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Esterification Reaction for Novel Synthesis Castor-Based Polyester and Formulation as Base Oil in Synthetic Drilling Fluid

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Abstract: ***Ricinoleic acid [hydroxyl fatty acid] is the meager constituent fatty acid in castor oil (85 – 95%). Castor oil is inedible oil which is one of the crops available, reachable oil in Egypt. Novel polyesters produced form esterification of different ratios of hydroxyl fatty acid (35, 55, and 75%) with glycerol and phthalic anhydride, at temperatures between 120 and 240°C. Three different novel polyesters were collected and designated as HD_{35}, HD_{55} and HD_{75} respectively. The average degree of polymerization is monitoring by determining the acid number of the aliquot of the reaction mixture and by measuring the volume of water evolved .The chemical structure of the new prepared polyesters were elucidated using Faurier transform infrared (FTIR) spectrophotometer, and the molecular weight determinations were conducted by Mass spectrophotometer. The average molecular weight of the novel polyesters compound ranged from 980 to 1500. The biodegradability of the new prepared polyesters gives us good indications the ability to be environmentally friendly. The new prepared polyesters were formulated and evaluated as a synthetic –based mud (ester–based mud) for oil–well drilling fluids .The evaluation includes study of the rheological properties, filtration and thermal stability of both reference commercial ester–based mud and ester based–muds formulated with the new prepared polyesters according to AIP specifications.***

Keywords: Inedible Oils, Castor Oil, Ester–Based Mud, Biodegradation.

1. Introduction

Drilling fluids are required for drilling oil and gas wells. During drilling, drilling fluid is circulated down the hollow drill pipe, through the bit and up the annulus between the drill pipe and the borehole. The fluid carries drill cuttings (crushed rock produced by the drill bit) to the surface [1]. The separated cuttings are in most cases, contain 5 to 15% adhering drilling fluids [2]. The physical as well as the chemical properties of the mud must be carefully controlled; Synthetic based drilling fluids SBFs are a relatively new class of drilling mud that is particularly useful for deep water and deviated hole drilling. They were developed to provide an environmentally superior alternative to oil based drilling fluids OBFs [3]. The synthetic base fluid is a drilling fluid ,where the base fluid consists of non-water soluble organic compounds, have a high biodegradability .There washave several quantifiable benefits compared to OBMs ,low toxicity and reduced irritant properties improve worker safety, elimination of diesel as a mud base reduces pollution hazard and risks and improves worker safety[4]. Biodegradation rates are influenced by different factors like temperature, fluid concentrations, and surface area size of target material. Ester-based mud has been proven to biodegrade more rapidly than other base fluids currently in use [5]. The use of vegetable oils in non-food applications has attracted appreciable interest because of their biodegradability, ability to undergo chemical modifications and renewable nature [6]. Ricinoleic acid (hydroxyl fatty acid) is the meager constituent fatty acid in castor oil (85 – 95%). Castor oil is inedible oil which is one of the crops available, reachable oil[7, 8].The vegetable oils are also used to prepare different kinds of other polymeric resins, such as epoxy, polyester amide[9], polyurethane[10]and others. The traditional seeds like linseed, soybean, coconut and castor oil have been used successfully for the above purpose[11-14]. These resins have been used in different fields of applications such as paint, coating, adhesives, binder for composites, etc.[15 -17]. Based on our literature search, there are very few reports on the use of castor oil or its directives alone in making polyester for based-mud application. The first attempts to prepare ricinoleic acid were made by Friedrich Krafft[18].

Some of article research modified vegetables oil with other chemicals to form the polymers with improved properties [19, 20]. In the present study, the synthetic ester based-mud was synthesized in the transestrification process. The method for the production of ester transestrification reaction was described by Patton[21].To perform all the functions of drilling fluids effectively, the properties of formulated drilling fluids must conform to the API 13B Specifications. The main property that indicates the performance of the drilling fluid is the rheology of the fluid[22]. Rheology off drilling fluid includes the apparent viscosity, plastic viscosity and yield point. Plastic viscosity relates to the potential of flow resistance due to mechanical friction [23]. The yield point is the key rheological parameter for evaluating hole cleaning, barite sag, equivalent-circulating density, surge pressure and it indicates the ability of the drilling fluid to carry the cutting to the surface [24]. Other properties include pH of the fluid, the electrical stability to ensure the stability of the emulsion and high pressure high temperature filtrate properties to provide the drilling fluid loss measurement during the drilling operation[25].

