Esteramide As an Enviromentally Friendly Synthetic Based Driling Fluids

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Abstract: Novel oleate esters of lauricamide were prepared by the reaction of oleic acid and lauricamide (derived from the reaction of lauric acid and diethanol amine) .The chemical structure for the new prepared lauricamide-mono and di-oleate esters were elucidated using elementary analysis, (FTIR), H^1NMR and chemical ionization mass spectra(CI/Ms) spectroscopic techniques. The new prepared esters have high biodegradability and a lower toxicity (environmentally friendly) so they were 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 properties of the ester based–muds formulated with the new prepared esters compared to the reference commercial synthetic–based mud.
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Key words: - Drilling Fluids –Rheological Properties, Biodegradation.

1. Introduction

It is a matter of common experience in the oil and gas industry that the drilling of oil or gas wells is carried out with the aid of circulating drilling mud or drilling fluids. So, the success of any well drilling operation depends on many factors, one of the most important of which is the influence of the drilling fluid. The fluid performs a variety of functions that influence the drilling rate, the coast, efficiency and safety of the operation **[Holland D., et al., (2003)].** Historically, water-based mud (WBMs) or oil-based mud (OBMs) has been used for offshore wells. But recently, the U.S. Environmental Potential Agency (EPA) regulated drilling operation **[Christopher J., et al, (1995)]**. SBMs have 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, some of an important reason can be listed blow **[Moritis G., (2011)]**. The synthetic based fluid is a drilling fluid where neither the base fluid nor the additives are of petroleum origin so, they are environmentally friends and have a high biodegradability, low toxicity. Salt brains usually is dispersed in the synthetic phase to form an emulsion, the other ingredients of the SBF include emulsifier, barite, clays, lignite and lime. A whole new class of non-toxic drilling fluids have been developed in the last two decades.

This mud formulated with a variety of synthetic organic base fluids. The resulting so-called synthetic based mud (SBMs), which are also known as pseudo oil- based mud **[Veil J.A., et al., (1999); Growcock F. B, et al., (2002)].** Ester-based organic compounds are one type of synthetic base fluid added to drilling mud used during offshore oil-drilling operations **[Dardir et al, (2011 b)]**. Esters are relatively stable under neutral conditions, but may undergo hydrolysis and revert back to the acid and alcohol under basic or acidic conditions. Esters are commonly used in the North Sea and have been used extensively in the Gulf of Mexico **[Candler J.E., et al., (1993)]**.

2. Material and Experimental Techniques

Preparation of N, N- di ethanol lauricamide

Lauric acid (1mol) was added to diethanolamine (1mol) in three necked flask, (0.02mole) of sulphuric acid as a catalyst and xylene was added as a solvent. The Temperature was raised slowly up to 50°C .Nitrogen gas was passed in with continuous stirring. The reaction mixture was heated with continuous stirring until the theoretical amount of water was collected, solvent was distilled off. The product was purified by washing with hot solution of (5%) sodium bicarbonate then dissolved in petroleum ether (B.p.40-60°C) . The organic layer was separated. N, N-diethanol lauricamide **(A_2)** was the yellow oily product obtained after collecting 18 gm of water [**Vogel, A., (1956); Ibrahim S., (2006)]; Manawwer Alam, S.M. et al., (2008)].** The elemental analysis and Infra-red spectrum of the product was carried out by Fourier Transform Infrared (FTIR) spectrophotometer.

Esterification of N, N- di ethanol lauricamide

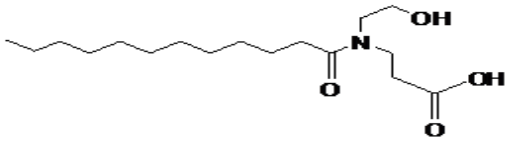
1 mole of the prepared fatty amide (N, N-diethanol lauricamide) (A_2) was added to olic acid (1 mole) or (2 mole) in three necked flask in presence of (0.005 mole) of solid p-toluene sulfonic acid as a catalyst and xylene as a solvent, The reaction mixture was heated with continuous stirring until the theoretical amount of water was collected in Dean-Stark tube.

The products were purified by washing with(5%) sodium bicarbonate solution then dissolved in petroleum ether _(b.p 40-60 C°).The organic layer

was separated and the solvent was distilled off **[Lietz et al., (1999) – Pouilloux et al., (1999) – Sekula et al., (2000)]**. The products obtained were as follows:

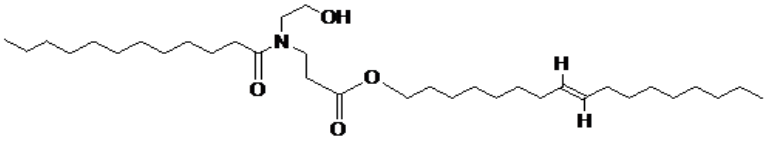
1. N-ethanol N'-(ethyl oleate) lauricamide (S_1) pale brown oily product was obtained after collected 18 ml water from the reaction.
2. N, N-di (ethyl oleate ester) lauricamide (S_2) brown oily product was obtained after collected 36 ml of water.

