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Potential of Ethylhexyl Ester Oil to Enhance Drilling of HTHP Wellbores

Abstract- Ester-based drilling fluids have been accepted as an alternative to mineral oils in drilling applications and currently being utilized to drill oil or gas wells around the world. However, the ester-based fluids have deficiencies that limit its ability to carry and transfer drilled solids, stabilize the wellbore and drill the extended reach wells. Several approaches have been considered to overcome the ester limitations. Thus, the main aim of this study is to overcome these limitations by developing the high performance ester-based green drilling fluids for deep and ultra-deep wells. The low-pressure technology was applied in the synthesis of the ester to minimize ester hydrolysis and thermal instability issues during the drilling operation. The rapid ester synthesis involved the 2-ethylhexanol and vegetable oil-based methyl esters C12 in the presence of sodium methoxide as the catalyst. Performances of 2-EH ester-based drilling fluids behaviour was assessed under different hot rolling temperatures (121, 149, 177, and 200oC) for 16 hours. The rheological properties in terms of low shear rate of 6 and 3 rpm were superior which verified that these ester-based muds could be used in deep and ultra-deep wellbores without sagging, pipe sticking and unbalanced wellbore problems.

Keywords- ester-based mud; drilling fluid formulation; high temperature; thermal stability; rheology.

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1. Introduction

High temperature high-pressure (HTHP) wells are that wells with bottom-hole temperatures ranging from 149°C to 250 °C and pressures from 10,000 to 25,000 psi. In such these fields, the rheological parameters of drilling fluids are difficult to control at extreme temperatures and pressures [1], thus requiring the use of special formulations and systems. Oil-based drilling fluids are the best candidates because they possess high thermal stability. However, their use has been banned by environmental legislations. This has encouraged the use of environmentally adaptable base oils such as green esters, new additives and specialized formulations, specifically for extreme temperature applications.

Ester-based drilling fluid is the earliest synthetic based fluid. It exhibits high environmental performances, specifically low toxicity and high biodegradability, thus making ester the best base oil for synthetic drilling fluids. However, this oil still has deficiencies such as high kinematic

viscosity, causing an increase in friction that impedes the circulation of the drill string, resulting in stuck pipe and finally failed oil/gas well bores.

High viscosity is believed to be crucial in deep oil/gas wells where the absence of overburden results in a severely-narrowed the window between pore pressures and fracture gradient. Furthermore, hydrolysis is another disadvantage of using ester-based mud, especially at high pressure and high temperature, which leads to the instability of drilling fluid to tolerate rock cuttings to the surface because of reactions with the formulations through drilling operations [2]. A limitation of oil/water ratios, mud weights and drill solid tolerances are among the repercussions of higher viscosities [2-3].

Ester-based fluids are usually prepared from renewable resources such as vegetable and animal oils (triglycerides) including palm oil, rice oil, coconut oil, fish oil, and whale oil. Vegetable oils have the disadvantages of being chemically

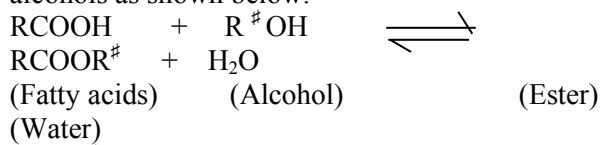
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reactive, where the oil tends to undergo alkaline hydrolysis at high temperatures that causes an increase in the thickness of the filter cake and filtrate volume loss. Furthermore, vegetable oils have high viscosity at low temperature, which renders them unstable in deep water wells. As highlighted in several US patents [(5,403,822), (36,066) and (5,252,554)] esters from natural origin vegetable or animal oils are not suitable as substitutes for mineral or diesel oils [4-6]. In contrast, esters of carboxylic acids with monofunctional alcohols derived from these normal origins or free fatty acids are more suitable as base oils in drilling fluid.

The synthesis of esters is usually conducted via esterification reaction between fatty acids and alcohols as shown below.



