ft^2)
Thixotropy (1b/100ft^2): Gel Strength at 10 min - Gel Strength at 10 sec.

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