2. Materials and Techniques

A. Materials

All chemicals that were used throughout this investigation are of analytical grade and used as they are without more purification. Castor oil (BDH, England), Glycerol (Al-Gomhorya Co., Egypt) and Phthalic anhydride (Aldrich Company), while Ethanol, Toluene, Potassium Hydroxide

and Potassium Hydrogen Phthalate were used as purchased (Morgan Co., Egypt).

B. Techniques

Preparation of the Main Target Compounds

Preparation of the main target compounds synthesis through:

a. Extraction of ricinoleic acid (hydroxyl fatty acid) from castor oil.
b. Syntheses of novel polyesters form different ratios of hydroxyl fatty acid (35, 55, and 75%).

Extraction of Ricinoleic Acid from Castor Oil

Average composition of castor seed oil [Ricinoleic acid (85 – 95%) Oleic acid (2 – 6%) Linoleic acid(1 – 5%) α-Linolenic acid (0.5 – 1%) Stearic acid (0.5 – 1%) Palmitic acid (0.5 – 1%) Dihydroxystearic acid (0.3 – 0.5%) ,Others (0.2 – 0.5%). Into a 1L two neck round bottom flask attached to reflux condenser and mechanical stirrer, add (200g) of castor oil, (100g) of KOH and (80 ml) of ethanol. The reaction mixture was refluxed until no oil globules are present. The reaction mixture was distilled to recover the alcohol. The residue was dissolved in (300 ml) hot water and stirred for (90 min.) until the mixture becomes almost clear. Then a diluted of 300 ml of sulfuric acid (98%) in 700 ml water. the diluted solution with added with continuous stirring for (5 min). The oily layer was separated and filtrated in steam-jacketed funnel and finally allowed to cool. The first attempts to prepare ricinoleic acid were made by Friedrich Krafft[18].

Preparation of Polyester with (35, 55 & 75%) Ricinoleic Acid Ratio

Three different polyesters formulated according to the ratio of ricinoleic acid (35, 55 &75%) have been prepared by polyesterification reaction according to the procedure of Patton[19]. pre-weighed ingredients according to the formulated ratio of glycerol , phthalic anhydride and ricinoleic acid in present of CaO (Catalyst) and xylene(solvent) were charged respectively into a 1L four-neck round bottomed glass reactor equipped with a condenser, thermometer, mechanical agitator and a Dean-Stark decanter for separating the water evolved from the reaction. The mixture was stirred and temperature was raised to 120–180 °C for 1 h. The temperature was subsequently increased and maintained at 220–240°C. The reactions were completed after the by-product (i.e. water of reaction), was collected to an amount according to that calculated from the reaction stoichiometry. Progress of the polyesterification reaction during the synthesis of samples, was monitored by periodically checking the acid number of the reaction mixture at intervals time to determine drop in acid value. Three novel polyesters were collected and coded as HD_{35}, HD_{55} and HD_{75} respectively. The Ingredients of the formulation and properties of the collected alkyls were given in Table (1).The chemical structures of the new prepared polyesters were elucidated using: Infra-red spectra of products were carried out by Fourier transform infrared (FTIR) spectrophotometer ATI Mattsonm infinity series TM, Bench top 961 controlled by win first TM V 2.01 software (in the Range 400-4000 cm^{-1}), and the Molecular weight determinations were conducted by (Mass spectrophotometer Hp- Model, Ms 5988).

Biodegradability Test of the New Prepared Polyesters.

The biodegradation ability of the new prepared polyesters was studded using different micro-organisms (natural flora) in Egyptian local media. In 100 mL batch flasks containing 20 mL basal salts medium with initial pH 7. The emulsion samples of prepared polyesters (HD_{35}, HD_{55} and HD_{75}) were prepared according to Piddington, CS.[28]. Incubation period was seven days at 30C^{o} in a shaking incubator (150 rpm). Growth was monitored by total viable count (TCFU) technique on tryptone glucose yeast extract medium (TGY) prepared according to Benson, HJ. after seven days[29].

Mud Formulation :to determine the potential of castor oil base polyesters as base oil for synthetic drilling fluid, it formulated with 100% synthetic ester (all oil system).Synthetic- based ester mud was performed by using the novel prepared polyesters (HD_{35}, HD_{55} and HD_{75}) compared to the imported synthetic- based ester mud (reference sample R). All samples were prepared according to American Petroleum Institute (API-1998)**[30]** .All additives for ester based mud and the imported ester -based mud M_R were obtained from PICO Company .So we have (3) mud formulations and a reference sample mud.

