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Effects of Blended Chemical Additives on Waxy Deposition Tendency of Nigeria Waxy Crude Oil

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ABSTRACT
The build up of paraffin wax in well bores and pipelines is still a major problem for the petroleum industry since it solidifies over time and is challenging to remove. This results in production losses. In this study, the influence of chemical additive blends (xylene, castor oil, and nanoparticles of zinc oxide and aluminium oxide) as wax inhibitors and flow improvers in Nigerian waxy crude oil was investigated. Samples of waxy crude oil from the Niger Delta of Nigeria were analyzed to ascertain their wax deposition tendencies, and the effects of the additive blend on those tendencies were assessed using a cold finger test at room temperature and 40^oC. The additives were blended in the ratios 1:1, 2:1, and 1:2. The findings indicated that the combination of all additives significantly reduced the crude oil samples' propensity to deposit wax during the cold finger test. The reduction of wax deposition tendencies of the waxy crude oils was best observed when castor seed oil CSO and zinc oxide were combined in a 2:1 ratio. For the crude oil samples, the paraffin inhibition efficiency (PIE) attained under these circumstances was a minimum of 15.39 percent at a concentration of 0.1 percent by volume of additive with crude oil. The samples were characterized, and it was found that sample B had the largest composition of hydrocarbons, primarily composed of compounds C_8–C_{18}.
Keywords: *chemical additives, wax deposition, paraffin inhibition efficiency*

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I. INTRODUCTION

Wax deposition is a well-known issue that has significantly raised production costs in the petroleum sector. At certain phases, this phenomenon also has a negative impact on manufacturing and refining processes. Although reducing wax precipitation is a top priority for the energy sector, the primary mechanisms of wax deposition are still not well understood. The temperature may drop below the threshold needed to keep crude oil fluid due to variations in the geothermal gradient and reservoir heterogeneity (Van Engelen et al., 1979; Udourioh et al., 2014).

At higher temperatures, high molecular weight paraffin (wax) dissolve in crude oil. However, as the temperature falls, the wax molecules split off from the crude oil. At a very low temperature below the cloud point, heavy paraffins and asphaltenes combine to form larger molecules that are not soluble in crude oil. The heavier components eventually settle to form a solid surface on the pipeline/container wall, production machinery, and wellbore (Hart, 2014). Crude begins to build up on the surface after a significant expansion in deposition. So, they stop using the tubing and pipe lines after a specific amount of time. The wellbore's permeability is decreased by the deposits (Amaefule and Charles, 1994). The production of the oil wells is significantly reduced as a result of all of these issues.

There are many methods for regulating and preventing wax deposition, including thermal, mechanical, chemical, and biological ones. The well tube and flow lines are often heated oiled when using thermal techniques. The mechanical techniques include scrapers that are transported by wire lines, sucker rods, and work strings often. Chemical strategies include things like solvents, dispersants, surfactants, and wax crystal modifiers, to name a few. The microbial approaches use bioproduction of surfactant and paraffin solvents to solubilize the paraffin fractions and remove skin damage caused by paraffin from the well bore (Mahto et al. (2010); Banat et al. 2000). Chemical procedures are the most practical and cost-effective way to prevent the wax from waxy crude oil from precipitating, where polymeric ingredients are added to the crude oil or blended in to reduce the pour point and increase the crude oil's flow capacity at lower temperatures (Deshmukh and Barambhe 2008; Mahto, 2010).

Wax deposition issues might cause dangerous circumstances, production to stop, costly workovers, output losses, and even irreversible damage necessitating equipment abandonment and replacement (Adewusi, 1997; Kok and Saracoglu, 2000). Wax deposition has been confirmed on every part of the production system, including the reservoir, wellbore, tubing, flow lines, and surface facilities. Wax deposition issues have occurred previously in the Niger Delta area (Sulaimon et al., 2010). Because of the frigid seabed temperatures, paraffinic fractions solidify in deep water fields, causing a gradual build-up of wax layers in pipelines and flowlines (Carmago et. al., 2004; Lee, 2008).