The $\text{R}^{\#}$ is methyl ($-\text{CH}_3$). However, these fatty esters will hydrolyze under high temperature and excessive alkalinity to produce calcium soap, which affects the rheology and corrosiveness of the drilling pipes. Thus, most of reported ester-based drilling fluids were not stable beyond 177°C . However, in this study, the new ester (2-EH C12) was found to be very stable even at temperature above 200°C . This ester was synthesized via a transesterification reaction between C12 ME and 2-ethylhexanol ($\text{C}_8\text{H}_{18}\text{O}$) alcohol in the presence of (CH_3ONa) as a catalyst using Low Pressure Technology (LPT) to minimize ester hydrolysis and thermal instability issues during the drilling operation. Furthermore, the required properties of the base oil for ester-based drilling fluid are kinematic viscosity at 40°C between 2.3-3.5 cSt, flash point above 66°C and a pour point less than ambient temperature [7]. The prior ester-based oil was also blended with low toxicity mineral oils to reduce its viscosity [6]. To overcome the hydrolysis and thermal instability of esters, lime was replaced with acetic acid to have thermal stability up to (177°C) [8]. However, the synthesis of an ester based drilling fluids without any blending of ester with mineral oils and stable up to (200°C) has not yet been reported.

2. Methodology

I. Synthesis of drilling fluid formulations

The drilling fluid formulation was conducted using the synthetic 2-EH C12 ester and C12 ME as base oils. 2-EH C12 ester was synthesized using vacuum technology proposed by Yunus and

co-authors in 2005 to minimize reserve and time reaction (Robiah et al, 2005). C12 ME was bought from Emery Oleochemicals Company. In tables 1, 2, 3, and 4, the formulation was prepared using the drilling fluid calculator software; all amounts of additives were weighed in grams. Inputs of software for each formulation in Tables 1, 2, 3 and 4 are mud weight, which was 12 lb/gal (1.44 g/cm^3), water to oil ratio of 15/85 and specific gravity of base oil. The physical properties of the 2-EH C12 ester were as follows: kinematic viscosity was: 40°C ($5.2 \text{ mm}^2/\text{sec}$) and at 100°C ($1.5 \text{ mm}^2/\text{sec}$), 0.854 specific gravity, 170°C flash point, and -7°C pour point. C12 ME of kinematic viscosity, specific gravity, flash point and pour point are $2.3 \text{ mm}^2/\text{sec}$, 0.865, 130°C and 1.5°C respectively.

The required amount of base oils (2-EH C12 ester, C12 ME) was weighed with a 350 ml mixing cup and the sample was then set using a Hamilton beach mixer. There are in fact three types of additives used in the formulation depending on the aging temperature level: type 1 (conventional additives) for a temperature range from (54 - 135°C), type 2 (advanced additives) for temperatures of (121 - 177°C), and type 3 (ultra-advanced additives) for temperatures of (177 - 250°C). Primary and secondary emulsifiers (metal soap of fatty acid) were added to produce and conserve the invert emulsion. A viscosifier agent (organophilic bentonite, hectorite and attapulgite) was used to disperse solids in the mud, a fluid loss agent (gilsonite, high softening point gilsonite, and synthetic polymer from gilsonite) was utilized to prevent mud flow to the formation, mixed brine (CaCl_2 of 25% + 75% water), barite and finally drilled solids were added as weighting agents to the mixture. The duration of mixing procedure was 60 minutes. Tables 1, 2, 3, and 4 show the samples with different types and amounts of additives. Samples 1-5, known as conventional formulations at temperature range of (54 - 121°C), samples of 6-15 used various additives that can stabilize the drilling fluid from (121 - 177°C); the rest used chemicals that have thermal stability from (177 - 250°C).

II. Drilling fluid properties

Drilling fluid is a complex blend of interacting elements; its characteristics change markedly with alterations in temperature, shear rate and shear history. To test the potential of 2-EH C12 ester as a base oil in drilling fluid under different ranges of hot rolling temperatures and pressures, API 13B-2 procedures were closely adhered to [9]. The Fann 35 SA equipment was used to investigate

drilling mud rheology using six speeds (600, 300, 200, 100, 6, 3 rpm) before and after hot rolling. The readings of shear stress under these six shear rates measured at 120°F (49°C) were used to compute the rheological properties of the mud which are plastic viscosity (Pv), yield stress or point (Yp), and gel strength at 10 seconds and 10 minutes. Pv and Yp indicate the ability of the mud to carry and transport cuttings from down-hole to the surface. For gel strength, at 10 sec and 10 minutes point to the capability of the mud or drilling fluid to suspend the weighting agents or barite particles without allowing settling. For synthetic-based mud or drilling fluid, the range of acceptable Pv is 10-60 mPa.s, but preferably from 15-40 mPa.s. The Yp ranges from 5 to 40 lb/100 ft² (244.1-1952.8 g/m²) preferably in the range of 10 to 25 lb/100 ft² (488.2-1220.5g/m²) [6]. ASME [10] highlighted the acceptable amount of filtrate, which is less than 10 ml.