M_R: Mud formulation with the imported ester mud (R).
M_1: Mud formulation with the new prepared polyester (HD_{35}).
M_2: Mud formulation with the new prepared ester (HD_{55}).
M_3: Mud formulation with the new prepared ester (HD_{75}).

Rheological Properties: The rheological properties synthetic-based muds Comprises of Apparent viscosity (A.V), plastic viscosity (P.V) and yield point (Y.P) and gel strength. The rheology of the fluid was measured by Fann 35 viscometer. According to API recommended practice for field testing oil-based drilling fluids ,API RP 13B-2 , the viscosities of the samples were measured with 6 different speeds,3,6,100,200,300 and 600 .rpm . Apparent viscosity (A.V), plastic viscosity (P.V) and yield point (Y.P) were calculated using formula (1), (2) and (3).

A.V = Reading at 600 rpm / 2 (1)
P.V = Reading at 600 rpm - Reading at 300 rpm (2)
Y.P = Reading at 300 rpm – plastic viscosity (3)

The gel strength of the mud is a measure of the minimum shearing stress necessary to produce slip-wise movement of fluid. It was determined by stirring the sample thoroughly at 600 rpm .then the was set off and the readings are generally taken **(1)** after 10 sec rested agitation of mud in the cup (G_{10} sec) **(2)** After the mud in the cup has been rested for 10 min rested (G_{10} min). Thixtropy of the mud is the difference between the reading after 10 sec and 10 min.

High Pressure- High Temperature Filter Press

The test method for filters loss is performed by using standard HP- HT filter loss model (107c). The test was run at (350^{o}F and 500psi) and the volume of filtrate recorded from the graduated cylinder at the end of cylinder 2, 5, 10, 15 and 30 minutes. The relation between time and volume of filtrate was plotted to calculate the corrected filter loss.

Thermal Stability Tests

The thermal stability of the synthetic polyester- base mud done to check the ratio of deterioration in filtration and rheological properties of synthetic polyester- base mud under high temperature, high hydrostatic pressure and continuous circulation the following test was carried out. Prepare synthetic polyester- base mud formulation for each of new prepared polyesters (HD_{35}, HD_{55} and HD_{75}) and reference mud (R) with ratio 100% ester base mud. The samples were placed in a rolling oven operating at 350°F for 16 hours. The samples were removed and cooled for 20 minutes in a cold water bath. Samples were then blended in a high speed blender for few minutes; A.V, P.V, Y.P, G_{10}sec, G_{10}min and filter loss were determined. The rheological properties were compared before and after thermal stability test [31].

3. Results and Discussion

Fig. (1) depicts one of the plausible mechanisms of Polyesterification Reaction Mechanism. The average degree of polymerization is monitoring by determining the acid number of the aliquot of the reaction mixture and by measuring the volume of water evolved [32-34] Table (1) was given the ingredients and properties of the prepared samples.

KOH Titration: Monitoring the reaction using acid number of in-process samples taken at intervals were determined by titrating with a (0.1M) KOH solution to the phenolphthalein end point after dissolution in a mixture of toluene and ethanol (1:1) [35,36].