Elemental analyses were determined on a Perkin-Elmer 240C micro-analyzer; Infra-red spectra of products were carried out by (FTIRs), Molecular weight determinations were conducted by (Mass spectrophotometer Hp- Model, Ms 5988) and H^1NMR spectra was measured on a Varian GEMINI 200 (200 MHz) for each products (S_1) and (S_2).



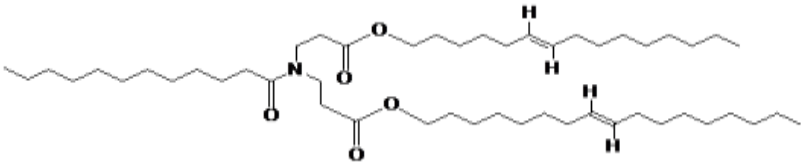
A_2

N, N- di ethanol lauricamide



S_1

N-ethanol N'-(ethyl oleate) lauricamide



S_2

N,N-di (ethyl oleate ester) lauricamide

Fig (1) : The chemical structures of the prepared compounds (A_2),(S_1)and (S_2)

Tests of Synthetic – Based Mud

Work for synthetic- based invert emulsion mud (ester- based mud)was performed by using the new prepared esters (S_1) and (S_2) compared to the imported known fatty acid ester (reference sample R) with 100% synthetic ester (all oil systems) . All samples were prepared according to American Petroleum Institute (API 1998) . All additives for ester based mud and the imported fatty acid ester R were from Baroid Company.

Mud Formulation

Ester oil 500 ml+ polar activator (0.2 ml, 0.025 ppb) + 8.5 ml primary emulsifier + 6 gm lime + 8 gm filtration control agent + 6 gm viscosifier + 0.95 ml rheological modifier + calcium carbonate as weighting material. For all mud formulations, all chemical additives were added slowly using stirring and mixed well in the mixer.

So we have (2) mud formulations and a reference sample mud, (100%) synthetic ester (all oil system).

M_R : Mud formulation with the imported ester mud (R).

M_{S1}: Mud formulation with the new prepared ester (S_1) N-ethanol N'-(ethyl oleate) lauricamide.

M_{S2}: Mud formulation with the new prepared (S_2) N,N-di (ethyl oleate ester) lauricamide.

Rheological Properties

Rheological properties of the synthetic-based muds were measured by using a chandler engineering laboratory model (API) viscometer chan 35 Model (3500). Apparent viscosity (AV), plastic viscosity (PV) and yield point (YP) were determined by making a relation between the share rate and share stress, where shear stress was taken from the dial reading which is in degree of the circle and shear rate (sec^{-1})= rpm x 1.067 . Unit of: PV in centipoises (CP), AV in centipoises (CP) and YP in 1b/100 ft^2.

Determination of Gel Strength and Thixtropy of a Mud

The gel strength of the mud is a measure of the minimum shearing stress necessary to produce slip-wise movement of fluid. Two readings are generally taken (1) after 10 second (G_{10} sec) (2) After the mud in the cup has been rested for 10 minutes rested (G_{10}

min). Thixtropy of the mud is the difference between the low reading after 10 sec, and 10 min.

Effect of Temperature on the Rheological Properties

Viscosity of the mud is a function of temperature more than pressure. It is necessary to measure viscosity at elevated Bottom Hole Temperature. This is done by using the viscosity-cup heater which is thermostat-controlled unit for heating the mud sample directly on a viscometer.

High Pressure- High Temperature Filter Press

The test method for filter 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 the volume of filtrate was plotted to calculate the corrected filter loss.

Thermal Stability Test

To test the thermal stability of the synthetic ester- base mud and to check the ratio of deterioration filtration and rheological properties of synthetic ester- base mud under high temperature, high hydrostatic pressure and continuous circulation the following test was carried out.

Prepare synthetic ester- base mud formulation for each of new prepared ester (S_1, S_2) and reference mud (R) with ratio 100% ester base mud. The samples were placed in a rolling oven operating at 350^{o}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; PV, AV, YP, G_{10}sec and G_{10}min and filter loss were determined. The rheological properties before and after the thermal stability test were compared **[Lahalih et al., (1989)]**.

Biodegradability of emulsion samples by using different organism

In 100 mL batch flasks containing 20 mL basal salts medium with initial pH 7. The emulsion samples [prepared esters (S_1, S_2)] were prepared according to **[Piddington, CS., et at., (1995)]**. The incubation period was seven days at 30C^{o} in a shaking incubator (150 rpm). Growth was monitored by total viable count (TCFU) technique of tryptone glucose yeast extract medium (TGY) prepared according to **[Benson, H.J., (1994)]** after seven days.