The electrical stability denotes the compatible stability of oil/brine emulsion. To maintain the well bore stability, the filtrate loss to the permeable formations at high temperature and high pressure has to be as low as possible. This is to avoid shale hydration and chemical interaction between mud and the formation. Furthermore, to prevent stuck pipes, the mud cake has to be thin and have rheology in acceptable range to allow the drill string to continuously rotate and the drilling fluid to penetrate. The electrical stability tester was used to evaluate the stability of the emulsifier system with oil to form a stable emulsion before and after thermal aging for 16 hours. The most important test is the high temperature high-pressure fluid loss, which measures the volume of filtration and the thickness of the mud cake using a static filtration tester. This device works under different temperatures and pressures, and uses

nitrogen as a carrier gas. However, the differential top and bottom pressure of the device was fixed at 500 psi (34.47 bar). Different filter papers were used for temperatures up to (149°C) and up to (200°C), while a stainless steel disc (Dynalloy X-5) was used for temperatures above (232°C). The filtrate testing was performed for 30 minutes and the filtration amount was doubled based on the differences in the Filtration area of high and low pressure cells: 45.8 cm² and 22.9 cm², respectively.

3- Results and Discussion

The significant characteristics under consideration in the performance of drilling muds with new formulations are their rheology and stability in both conventional and geothermal conditions. Table 1 shows the formulation components used to obtain the best mud formulation in accordance with API standards procedures. The conventional condition of (121 °C) for periods up to 16 hours (standard time of mud circulation inside the well) was employed. The rheological properties (PV, yield point (YP), and gel strength for short and long periods), preferred low shear rate (θ_3, θ_6 at 8–12 cP), and filtration properties (30 min at 500 Psi of differential pressure), were then determined. The kinematic viscosity, specific gravity, flash point and pour point, of the commercial methyl ester (ME) based Mud 5 are (2.3 cSt, 0.865, 130 °C, and 1.5 °C respectively) and the newly synthesized base oil, 2-EH C12 ester Muds (1-4) are (5.2 cSt at 40 °C and 1.5 cSt at 100 °C, 0.854, 170 °C, and -7 °C respectively). A comparison study of ME based mud and 2-EH ester based muds performance was made in Figure 1.

Table 1: Ester based mud formulations with conventional type of additives at (121 °C)

Materials	1/12ppg, 121C	2/12ppg, 121C	3/12ppg, 121C	4/12ppg, 121C	5/12ppg, 121C
2-EH C12 E,ml	196.24	196.56	193.17	190.557	0
C12 ME, ml	0	0	0	0	204.45
Confi mul p, g	3	4	4	4	4
Confi mul s, g	6	6	6	6	6
Confi gel ht,g	1	1.3	1.3	1	1
Confi trol, g	4	6	8	12	8
Lime, g	5	2	2	2	2
Water, ml	40.55	40.2	40.31	39.377	39.92
Calcium chloride, g	14.48	14.36	14.6	14.267	14.46
Barite, g	213.93	215.78	203.53	214.99	215.66
Rev Dust, g	20	20	20	20	20

Figure 1 indicates that Mud 4 exhibits superior performance than a commercial ME-based mud

(Mud 5) in terms of the amount of filtration as well as the rheological properties under the conventional conditions (121°C). Moreover, the 2-EH C12 ester is superior as ME-based mud formulation. The filtration enhancement in Mud 4 using 12 g of conventional fluid loss agent (Gilsonite) is demonstrated in Figure 1. The result is not attributable only to filter paper plugging, but also the reduction from 5 to 2 g of the amount of

lime. Mueller et al. [6] claimed that using 2 g of lime in ester-based muds minimized the hydrolysis reaction. For the 2-EH ester in this study, the fatty acid ester hydrolysis issue was resolved because the 2-EH ester was produced from transesterification of methyl ester with 2-EH alcohol using Low Pressure Technology method proposed by Yunus et al. [11]. However, the 5 g of lime may affect the hydrolysis of the emulsifier.