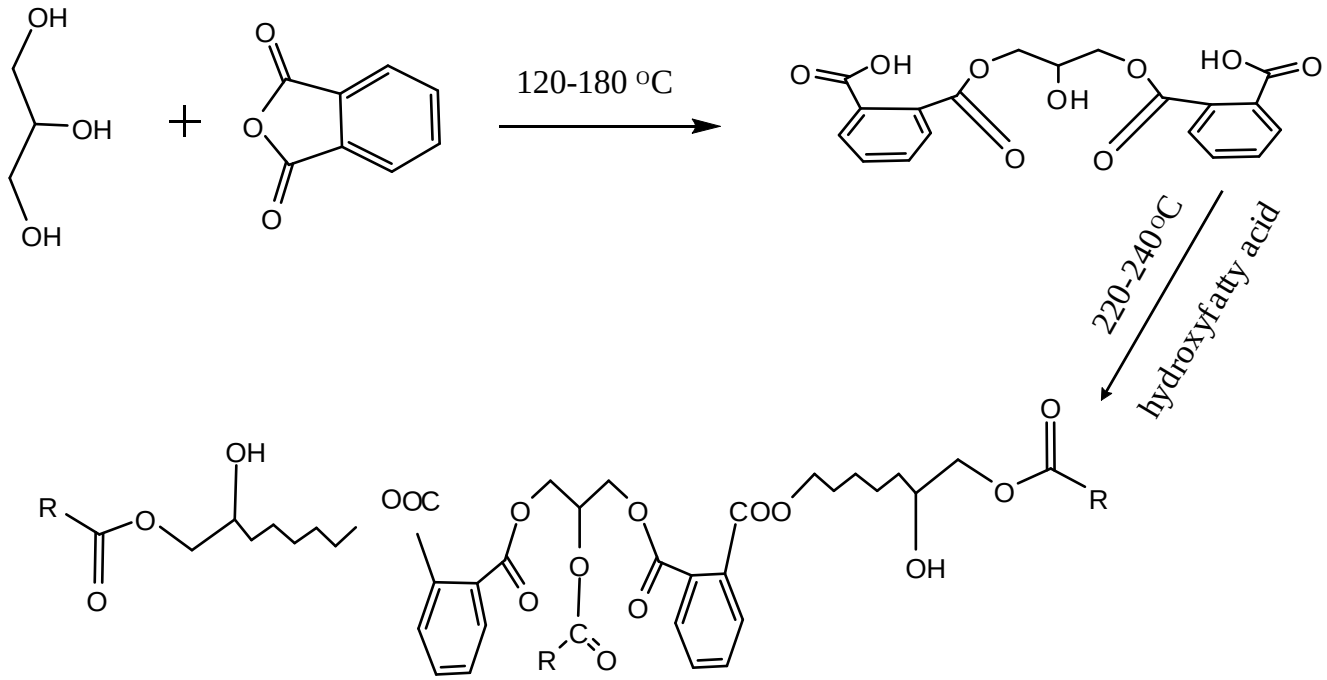

Figure 1: Expecting Mechanisms for the Prepared Polyesters (HD_{35}, HD_{55} and HD_{75})

Table 1: The ingredients and properties of the prepared samples

Ingredients	*Polyesters*		
	HD_{35}	HD_{55}	HD_{75}
Hydroxyl fatty acid(%)	35	55	75
Glycerol (%)	35	25	15
Phthalic Anhydride (%)	30	20	10
Water collected from the reaction (ml)	18	36	54
Acid value (mg KOH g^{-1})	12	8	5
Properties of Polyesters			
Molecular weight	971	1223	1518
Color	Dark	Brownish	Light

The chemical structures of the new prepared polyesters (HD_{35}, HD_{55} and HD_{75}), was confirmed by:

Infrared Spectroscopy (IR): FTIR spectra of polyester samples and ricinoleic acid were recorded to confirm their structures, Fig. (2).The strong band at 1,730 cm-1 is due to the carbonyl group in ester linkages. The weak absorption bands at 1,580 and 1,599 cm-1 arising from C=C are due to the aromatic rings in phthalic anhydride. Free hydroxyl groups are expected to be present at 3,486–3,524 cm-1 resulting from stoichiometric excess of glycerol in poly esters formulation and these groups are present in oleic acid by low intensity. Bands were observed at 3,004–2,854 cm-1 for C–H stretching aromatic and aliphatic, 1,458 cm-1 for C–H bending, 1,282 and 1,125 cm-1 for C–O–C stretching of ester. All these characteristic absorption bands support the structure of polyesters samples formed from ricinoleic acid.