3. Results and Discussion

N, N- diethanol lauricamide (A_2) was prepared through elimination of water molecule and produce amide linkage and the ester products (S_1) N-ethanol N'-(ethyl oleate) lauricamide , (S_2) N,N-di (ethyl oleate ester)lauricamide were prepared through elimination of water and produce ester linkage. The chemical structures of the prepared compounds A_2, S_1 and S_2 were confirmed by:

The physic-chemical characteristic of the prepared compounds (A_2), (S_1) and (S_2) were listed in Table (1).

Table (1): Physic-chemical characteristic of the prepared compounds (A_2), (S_1) and (S_2).

Cpd.	Mol. Formula	Exp. M.Wt	Ref. Index	Density@20°C	P.p, °C
A_2	$C_{16}H_{33}NO_3$	288.64	1.480	0.984	3
S_1	$C_{34}H_{65}O_4N$	552.8	1.478	0.937	-1
S_2	$C_{52}H_{97}O_5N$	816.9	1.497	0.921	0

Elemental analysis of prepared compounds (A_2), (S_1) and (S_2) shows good coincident between the calculated and found values of C, H, O and N (%) Table (2).

Table (2): Elemental analysis of prepared compounds (A_2), (S_1) and (S_2).

Cpd.	Elemental Analysis					
	C%		H%		N%	
	Found	Cal.	Found	Cal.	Found	Cal.
A_2	59.03	59.11	10.41	10.34	6.90	6.89
S_1	73.99	73.92	11.77	11.87	2.62	2.54
S_2	76.39	76.51	11.46	11.98	1.52	1.72

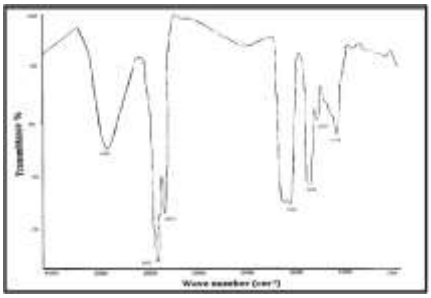
FTIR spectra of N, N- diethanol lauricamide (A_2) shows characteristic bands of the amide link and the characteristic bands of the ester links of (S_1) N-ethanol N'-(ethyl oleate) lauricamide,(S_2) N,N-di (ethyl oleate ester) lauricamide were listened in Table (3-4) and Fig. (2):

Table (3): FT-IR spectroscopic analysis of N, N- diethanol lauricamide (A_2).

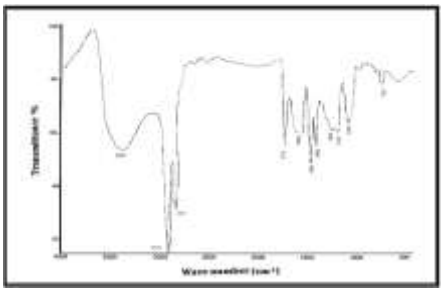
Functional groups	FT-IR Bands (cm^{-1})
	A_2
υ OH stretching	3402
υ C-O stretching	1174
υ C-H $_{sym}$ and C-H $_{asym}$ stretching	2855-2925
υ C= O (amide) stretching	1624
υ C-N (amide) stretching	1402

Table (4): FT-IR spectroscopic analysis of the prepared compounds (S_1),(S_2).

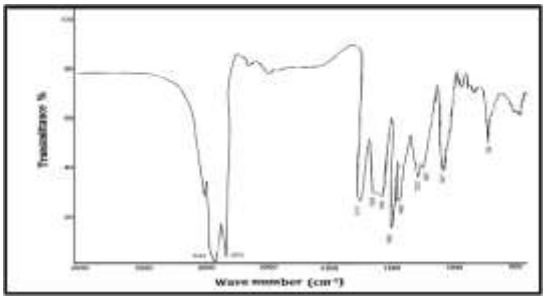
Functional groups	FT-IR Bands (cm^{-1})	
	S_1	S_2
υ C-O (ester) stretching	1179-1243	1207-1253
υ C=O(ester) stretching	1715	1719
υ C-H $_{sym}$ and C-H $_{asym}$ stretching	2855-2924	2855-2925
υ C= O (amide) stretching	1619	1622
υ C-N (amide) stretching	1407	1408



(A_2)



(S_1)