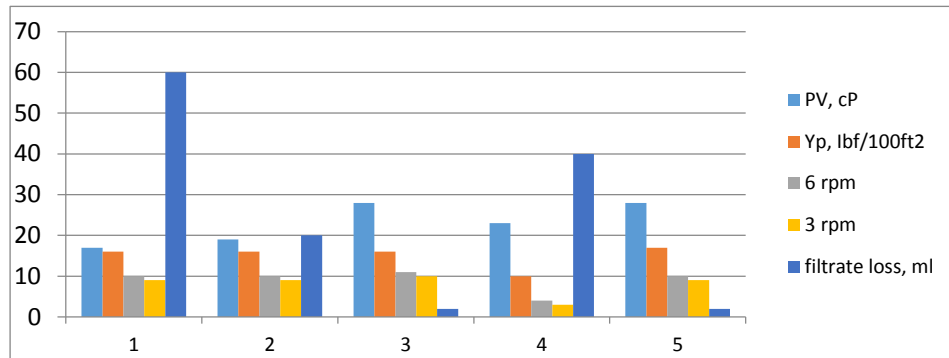


Figure 1: Comparison between C12 ME and 2-EH C12 ester at (121 °C)

Table 2 describes the Muds 6–15 which contain an advanced type of additives (Confi Trol HT), and two types of ester base oils (2-EH ester, and ME). The results are shown in Figure 2 which also depicts the comparison of ME based muds (6-10) and 2-EH ester (11-15) at 149°C. In spite of the unique rheology of samples 7, 8 and 10, their amount of filtration was high. This may be due to

the hydrolysis of fatty acid esters to its components (fatty acid plus alcohol) under high temperatures (149°C) and in an excess of lime, which was used to activate the emulsifier system. While Mud 15 was very stable before and after hot rolling, with just 2 ml of filtrate and a mud cake thickness of 1 mm, as shown in Figure 2.

Table 2: Ester-based mud formulations with advanced types of additive

MATERIAL	6	7	8	9	10	11	12	13	14	15
	149C	149C	149C	149C	149C	149C	149C	149C	149C	149C
2-EH C12 E, ml	0	0	0	0	0	189.4	187.7	187.6	187.4	0
C12 ME, ml	204.05	199.4	197.6	196.77	191.5	0	0	0	0	0
Confi Mul P, g	4	4	4	0	4	4	4	4	4	4
Confi Mul S, g	6	6	6	1	8	6	8	8	8	8
Confi Mul HT, g	0	0	0	10	0	0	0	0	0	0
Confi Gel HT, g	1	1.25	1.5	1	1	1	1	1.25	2	2
Confi Trol HT, g	8	10	12	12	12	12	12	12	12	15
Lime, g	5	5	5	5	5	5	5	5	5	5
CaCl ₂ , g	40.2	40.7	40.3	40.1	39.1	39.1	38.8	38.8	38.7	38.5
WATER, ml	14.6	14.6	14.398	14.4	13.9	14	13.9	13.8	13.8	13.8
BARITE, g	201.3	205.6	203.9	203.95	209.7	211.2	211.3	211.2	210.7	212.02
Drill solid, g	20	20	20	20	20	20	20	20	20	20

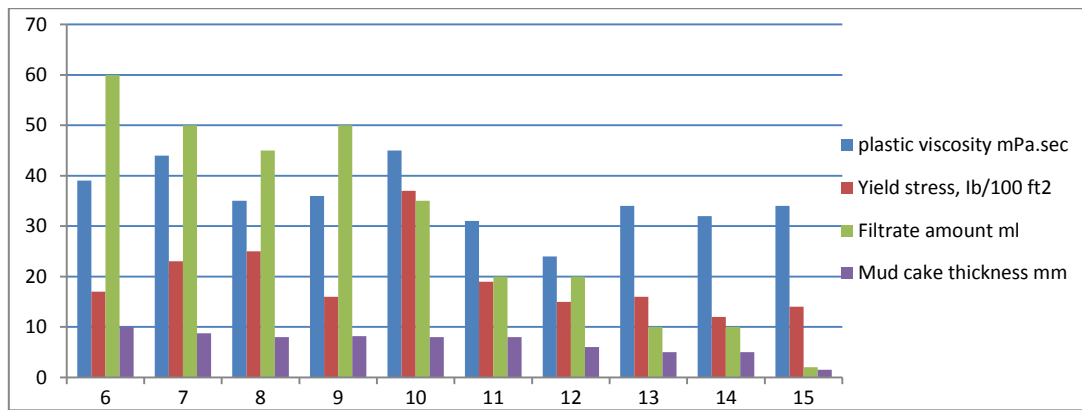


Figure 2: Comparison between C12 ME & 2-EHC12 E at 149°C

A comparison study was made between synthetic 2-EH ester based muds (Mud 13 and 15) and Nasiri et al. Mud 26 and 27 as illustrated in Figure 3. It is obvious the PV of the 2-EH C12 ester is closed to that of Nasiri at (149 °C), while the YP is better than that of Nasiri, enabling the 2-EH C12 ester to carry cuttings. Moreover, the filtration amount and mud cake thickness of the 2-EH C12 ester were less than those obtained by Nasiri et al.

