RESEARCH PAPER

Comparative analysis of the effect of plant-based and petroleum-based wax inhibition additives on heavy crude oil in the Niger-Delta

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Abstract

This study investigates the use of plant-based oils—soybean oil (SO), coconut oil (CO), and their biofuels, and petroleum distillates, namely automotive gas oil (AGO) and premium motor spirit (PMS) as potential wax inhibitors. At various volume concentrations (3 %, 5 %, 10 %), the impact of the additives on the pour point, rheology, and wax deposition of a heavy waxy crude oil sample from the Niger-Delta was investigated. The ASTM standard test procedures were used, using the cold finger apparatus for wax deposition test and paraffin inhibition efficiency determination. It was observed that though all the additives tested could reduce crude oil viscosity, SO and CO had the least effect compared with their biofuels and petroleum distillates (which had the greatest effect). PMS reduced the yield point (YP) significantly at all concentrations, while AGO reduced it only at a low concentration (3 %). The plant oils and biodieselts had a poor effect on YP. Again PMS had the most effect on pour point reduction, followed by AGO. SO and SO biodiesel (SOBD) showed a similar trend, raising the pour point at low concentrations, while reducing the same at higher concentrations. CO and COBD both reduced the pour point at all concentrations. The cold finger wax deposition test ultimately revealed that SO is a good wax crystal modifier. At a high concentration, its paraffin inhibition efficiency is almost comparable to that of AGO and PMS at reduced concentration. Its flow improvement property is however relatively poor, as it could not improve the YP and pour point of the crude oil significantly. In comparison with CO, however, SO shows greater potential for wax inhibition and flow improvement, while AGO and PMS show excellent results. The plant oil biodiesels (SOBD and COBD), however, showed more promise than the original plant oils (SO and CO) in flow improvement, but are less attractive in wax inhibition.

Keywords: Coconut oil, Cold finger, Pour point, Soybean oil, Viscosity, Wax

1. Introduction

The goal of every production operation is to maximize output in the safest possible way, thereby growing and sustaining the economic profile of the business venture. In a typical oilfield production this goal, however, is subject to numerous constraints limiting the production output. Wax precipitation and deposition in the oil stream during production is one of such concerns plaguing the upstream oil and gas industry. Waxes are higher molecular weight organic solids (saturates) present in the raw petroleum. As the raw petroleum rises to the surface through the tubing or through subsea pipelines, temperature decreases and eventually gets to the wax appearance temperature (WAT) or cloud point temperature. When the temperature of the pipeline or tubing is lower than the WAT and the bulk crude

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temperature stays higher than the pipeline temperature, the temperature gradient causes diffusion and concentration of wax molecules toward the region of lower temperature (pipe walls) resulting in the wax deposition phenomenon.[1] This process is known as molecular diffusion. The effect often results in reduced production, shutdown, and equipment failure, reducing total income and incurring more expenses in remediation management.[2] Chemical methods are notable for wax prevention. This involves the use of a variety of chemical inhibitors that interact with either the crude oil molecules or the pipe to inhibit crystal growth formation. It is determined that there are three different kinds of wax chemical inhibitors: wax crystal modifiers, wax dispersants and pour point depressants.[3] Wax dispersants are surface-active substances that change the wax-holding capacity of the pipe walls by adhering to the surface of the wax crystals and the interior walls of the pipe. This prevents the deposition of wax crystals. Pour point chemicals known as depressants lower the temperature at which gel forms during cooling, thereby lowering the consolidation of wax crystals, while chemicals that resemble wax and have comparable chemical structures are known as wax crystal modifiers. They are composed of polar part and hydrocarbon chains. Because of this structure, the chemicals may co-crystallize with wax molecules and take up their place in the structure of the lattice by way of hydrocarbon chains. To stop the wax particles from forming crystals, they further provide a steric barrier to the crystal.[4]