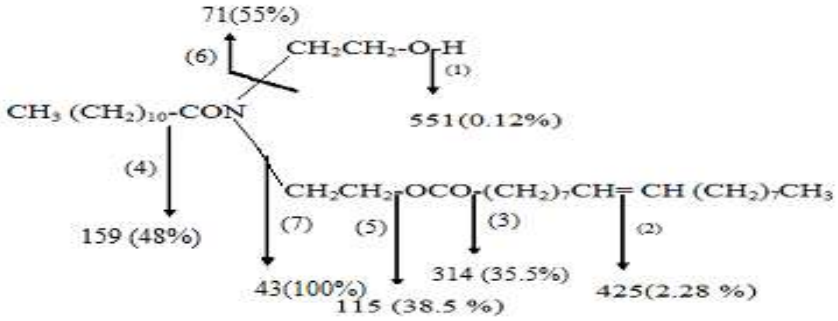


(S_2)

Fig.(2): FT-IR spectroscopic analysis of the prepared compounds (A_2), (S_1) and (S_2)

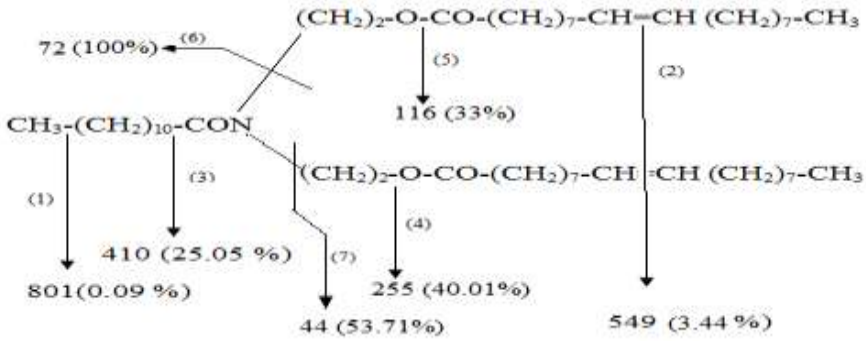
Chemical ionization mass spectra (CI/M_S) of S_1 and S_2 show in Schemes (1-2) and Fig (3) respectively. The mass spectrum of the major component shows mass peaks of (m/z) (abundance %) **[Maclafferty, F.W., (1980)]**.

The mass spectrum (CI/Ms) of N, N-di (ethyl linolineute ester) lauricamide (S_1) showed the base peak m/e at 43 (100%) which can be attributed to $\overset{O}{\overset{\|}{C}}-N$. The fragmentation can be schematically summarized as follows:

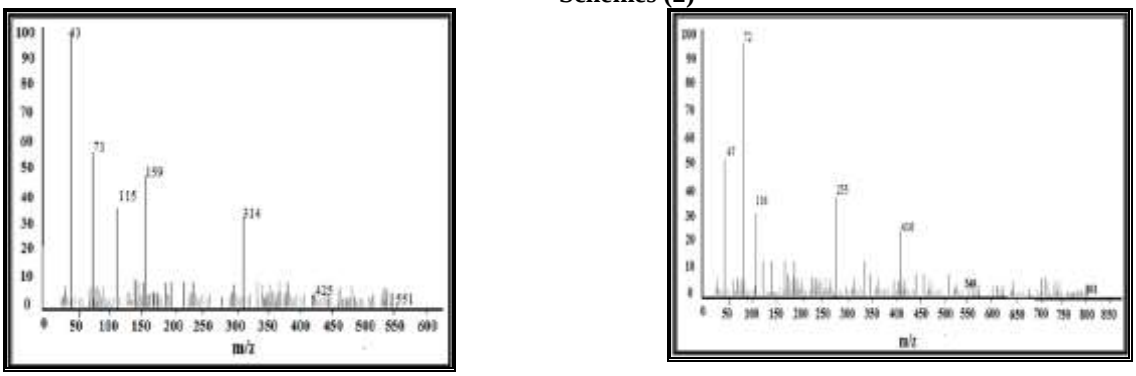


Schemes (1)

The mass spectrum (CI/Ms) of N,N-di (ethyl oleate) lauricamide (S_2) showed the base peak m/e at 72 (100%) which can be attributed to $\overset{O}{\overset{\|}{C}}-N-CH_2-CH_2$. The fragmentation can be schematically summarized as follows:



Schemes (2)



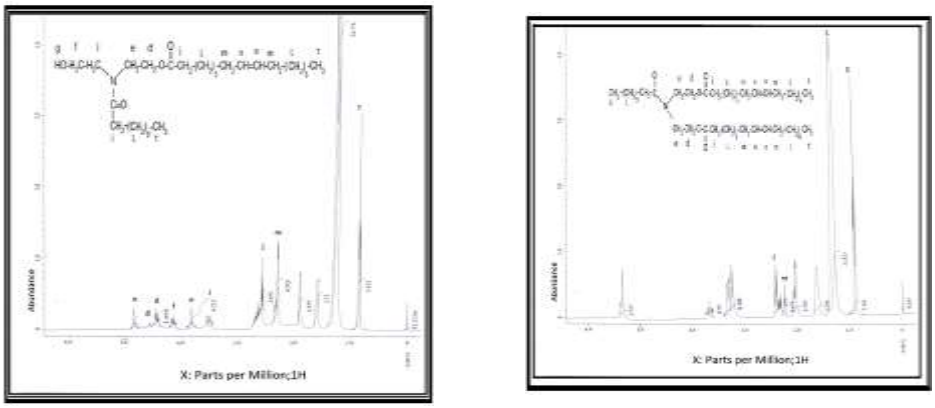
(S_1) (S_2)