[12]. This comparison proves the superiority of 2-EH ester-based mud, in which the base oil is pure synthesized 2-EH ester, without mixing with any mineral oil, not as in Nasiri et al. [12]. Their synthesized ester-based muds were carried out using a mixture of fatty acid ester and linear alphaolefin to overcome the high viscosity of the ester.

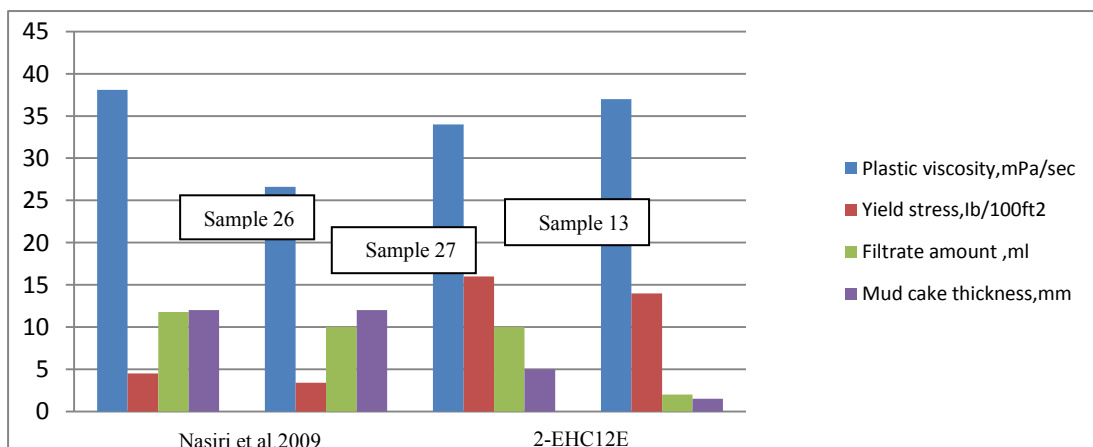


Figure 3: comparison between Nasiri et al. [12] ester based mud and 2-EHC12 E based mud at (149°C)

In our study, various mud samples were investigated at 177°C using different types of additives, described in Table 3. The fluids were formulated to simulate a geothermal well whereby the combination of advanced and ultra-advanced additives enhanced the rheological behaviour and exhibited a low rate of filtration, as well as thin mud cake. Apparently, Mud 19 was a good formulation at 177 °C, with an excellent rheology; filtration, and mud cake properties, as shown in Figure 4. Figure 4 shows a comparison between Mud 34 and 35 reported by Nasiri et al. [12] and 2-EH ester Mud 18 and 19 at 177°C. It is clear that the 2-EH ester from palm kernel oil exhibits better qualities than the base oil blend of fatty acid ester

and linear alphaolefin reported by Nasiri et al. [12]. The most obvious point to emerge from this comparison is that the newly synthesized ester-based oil with a 5.2 cSt kinematic viscosity showed superior performance than the blended oil with only 3.4 cSt kinematic viscosity. These formulations contained both advanced and ultra-advanced additives.

Table 4 illustrates the performance of mud samples formulated using ultra-advanced additives. Rheology of Muds (20-23) confirms that Mud 22 performed better than others, which possess superior rheology with the required amount of filtration at this high temperature.