Several literatures are available on the use of chemicals for wax prevention, Nwankwo et al.[5] compared the efficacy of wax dispersants and crystal modifiers by continuous injection of the chemicals into a producing well, and observing their effect on pressure differential. They observed that wax crystal modifiers are more efficient than dispersants. Adeyanju and Layioye[6] investigated the potential of kerosene and premium motor spirit (PMS) as pour point depressants and wax inhibitors. They measured the mass of wax deposition inside a flow loop containing PMS and kerosene. Large amounts of solvents as high as 60 % are required to lower the pour points of light and medium crude by 8 and 2°, respectively. Chemicals such as xylene and toluene have been found to be most effective as wax inhibitors compared with diesel and PMS according to Straub et al.[7] and Anyanwu et al.[8] Current challenges posed by using conventional chemicals include environmental risks associated with spills or leaks, cost effects, and sustainability. Natural-based additives are therefore currently being studied to overcome these challenges.[9,10] Several researches have shown that plant oils can be a suitable replacement for these commonly used chemical additives like xylene and toluene for wax control. Amni et al.[10] investigated the impact of crude palm oil, crude palm kernel oil, and jatropha seed oil on paraffin prevention efficiency. Fadairo et al.[11] also examined the impact of castor and rubber seed oils on the rheological characteristics of waxy crude oil from the Niger-Delta. Coconut oil (CO) and moringa seed oil were investigated by Olusegun et al.,[12] cashew nut seed oil and orange seed oil by Eke et al.,[13] and Fadairo et al.,[14] respectively. These studies show great potential for plant-based seed oils for wax inhibition. However, there is no known record of research on the use of either soybean oil (SO) or its biodiesel as a wax inhibitor. Meanwhile, SO has great potential to be a wax crystal modifier as its molecular structure is composed of both polar and nonpolar parts. Its molecular flexibility and steric hindrance can also enhance co-crystalization with wax molecules thereby preventing its aggregation.[15] There is also limited data on the use of CO, automotive gas oil (AGO), and PMS as wax inhibitors. This study therefore aims to primarily understudy the effect of SO, CO, and their biofuels in comparison with AGO and PMS (petroleum distillates) on wax inhibition and flow improvement of heavy crude oil.

2. Experimental work and theoretical calculations

A waxy crude oil from the Niger-Delta region of Nigeria was examined in the laboratory for its physical properties such as density, specific gravity (SG), and API gravity. Density was measured using the ASTM D1298 Density tester. Further tests carried out on the crude oil sample include wax content determination, rheology, pour point, and paraffin deposition cold finger test (Table 1). Properties of the inhibitors were also examined before blending with the crude oil (Table 2). The mass of a specific volume (50 ml) of the fluid was determined using a pycnometer bottle and an analytical balance. Density was determined by dividing its volume (50 ml) by the difference between the mass of the pycnometer in its empty and full states. The pH of all samples was determined using the Jenway 3510 Standard Digital pH Meter.

2.1. Wax content determination

The total wax content of the crude oil was determined using the modified UOP 46–64 method

Table 1. Physical properties of crude oil sample.

Parameter	S.G	API	Pour Point	300 RPM	600 RPM	AV (cp)	PV (cp)	pH	Wax content (W%)	Yield Point (lb/ft^3)
Result	0.9273	21.1	−5	160	301	151	142	7.02	17.5	18

Table 2. Physical properties of additive.

Properties	Sample					
	SO	SOBD	CO	COBD	AGO	PMS
Density (g/cc)	0.8868	0.8416	0.856	0.8286	0.7782	0.6832
Specific gravity	0.8840	0.8390	0.8478	0.8260	0.7757	0.6810
Reading at 600 RPM	85	13	71	58	7	2
Reading at 300 RPM	44	7	35	30	4	1
Plastic viscosity (cp)	41	6	36	28	3	1
Pour point (°C)	−1	−10	12	9	< −15	< −15
pH	4.12	6.91	3.85	6.58	10.99	6.73

adopted by Eke et al.[13] A measure of 10 g of crude oil was mixed with 100 ml of toluene solvent. The mixture was heated and stirred for about 30 min to completely dissolve the oil and its soluble components. The residue (wax and asphaltene) was filtered, washed with cold toluene, and dissolved in 200 ml of 3:1 mixture of petroleum ether and acetone. The mixture was then cooled to −20 °C for 24 h for the wax to be precipitated out of solution. The pure wax was then filtered, dried, and weighed. The percentage by weight of the pure wax was then determined. All measurements were made at an ambient temperature of 28 °C.

2.2. Bio-diesel extraction

The biofuels of plant oils, SO and CO, were extracted by transesterification reaction.[14] A measure of 2 g of NaOH pellet was weighed and added to 40 ml of methanol and stirred until suspension was completely dissolved. After adding the methanol/NaOH combination to 200 ml of SO, the mixture was agitated for around half an hour at 60 °C. After letting the mixture settle for a full day, the glycerol at the bottom and the biodiesel on top were separated using a decanter. A measure of 100 ml warm water was added to the biodiesel to dissolve excess methanol and NaOH. The processed biodiesel was finally decanted after it had settled. This procedure for extracting soybean oil biodiesel (SOBD) was repeated for coconut oil biodiesel (COBD).