The wide range of studies in the literature that discuss issues related to deposition of wax in crude oil illustrates the wide range of themes in this field. Many of these researchers have used successful methods to deal with waxy crude oil by using flow-improving compounds that are able to lessen the crude oil's tendency to deposit wax. Pour point depression of crude oil is important for assessing flow behavior and storing crude samples because it helps to prevent deposition of paraffin wax (Akinyemi et al., 2016, Adewusi, 1997). In order to better understand how natural non-edible plant seed oil, specifically, castor seed oil and a chemical blend (including xylene and nanoparticles) affect the tendency of Nigerian crude oil to deposit wax, this study was created.

II. MATERIALS AND METHODS

Castor seed oil was obtained from a local market in Epe local government of Lagos State Nigeria. BDH Chemical Ltd., Poole, England, produced the analytical grade (xylene) that was used. The zinc oxide, aluminium oxide nanoparticles were obtained from analytical chemical sales point in Nigeria while two crude oil samples were obtained from the Niger Delta region of Nigeria.

Last but not least, waxy crude oil's rheological properties at various temperatures were evaluated using a Brooke field viscometer. Several pour point depressants in varying quantities were present in this sample of crude oil. By measuring viscosity over a wide temperature range, the cloud point also known as the wax appearance temperature was discovered. It was thought to be the temperature at which wax solids begin to form in the oil and produce a deflection in the slope due to a departure from Newtonian behaviour. The Brooke field viscometer was used to measure viscosity under varied temperature and shear rate conditions.

2.1 Sample preparation

The two crude oil samples were reconditioned by heating them to a temperature of roughly 60°C for almost 10 hours, with hand-rocking occasionally during heating to remove any possible earlier history (Akinyemi et al., 2018). In order to remove all heat and shear histories and create homogeneous samples for testing, reconditioning the samples made sure that all pre-crystallized wax was re-dissolved into the oil.

2.2 Characterization of crude oil samples

The crude oil samples were characterised to determine their hydrocarbon composition using Agilent Technologies 6890N gas chromato-graph equipped with a flame ionization detector (FID) as described by Akinyemi et al., 2016. The pour point and the American Petroleum Institute gravity (APIg) of the crude oil samples were determined using ASTM D97 and ASTM D287 standard methods respectively. The viscosity of the crude oil sample was determined at 30^oC using rotational viscometer (Brook-field rotational viscometer: Ndj-5S)

2.3 Wax Deposition Tests

The wax deposition tendencies of the crude oil samples were evaluated under non-flow of bulk crude oil conditions using the procedure described by Bello et al (2005). For the cold finger test, the apparatus required 50mlof the crude oil sample. During the depositional procedure, the temperature of the bulk crude oil was maintained just above its pour point (30^oC for sample A, 40^oC for sample B). A cold patch (cold finger) was kept at 6^oC in the bulk crude oil during the testing process for each sample to produce a temperature gradient.
The sample was stirred using a magnetic stirrer. The cold finger was taken out of the equipment and weighed after a 60-minute deposition period. The technique was carried out using a pure crude oil sample first, and then a sample that had been treated with chemical additions. In the castor oil-nanoparticle mixture, chemical additives in the ratios of 1:1, 1:2, and 2:1 were utilized. Similar ratios were used for castor oil and xylene as well as for xylene-nanoparticle mixtures. Equation (1) was used to calculate the Paraffin-inhibition effectiveness (PIE) of each chemical additive evaluated.

$$\text{PIE} = \frac{Wp - Wa}{Wp} \times 100\% \qquad (1)$$

where Wp = quantity of paraffin deposited in a pure sample, in g
Wa = quantity of paraffin deposition with chemical additions in the sample g

III. RESULTS

The Characteristic properties of the Curde oil samples used are shown in Table 1

Table 1Characteristic properties of curde oil samples

Parameter	Sample A	Sample B
APIg	31.5	26.8
Pour point, °C	17	22
Viscosity mPa.s at 30°C	21.5	49.8