Fig.(3): CI/Ms Spectrum of prepared compounds (S_1) and (S_2)

Proton nuclear magnetic resonance (H^1NMR) confirmed the chemical structure of S_1 and S_2 were listed in Table (5) and shown in Fig. (4).

Table (5): H^1NMR spectra of the prepared fatty ester amides $S_1$and S_2.

H^1-NMR spectra (ppm, $CDCl_3$)
For N, N-di (ethyl linolineute ester) lauricamide (S_1) : [0.88 (terminalCH_3 fatty chain)], [3.39, 3.48 (CH_2 attached to amide nitrogen)], [4.78 (O–H)], [3.61 (CH_2 attached to –OH], [5.48 (–CH=CH– protons attached to double bond of unsaturated fatty acid)], [1.29, 1.64, 2.18 (CH_2 fatty chain)], and [2.32 (CH_2 attached to C=O ester)] Fig. (3).
For N,N-di (ethyl oleate) lauricamide (S_2) : [0.88 (terminalCH_3 fatty chain)], [3.48 (CH_2 attached to amide nitrogen)], [5.48 (–CH=CH– protons attached to double bond of unsaturated fatty acid)], [1.26, 1.29 1.31, 1.53 (CH_2 fatty chain)], and [2.51 (CH_2 attached to C=O ester)] Fig. (3).



(S_1) (S_2)

Fig. (3): H^1NMR spectra of the prepared fatty ester amide S_1, S_2

Biodegradation of the prepared ester

The results show in Fig (4) and Fig (5) indicated that 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 esters (S_1, S_2) 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) **[STEBER, J., et at., (1995)].**

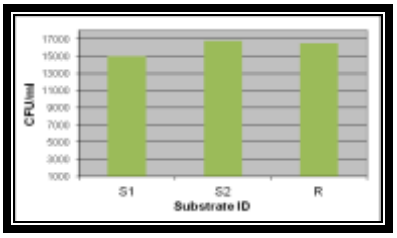


Fig. (4): Growth of Bacillus sphaericus HN1 on tested compounds

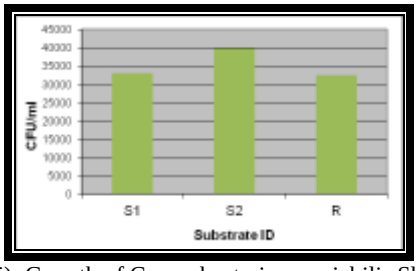


Fig. (5): Growth of Corynebacterium variabilis Sh42 on tested compounds

Evaluation of the prepared esters:

The new prepared esters (S_1, S_2) were evaluated as a synthetic based mud (ester-based mud) for oil – well drilling fluids. The mud formulation of synthetic – based muds were all oil systems - (100%) synthetic ester this formulation was considered as the control sample (reference) for the evaluation measurements of the new ester – based mud. All synthetic – based muds were prepared according to the American petroleum institute (API 1998), and this muds were evaluated as a synthetic based mud, for oil – well drilling fluids. In this research, the evaluation incorporates the following:

Rheological properties

The rheological properties of ester – based muds composed of esters mud (M_{S1},M_{S2}) were measured compared to the field ester – based mud formulated by the imported ester mud as a reference sample (M_R) . Rheological results at 77 ^oF were illustrated in Fig (6).

For both of (M_{S1}, M_{S2}) the apparent viscosity (AV) were (175 cp) which is more than the

apparent viscosity of the reference mud sample (26 cp). The plastic viscosity (PV) changing from (50 to 80 cp) for the new based mud compared to reference mud sample M_R which is equal to (18.5 cp), and the yield point (YP) ranges from (190 to 250 1b/100ft^2) for the new esters – mud where the yield point of the reference mud sample (M_R) is equal to 17 1b/l00ft^2.

From the above results, it had been shown that the rheological properties of the new ester – based muds (M_{S1}, M_{S2}), exhibit rheological properties value better than the reference (M_R) that's formulated with the imported fatty ester.