2.3. Determination of viscosity and yield point

The OFITE viscometer model 800, based on the API standard test for viscosity measurement,[9] was used to determine the samples' apparent viscosity (AV), plastic viscosity (PV), and yield point (YP). The pure crude sample was agitated and then placed in the rheometer cup. After lowering the instrument head to precisely the scribe line, the sleeve was secured in place. The speed was set at 600 and 300 revolutions per minute (RPM), and the dial was read for each speed after it stabilized. This procedure was repeated after the crude was injected with each additive at three distinct volume concentrations (3, 5, and 10 %). The three rheological qualities were identified as YP, plastic viscosity, and apparent viscosity. PV measures a fluid's non-Newtonian behavior, whereas AV measures a fluid's overall inability to move, considering both viscous and elastic features. The least amount of stress needed to start a flow or deformation is known as the YP. All viscosity/YP measurements were done at ambient temperature (28 °C):

$$\textit{Apparent Viscosity}\ (cp) = \frac{\textit{Reading at 600 RPM}}{2} \quad (1)$$

$$\textit{Plastic Viscosity}\ (cp) = 600\ \textit{RPM reading} - 300\ \textit{RPM reading} \quad (2)$$

$$\textit{Yield Point}\ (lb/ft^3) = \text{Reading at 300 RPM} - \text{Plastic Viscosity} \quad (3)$$

Amni et al.;[10] Ragunathan et al.;[9] Ajugwe et al.[15]

2.4. Cloud point and pour point measurement

The procedure for this test was the ASTM D5853-17a − a Standard test method for pour point of crude oils (Procedure A).[16] A measure of 40 ml of crude oil was placed in a clean test jar and a cork was fitted. An alcohol-in-glass thermometer was inserted into the test tube through the middle of the

cork. The test tube was kept in a deep freezer and the temperature observed every 3 min until the sample in the test tube began to cloud inside, indicating the WAT. The observation continued until a point where the sample does not show any movement for at least 5 s when the tube is placed in the horizontal position. This temperature minus 3 °C is the pour point of the sample. The crude was injected with each additive at volume concentrations of 3, 5, and 10 %, and the same procedure was followed to determine the impact of the additives on the pour point of the crude.

2.5. Paraffin inhibition efficiency (PIE)

The standard test procedure for determining paraffin inhibition efficiency (PIE) was the 'cold finger test,' adopted by Amni et al.[9] and Ragunathan et al.[10,17] A measure of 400 ml of the additive-free crude oil sample was heated to 50 °C before being added to the oil tank. By adding ice to the water tank to generate a sufficient 46 °C temperature differential, the bulk temperature was kept at 50 °C, allowing the cold finger detector to be set at 4 °C. Water was pumped through the steel tube (cold finger probe) that passes though the bulk crude oil sample (at 50 °C). After an hour, the wax layer on the cold finger probe was scooped and its mass measured. The procedure was repeated for crude oil doped with each of the additives at concentrations of 3, 5, and 10 %. The following formula was used to calculate each paraffin inhibitor's efficiency:

$$PIE\,(\%) = \frac{Wp - Wa}{Wp} \times 100\% \qquad (4)$$

where *PIE* is the paraffin inhibition efficiency; W_a is the mass of the deposited paraffin wax in the presence of chemical additive; and W_p is the mass of deposited paraffin wax in the absence of an inhibitor.[17]

3. Results and discussions

3.1. The additives and crude oil overview

According to Table 1, the crude oil sample is highly viscous with nearly neutral pH. SO and CO also have higher plastic viscosities compared with their biodiesels (SOBD, COBD). The crude oil and all the additives showed non-Newtonian fluid behavior, with their viscosities changing proportionally with shear stress. The high viscosities and pour points of the plant oils relative to the petroleum distillates can be attributed to the presence of high molecular weight long-chain fatty acid in the plant oil as evidenced by the pH values (Table 2). This further increases the likelihood of solidification, especially at moderate and low temperatures. These saturated compounds are not present in petroleum distillates.

3.2. Impact of additives on crude oil's rheological properties

All the additives decreased the crude's apparent and plastic viscosities at all concentrations. This is as a result of the significant difference in viscosity values between the individual additives and crude oil. Indeed as shown in Fig. 1, PMS showed excellent result in AV reduction followed by AGO and then SOBD and COBD, which seems to have the same effect at 5 and 10 %. A similar trend was observed for PV with CO having the least effect. At higher concentration though, AGO performed best followed by SOBD and PMS, which seems to have the same effect at high concentrations with COBD. At low concentration, however, SO showed better performance than the other additives except PMS (Fig. 2). In addition to viscosity reduction, petroleum distillates reduced the YP of the crude oil