3.1 The impact of additive mixes on wax deposition in sample A

From the result obtained, the paraffin inhibition efficiency of the chemical additive on sample A at temperature of 30°C decreases from (5.63 - 5%) as the percentage of Castor seed oil (CSO) in the CSO-xylene blend was varied with higher xylene percent from 1:1 to 1:2 (Figure 1). However, as CSO percentage increases further to a ratio 2:1, the paraffin inhibition efficiency of the blend on sample A increase progressively to 6.98%. The xylene – zinc oxide blend gave PIE of 5% when the crude oil was inhibited with same proportions of additives (i.e., 1:1). It was further observed as shown in Figure 1 that the (xylene-zinc oxide) concentration of the sample A increased the PIE progressively (5.71%) when doped further with the blend additive as the percentage of xylene in the blend increased from 1:1 to 2:1 of the mixture. Hence, the PIE decreased when the proportion of zinc oxide in the blend was favoured at a ratio of (1:2). This indicates that the blend with higher ratio of xylene in the blend tends to favour the mixture.

When Norrman *et al.* (2016) looked at the impact of polymer coverage and nanoparticles on wax inhibition, they found that lower xylene load ratio-samples (1:1 and 1:2) resulted in a larger amount of wax deposit. Similar to the previous case, wax may crystallize at various temperatures in different regions of the sample due to inhomogeneity non samples, which is likely brought on by the aggregation of zinc oxide nanoparticles. The PIE of all primary additives can generally be increased by adding xylene nanoparticles, but only when the concentration and load are favorable (Norrman *et al.* 2016). The sample test combined with xylene and aluminum oxide showed the same pattern.

The blend of CSO with aluminium oxide was found to be very low in PIE compare to blends of other additive. The CSO-zinc oxide blend gave a very low PIE value (2.5%) when mixed in equal ratio but the value increased further (4.34%) when the percentage of CSO was favoured (2:1). Hence, the blend of CSO with zinc oxide in proportion of 1:2 gave the highest PIE value of 7.5% the sample.

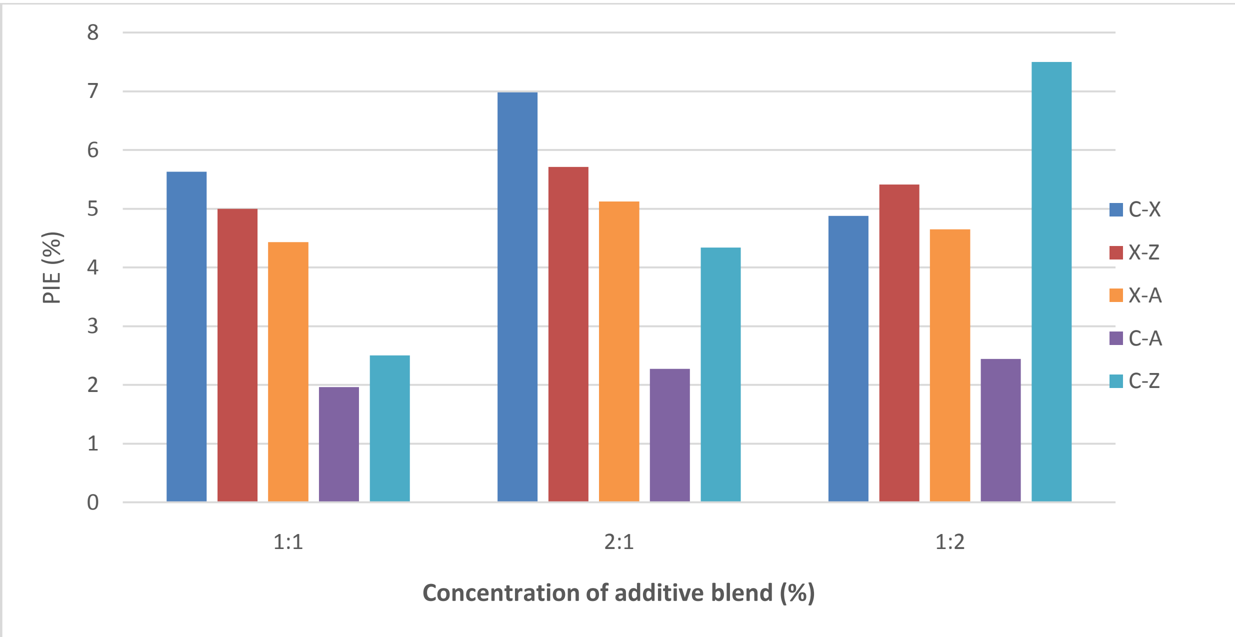

Figure 1: Optimum performance of additives on wax deposition tendencies of crude oil sample A at 30°C