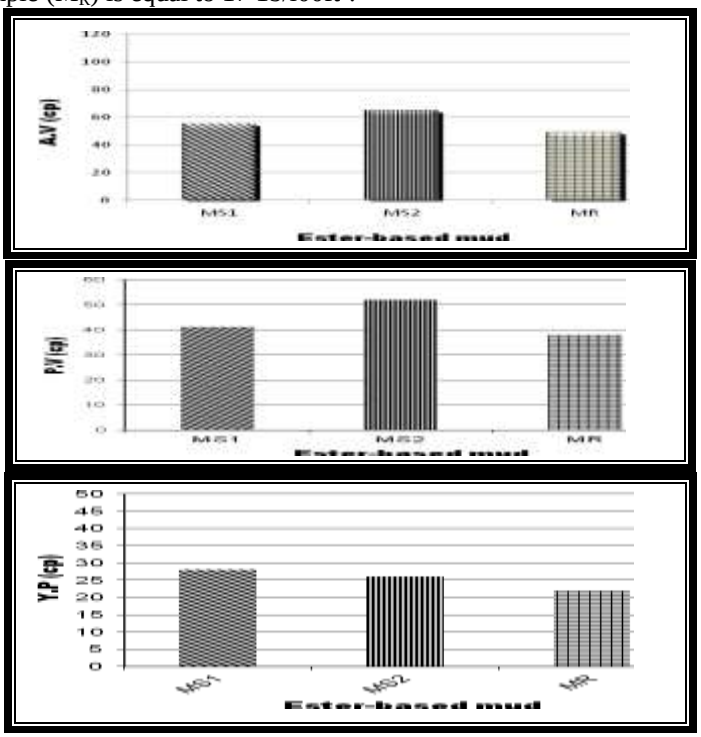


Fig.(6):Rheological properties of synthetic Esters-Based mud formulated with a new prepared esters (M_{s1}, M_{s2}), compared to refers sample (M_R)

Gel Strength

The gel strength of ester – based muds formulated by the prepared esters (M_{S1}, M_{S2}), were plotted in Fig (7) compared to reference mud sample (M_R).The Figure shows that the gel strength of esters – based mud (M_{S1}, M_{S2}), composed of new prepared (T_1, T_2) esters. Their values change from (3 to 5 lb/looft^2) after (10 sec), where the gel strength of the reference mud sample (M_R) was (3.51b/l00ft^2). The gel strength after (10 mint) varies from (6 to 8 lb/l00ft^2 for the prepared esters mud and was (6 1b/looft^2) for reference mud sample (M_R). The thixtropy of the prepared esters mud changes from (2 to 3 lb/l00ft^2) and the reference mud sample was (2.5 lb/l00ft^2). The results of gel strength of new prepared ester – muds change within acceptable range compared to the American Petroleum Institute [**API , (1998)].**

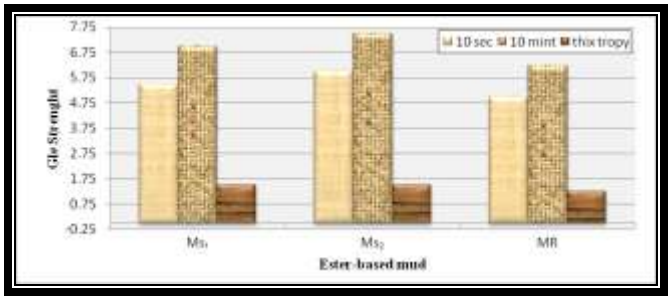


Fig.(7): Gel Strength of synthetic Esters-Based mud formulated with a new prepared esters (M_{S1}, M_{S2}), compared to refers sample (M_R)

Effect of temperature on the rheological properties of esters - based muds (M_{S1}, M_{S2}) and the reference mud sample (M_R).

Rheological properties vary under variable temperatures for (ester – based mud) formulated by the prepared esters (M_{S1}, M_{S2}),, Fig (8-10) shows the results of apparent viscosity(AV) , plastic viscosity (PV) and yield point (YP) for the ester – based muds compared to the reference (M_R), with temperature rises from 77 F° to 212 F^o .

Fig (8) show results of apparent viscosity, plastic viscosity and yield point for the new ester – based muds (M_{S1}, M_{S2}), compared to reference R, with temperature rises up to 212 F^o. The apparent viscosity (AV) was 175 cp and decreases to (17-25) cp for the new ester based muds respectively whereas the apparent viscosity of the reference (M_R) decreases from (26 cp to 10 cp).

In Fig (9) the plastic viscosity (P.V) was (85 cp and 100 cp) respectively for the new – ester – based mud (M_{S1}, M_{S2}), decreases to (15 cp and 24 cp) respectively when the temperature increases from 77 to 212 F^o the reference ester mud sample (M_R) Show reducing plastic viscosity from 18.5 cp to 8 cp.