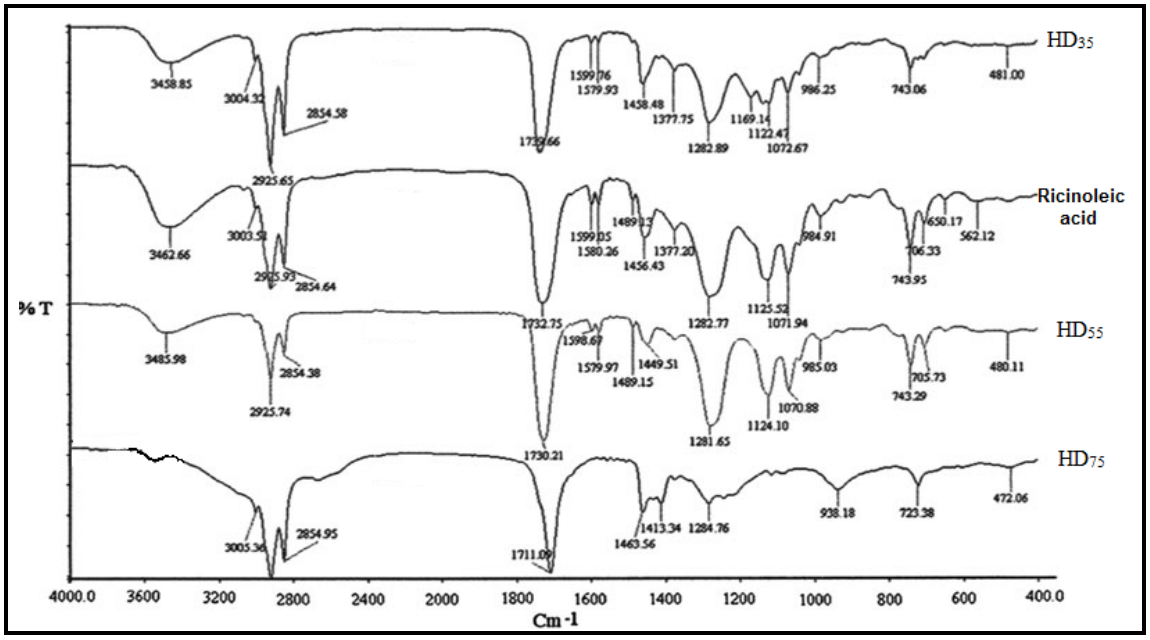

Figure 2: FTIR spectra of polyester samples and ricinoleic acid

Biodegradation of the prepared polyesters

This study aimed to investigate the ability of some microbial strains to utilize different emulsion samples as sole source for carbon and energy. Results show in Fig. (3) and Fig. (4) indicated the ability of the studied microbial strains to grow on the emulsions samples as a sole source of carbon and energy, indicating the emulsion of prepared polyesters (HD_{35}, HD_{55} and HD_{75}) biodegradability compared to the reference sample ester base (R) where CFU/ml is total count of the growth colliens of these organism in one mill liters (ml)[37].

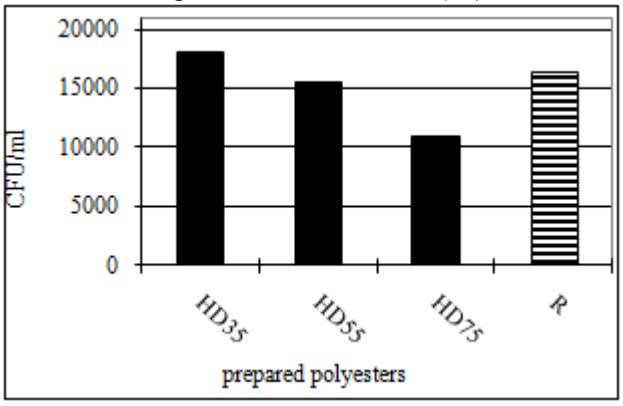

Figure 3: Growth of Bacillus sphaericus HN1 on tested compounds

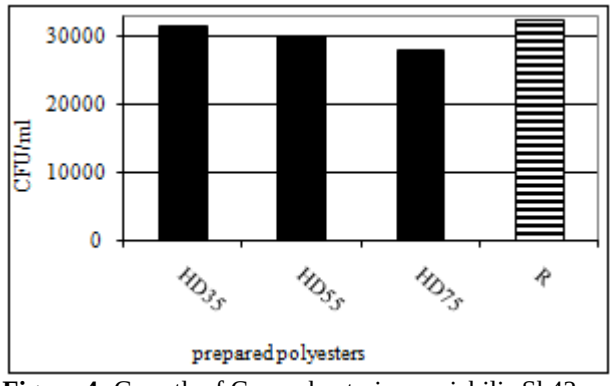

Figure 4: Growth of Corynebacteriumvariabilis Sh42 on tested compounds

Evaluation of the Prepared Esters as Ester-Based Mud

The new prepared polyesters (HD_{35}, HD_{55} and HD_{75}) were formulated as a synthetic based mud (ester-based mud) [All oil system-100% synthetic ester] . The formulations of the new prepared polyesters (M_1,M_2&M_3) were evaluated . The results were listed in Table (2) and were showed in Fig (5-8).