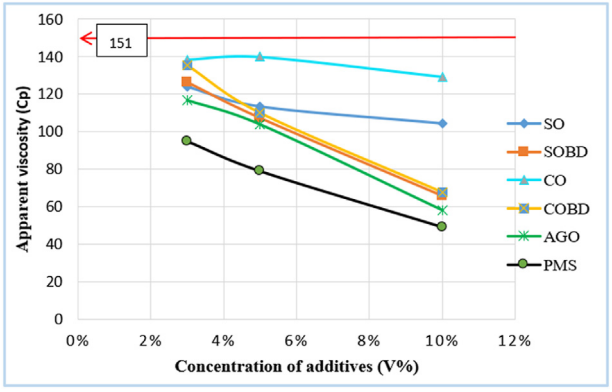

Fig. 1. Additives' impact on crude oil's apparent viscosity. Apparent viscosity of crude oil = 151 cp.

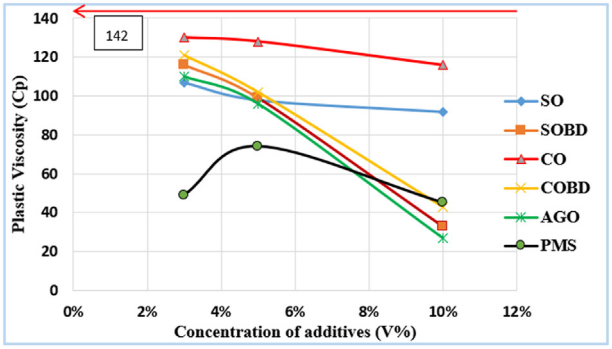

Fig. 2. Additives' impact on crude oil's plastic viscosity. Plastic viscosity of crude oil = 142 cp.

significantly compared with the plant oils. As shown in Fig. 3, PMS significantly areduced the YP at selected concentrations, AGO reduced it at 3 % and maybe at 5 % but it caused a high increase at 10 % similar to biodiesels. Their positive effect on YP is as a result of a combination of several properties of the distillates, including wax crystal modification, dispersion, solubility, and surface tension reduction. They tend to adsorb onto the surface of the wax particles thereby disrupting crystal growth by forming a thin layer that shears off the crystals easily.[3] This result also shows that indeed fatty acid content in plant oils can hamper the flowability of crude oil, as SOBD and COBD showed better performance than SO and CO, respectively. SO raised the YP at all concentrations while CO raised the YP at 5 and 10 % concentrations.

3.3. Impact of additives on crude oil's pour point

The crude oil's pour point is −5 °C, as shown in Table 1. This temperature is really the point at which clogging causes the oil to stop flowing to the surface through the tubing, as the oil stops flowing when positioned horizontally for 3–5 s. Both the closed-in tubing head pressure and flowing tubing head pressure are zero. At this point the well is considered dead until wax treatment is applied. As shown in Fig. 4, both SO and SOBD raised the pour point of the crude oil at a 3 % concentration, but lowered it at 5 and 10 % concentrations. Again PMS and AGO had the greatest effect in comparison with plant-based additives. As shown in Fig. 4, PMS and AGO have the greatest effect at a 10 % concentration only, while at 3 and 5 % they seemed to have the same effect as biodiesel. Their excellent pour point reduction ability also stems from a combination of different mechanisms including nucleation and steric hinderance. The additive's molecules once in contact with the wax molecules reorganize into micelle-like aggregates with a crystalline core, forming large amounts of smaller sized wax nuclei. This crystal size reduction mechanism keeps the wax particles small enough to remain stable in the oil phase. Also, because the petroleum distillates have similar chemical structures with waxes, with hydrocarbon chains (wax-like) and polar portions, they tend to co-crystalize with the wax molecules and occupy the position of the wax molecules in the lattice structure through the hydrocarbon chains.[17]

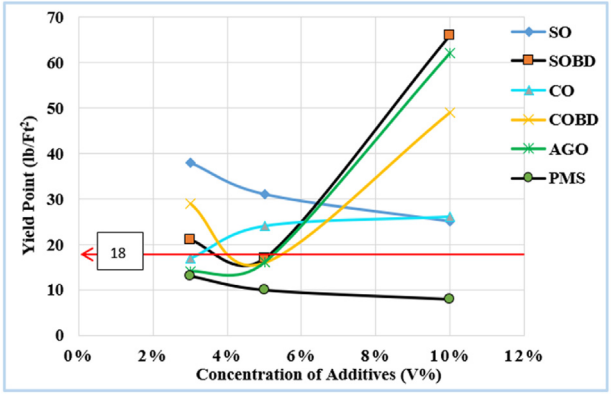

Fig. 3. Additives' impact on crude oil's yield point. YP of crude oil = 18 lb/Ft².