In Fig (10) the yield point (YP) of the new ester – based muds under varying temperature up to 212 F^o were (170 1b/looft^2 to 2151b/l00ft^2)the decreases was (6 -4 1b/l00ft^2) when the temperature increases from 77 F^o to 212 F^o .Testing results for rheological properties under variable temperatures indicate that the new ester – based muds (M_{S1}, M_{S2}), were more stable under high temperature than the imported ester – based mud when utilized in field synthetic – based mud.

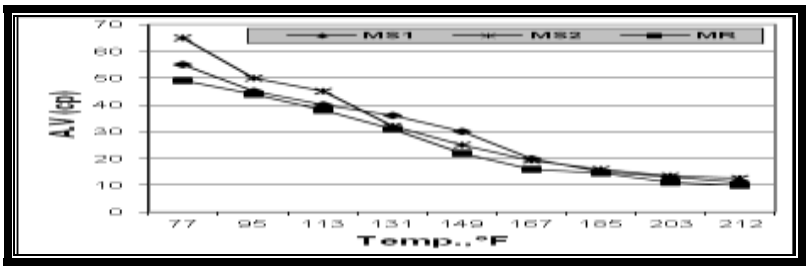


Fig.(8): Apparent viscosity(AV) -Temperature relationship of synthetic Esters-Based mud formulated with a new prepared esters(M_{S1}, M_{S2}), compared to refers sample ($_R$)

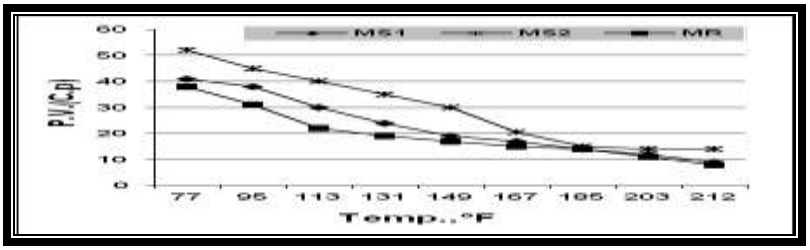


Fig.(9): Plastic viscosity(PV) -Temperature relationship of synthetic Esters-Based mud formulated with a new prepared esters (M_{S1}, M_{S2}), compared to refers sample (M_R)

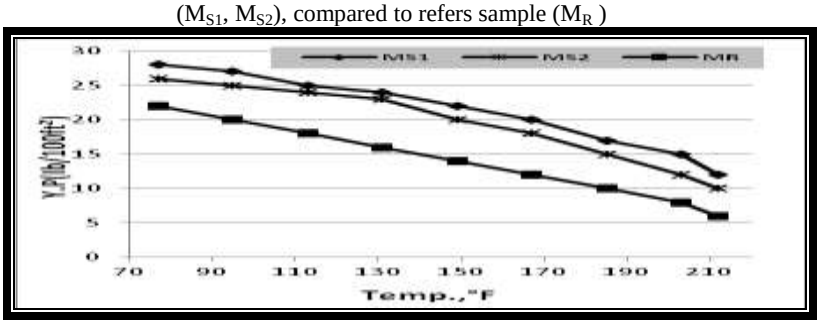


Fig.(10): Yield point (Y.P) -Temperature relationship of synthetic Esters-Based mud formulated with a new prepared esters (M_{S1}, M_{S2}), compared to refers sample (M_R)

Effect of temperature on gel strength of esters - based muds (M_{S1}, M_{S2}) and the reference mud sample (M_R).

The gel strength of the ester – based muds (M_{S1}, M_{S2}) composed of a new prepared esters changes with increasing temperature Fig (11) shows the effect

of temperature on gel strength, after 10 sec. ranging between 3.2-3 1b/l00ft^2 and when temperature increases from 77 F^o to 212 F^o the gel strength ranging between (1-2 1b/l00ft^2) while the reference ester based mud decreases from 5 to 2 1b/l00ft^2. While in Fig (12) the gel strength after 10 min. for the new ester – based muds ranging from (5.5to 5 1b/l00ft^2) when temperature increases from 77 F^o to 212 F^o where the reference sample (M_R) decreases from (8 to 3 1b/l00ft^2). So the muds are stable and they can keep their rheological properties for a period of time during the drilling operation.