Table 2: The evaluation results of the new prepared polyesters (M_1,M_2&M_3) .

Mud Evaluation	M_1	M_2	M_3	M_R	API 13B Specification
Apperant viscosity (cP)	52.5	60	65	40	35-65
Plastic viscosity (cP)	34	41	42	19	25-40
Yield point (1b/ft^2)	37	38	46	42	15-45
Gel strength 10 sec (1b/100ft^2)	5.5	6	6	5	8-20
Gel strength 10 min (1b/100ft^2)	7	7.5	7	6.25	8-30
Thixtropy (1b/100ft^2)	1.5	1.5	1	1.25	0-5
HTHP filtrate (ml/30 min)	2.3	2.2	2	2	<10 ml

Thermal stability

One of the major problems of drilling fluids is their instability to shear and thermal aging. In drilling operations, drilling fluids encounter geological formations with different temperature. The combination of thermal and shear stresses accelerates the degradation of the drilling fluids and results in significant reduction in its effectiveness. Table (3) illustrates the relative stabilities of ester–based mud formulated with the new prepared esters (M_1,M_2&M_3) compared to the reference ester–base mud (M_R) after aging for 16 hours at 350 F^o, high hydrostatic pressure and continuous circulation.

Table 3: The relative stabilities of ester-based muds (M_1,M_2&M_3) compared to (M_R)

Mud	Hours of aging at 350°F	A.V (CP)	P.V (CP)	Y.P 1b/l00ft^2	Gel strength 1b/l00ft^2		Filter loss (ml)
					G_{10}sec	G_{10}min	
M_R	0	40	25	42	5	6.3	2
	16	38	21	38	4	6	1.8
M_1	0	65	34	37	6	7	2.3
	16	52	30	33	5.5	6.5	2.1
M_2	0	60	41	38	6	7.5	2.2
	16	46	38	33	5.5	7	2
M_3	0	53	34	46	5.5	7	2
	16	41	29	39	5	6.5	1.7

4. Conclusion

In this study the ability castor oil (inedible oil) to undergo chemical modifications and renewable nature. Ricinoleic acid (hydroxyl fatty acid) is the meager constituent fatty acid in castor oil (85 – 95%) is a based component in the esterification reaction. Esterification Reaction of Ricinoleic acid (hydroxyl fatty acid) produces novel synthesis castor- based polyester". The based polyesters were successfully synthesized by using the one-step. The new prepared polyesters (HD_{35}, HD_{55} and HD_{75}) were chemically confirmed and have a high degree of degradability (Environmentally friendly). The polyesters-based mud (M_1,M_2&M_3) shows results combatable to API specifications and reference sample, which is accepted to the international company.

1) Rheological properties of the novel prepared polyester-based mud performed a superior results compared to the reference ester – based mud (M_R).
2) HP – HT filter lossat (350 F ^{o} – 500 psi) for the ester – based muds formulated with the new prepared polyesters (M_1,M_2&M_3) were compared to the reference ester – based mud (M_R. The results were 2.3 ml for ester – based mud (M_1) ,2.2 ml for ester – based mud (M_2) , while (M_3) ,2 ml same to (M_R) filter loss .both ($M_{1\&}M_2$) were computable with filter loss of the reference sample (M_R),
3) Ester–based mud formulated with the new prepared polyesters (M_1,M_2&M_3) give a good degree of stabilities compared to the reference ester–base mud (M_R) after aging for 16 hours at 350 F^o, high hydrostatic pressure and continuous circulation.

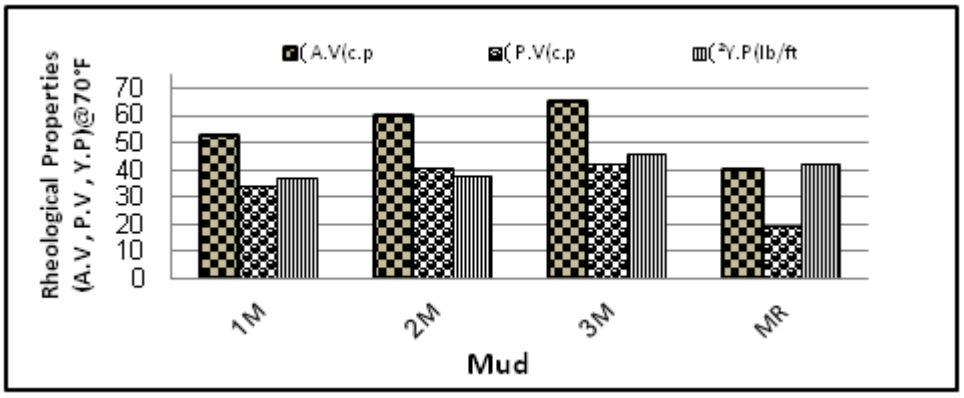

Figure 5: Rheological properties of synthetic esters-based mud (M_1,M_2&M_3) compared to refers sample (M_R)