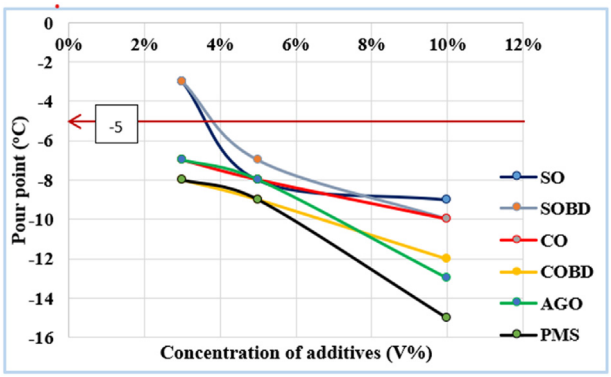

Fig. 4. Additives' impact on crude oil's pour point. Pour point of crude oil = −5 °C.

3.4. Wax deposition impact by additives

Table 3 displays the paraffin mass that is deposited at the cold finger probe at varying additive concentrations. An amount of 1.86 g of paraffin wax was deposited from the pure crude oil, additive-free. All the inhibitors were effective in reducing wax deposition, with AGO and PMS having a greater effect. PIE of each additive at various concentrations are as shown in Fig. 5.

From the figure, AGO exhibits the most effect as a wax inhibitor at lower concentrations than PMS with PIE of 34 and 55 % at 3 and 5 % concentrations, respectively, against PMS with 31 and 46 %

Table 3. Mass of Wax deposited on cold finger at different concentrations of additives.

Sample	Mass of Wax Deposit (g)		
	3 %	5 %	10 %
SO	1.67	1.29	1.04
SOBD	1.49	1.37	1.38
CO	1.74	1.62	1.60
COBD	1.51	1.46	1.57
AGO	1.23	0.84	0.78
PMS	1.28	1.00	0.70
PCO	1.86 g		

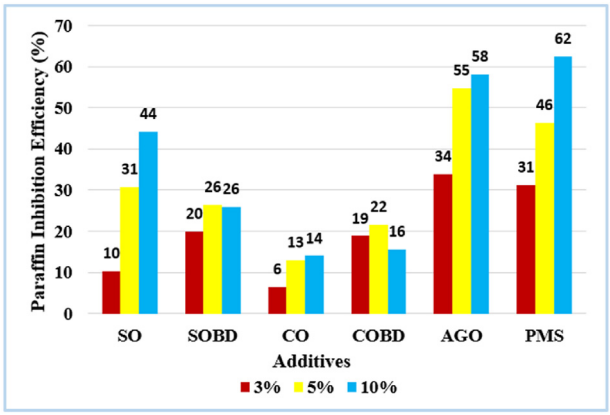

Fig. 5. Paraffin inhibition efficiency of additives at different concentrations.

efficiency. At 10 % concentration, PMS has a PIE of 62 % against 58 % for AGO. CO has the least efficiency of all concentrations, followed by COBD. CO has a PIE of 6, 13, and 14 % at 3, 5, and 10 % concentrations, respectively, while COBD has a PIE of 19, 22, and 16 % at 3, 5, and 10 % concentrations, respectively.

3.5. Conclusion

This study has shown that SO is a good wax crystal modifier. At high concentration, its PIE is almost comparable to that of AGO and PMS at reduced concentration. Its flow improvement property is however relatively poor, as it could not improve the YP and pour point of the crude. In comparison with CO, however, SO shows more potential in wax inhibition and flow improvement, while AGO and PMS show excellent results. The petroleum distillate's strong solvency qualities, similar chemical composition with wax, and dispersion abilities. Which guarantee that wax molecules are dissolved and keep them from precipitating out of solution, are responsible for their effectiveness in viscosity reduction, pour point lowering, and wax inhibition. The plant oil biodiesels however showed more promise than the crude plant oils in flow improvement, but are less attractive in wax inhibition.

Ethics information

This manuscript has not been submitted to more than one journal simultaneously for consideration. The submitted work is original and has not been published elsewhere in any form or language. The results presented are clear, honest, and without fabrication, falsification or inappropriate manipulation of data.

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Authors contribution

Conceptualization: T.M., S.A.A. Data curation: T.M., F.O.E., L.N.M. Project administration: T.M., S.A.A. Formal Analysis: T.M., F.O.E., L.N.M., L.D.F. Investigation: T.M., S.A.A., L.D.F., L.N.M. Writing (First draft): T.M. Writing (Review and Editing): T.M., S.A.A., F.O.E., L.N.M.

Conflicts of interest

There is no conflict of interest.

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