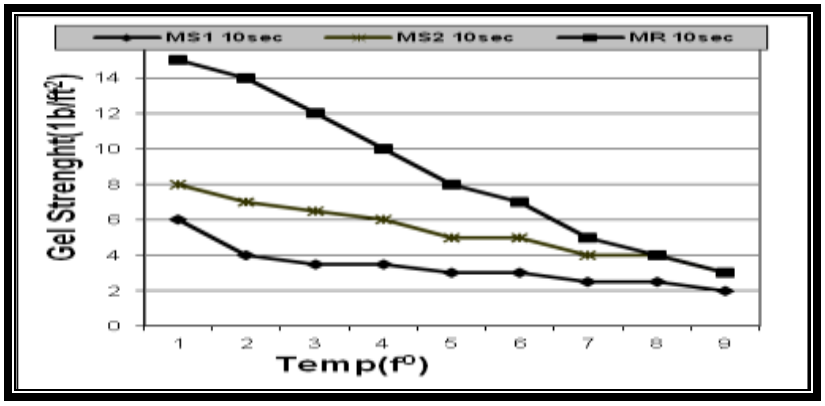


Fig.(11): G_{10} sec -Temperature relationship of synthetic Esters-Based mud formulated with a new prepared esters (M_{S1}, M_{S2}), compared to refers sample(M_R)

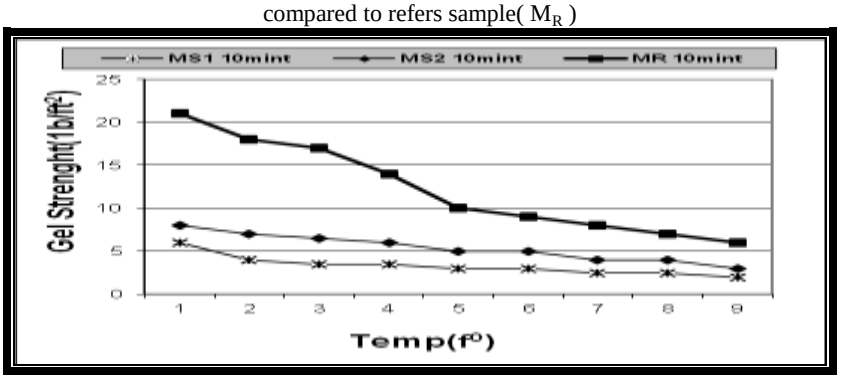


Fig.(12): G_{10} min -Temperature relationship of synthetic Esters-Based mud formulated with a new prepared esters (M_{S1}, M_{S2}), compared to refers sample (M_R)

Filtration

Table (6) shows that the HP – HT filter loss at 350 ^{o}F– 500 psi for the new ester – based muds formulated with the new prepared esters (M_{S1},M_{S2}) compared to the reference ester – based mud (M_R) (100%) ester mud. The results were 9 ml for ester – based mud (M_{S1}) which was computable with filter loss of the reference sample (M_R), while (M_{S2}) ester – based mud was 7.1 ml .The decrease of filter loss of the (M_{S2}) ester – based mud indicate their stability.

Table (6): Filter loss (ml) for the new ester – based muds (M_{S1}, M_{S2}) and reference ester mud (M_R).

Mud formulation	Filter loss(ml)
Reference mud (R)	9
M_{S1}	9
M_{S2}	7.1

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 (7) illustrates the relative stabilities of ester–based mud formulated with the new prepared esters (M_{S1}, M_{S2}) compared to the reference ester–base mud (M_R) after aging for 16 hours at 350 ^{o}F, high hydrostatic pressure and continuous circulation.

Table (7): the relative stabilities of ester – based muds (M_{S1}, M_{S2}) compared to the reference sample ester base (M_R) at 350 ^oF, high hydrostatic pressure and continuous circulation.

Mud	Hours of aging at 350^{o}F	Av (CP)	PV (CP)	YP 1b/l00ft^2	Gel strength 1b/l00ft^2	
					G_{10}sec	G_{10}min
M_R	0	80	60	38	18	24
	16	66	50	32	15	21
M_{S1}	0	55	41	28	6	7
	16	11	9	12	2	3
M_{S2}	0	65	52	26	8	10
	16	12.5	14	10	3	4

Conclusion

In this study experimental work and evaluation of the new prepared esters S_1-S_2 showed good results when utilized in the formulation of ester – based mud. Experimental work for all new prepared esters were conducted at the same time compared to field ester based mud (reference sample) with the international standards and specifications. From the evaluation data of the new prepared ester utilized in the ester-based mud we can conclude the following

1- Rheological properties of the most new prepared ester based mud performed a superior results compared to the imported ester – based mud (M_R), MS_2 showed the better result than MS_1 and reference.
2- The effect of temperature on the rheological properties of new ester – based muds (MS_1,MS_2) formulated with the new esters S_1-S_2 show a slight decrease by increasing temperature compared to field ester – base mud (M_R),also they are stable at high temperature and pressure with continuous circulation (thermal stability) .
3- Gel strength of ester – based muds formulated with the new prepared esters (S_1-S_2) showed a gradual decrease by increasing temperature as the field ester – based mud (M_R).
4- Filtration properties of ester – based muds formulated with the new prepared esters (S_1-S_2) showed low filter loss compared to the field ester – based mud (M_R).
5- The new prepared esters (S_1-S_2) have high biodegradable value compared to the field ester (R), S_2 showed the better result than S_1 and reference.

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