Table 3: Ester based drilling mud with advanced and ultra- advanced additives

MATERIAL	16 177C	17 177C	18 177C	19 177C
2-EH C12 E, ml	201.9	191.7	198.24	201.8
Confi Mul HT+Confi tech HT ,g	12	10+2	0	10+2
Confi MulXHT+Confi Tech HT ,g	0	0	10+2	0
Confi Gel HT ,g	0	1.3	0	0
Confi Gel XHT ,g	0.5	0	1	1.5
Confi Trol HT ,g	0	15	0	0
Confi Trol XHT ,g	7	0	6	5
LIME,g	5	2	2	2
CALCIUM CHLORIDE,g	14.9	14.1	14.6	14.9
WATER,ml	41.7	41.4	41	41.7
BARITE,g	208.6	210	216.4	211.9
Rev Dust,g	20	20	20	20

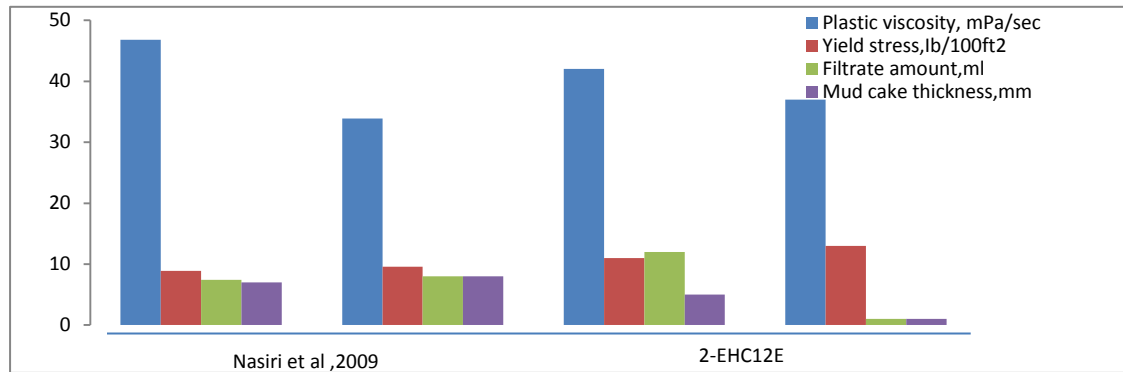


Figure 4: Comparison between Nasiri et al. [12] ester based mud and 2-EHC12 E based mud at (177°C)

Table 4: Ester based mud formulations and Rheological properties before (B) and after (A) 200°C

MATERIAL	20 200C	21 200C	22 200C	23 200C
2-EH C12 E, ml	201.9	198.237604	194.41	193.9
Confi Mul HT, g	12	0	0	0
Confi Mul XHT, g	0	12	12	12
Confi Gel XHT, g	0.5	1.5	1.5	1
Confi Trol XHT, g	7	6	5	6
LIME, g	5	2	2	2
CaCl ₂ , g	14.9	14.629	14.35	14.6
WATER, ml	41.7	40.963	40.17	41
BARITE,g	208.6	216.37	216.4	216.4
Drilled solid,g	20	20	20	20

Rheology	20		21		22		23	
	200C		200C		200C		200C	
	B	A	B	A	B	A	B	A
600 rpm	79	165	77	115	64	93	66	95
300 rpm	42	94	45	66	35	52	38	53
200 rpm	30	69	29	48	25	37	27	38
100 rpm	18	44	18	28	16	23	17	23
6 rpm	4	9	6	6	6	7	6	7
3 rpm	2	8	5	5	5	6	4	6
Pv, cP	37	71	32	49	29	41	28	42
Yp, lb/100 sq ft	5	23	23	17	6	11	10	11
Gel strength @ 10 sec	6	7	8	7	9	7	6	7
Gstrength @ 10 min	9	10	17	9	16	9	9	9
ES volt	646	636.43	1134	678	1217	997	1116	989
HTHP filtrate, ml		20		10		7.5		10
Mud cake thickness, mm		8		8		4		6

4. Conclusion

This study has successfully developed new formulations for ester-based drilling fluid, which are thermally stable up to 200°C. Based on the rheology of 2-EH C12 ester-based muds under high pressure high temperature conditions, these formulations would be able to perform the drilling fluid functions of suspending, carrying and transporting rock cuttings as well as well maintaining the bore stability. Based on the comparison study made between C12 ME of low kinematic viscosity and 2-EH C12 ester of high kinematic viscosity, the drilling performance of the 2-EH C12 ester was superior than that of C12 ME before and after hot rolling at these temperatures; 121°C, 149°C, 177°C, and 200°C. Adding lime and a small of calcium hydroxide to the formulation enhanced the mud properties especially at high temperatures. The presence of calcium hydroxide improves the hydrolytic issue while the use of ultra-advanced type of fluid loss agent affects the rheology.

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