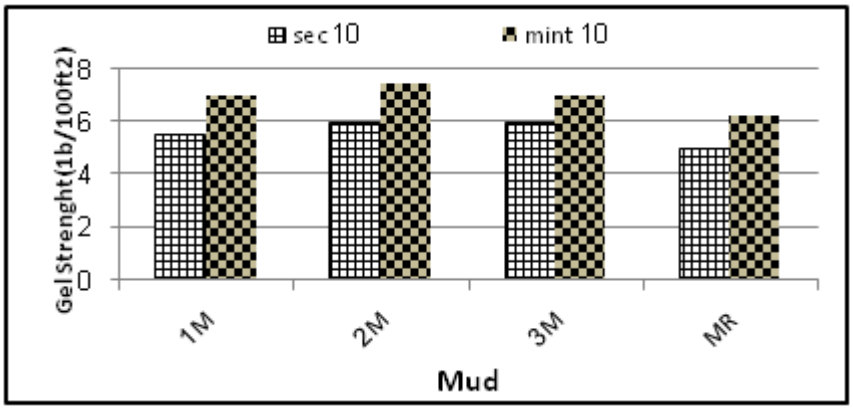

Figure 6: Gel Strength of synthetic esters-based mud (M_1,M_2&M_3) compared to refers sample (M_R)

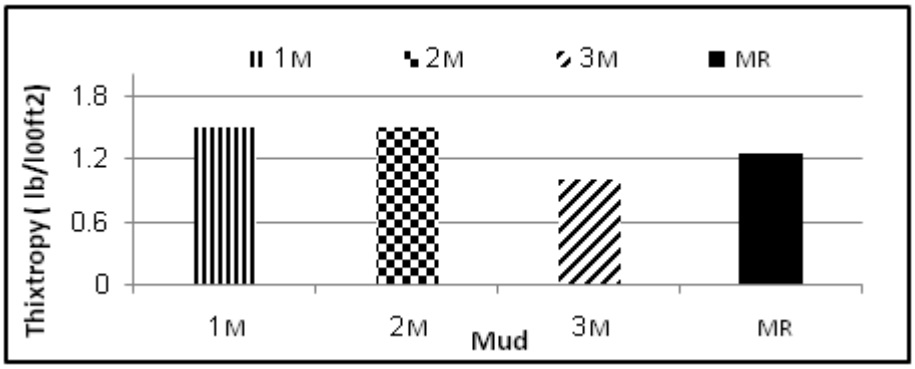

Figure 7: Thixtropy of synthetic esters-based mud (M_1,M_2&M_3) compared to refers sample (M_R)

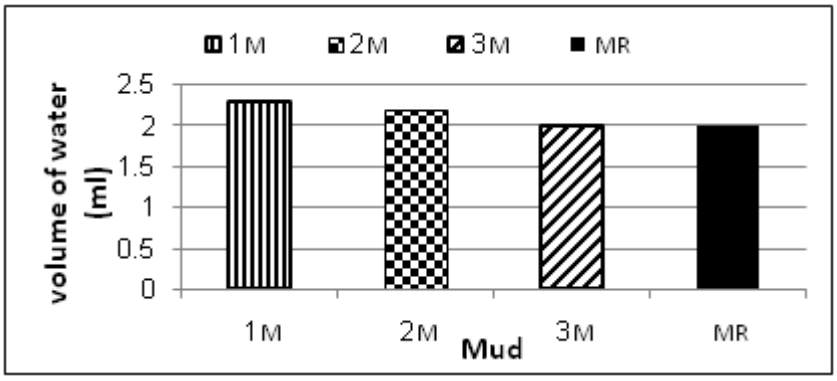

Figure 8: Filter loss (ml) of synthetic esters-based mud (M_1,M_2&M_3) compared to refers sample (M_R)

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