3.2 Effect of additives blends on wax deposition in sample B

When all additives were used in equal amounts with the CSO-aluminum oxide mixture, which produced the highest value of 6.22 percent, it was found that the PIE values were very low. However, it was found that when employed as a chemical additive to sample B at 30°C, a mixture of CSO-zinc oxide at a ratio of 2:1 offered the maximum wax inhibition efficiency of 15.39 percent (Figure 2). Blend of xylene and aluminium oxide (2:1, figure 4.2) came in second place and produced a PIE of 7.69 percent. The interaction between the oleic acid and ricin oleic acid molecules with the high paraffin molecules of the crude oil appears to be enhanced, which increases the prevention of wax deposition (Akinyemi *et al.*, 2018).

The best performance of additives on crude oil's wax deposition tendencies was obtained in sample B with a CSO-zinc oxide blend, demonstrating how effective CSO additives are as inhibitors.

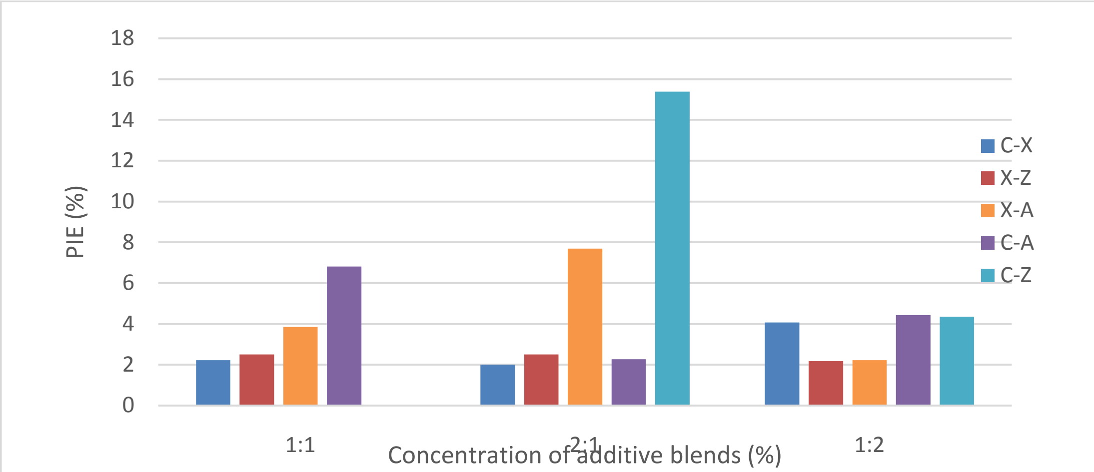

Figure 2: Optimum performance of additives on wax deposition tendencies of crude oil sample B at 30°C

3.3 Effect of additives blends on wax deposition sample A at 40°C

The seed oil's ability to block wax on sample A at 40°C was improved by blending CSO with xylene in an equal ratio (Figure 3). Due to the high concentration of oleic acid and its derivatives in CSO, this may be explained by the increase in oleic acid and its molecules in the blended combination. However, the PIE decreases when the CSO content in the CSO-xylene blend is raised (2:1). The same outcome was seen when xylene was given preference in terms of proportion (1:2).

The highest PIE value was produced by the CSO-zinc oxide mixture (13.16 percent). The sample with the highest PIE value, Sample B inhibited at 30°C, showed the same pattern (15.39 percent). This demonstrates that there is a synergistic interaction between the oleic acid molecules and the ricin oleic acid in the CSO-zinc oxide bent molecules, resulting in a higher contact with the high paraffin molecules of the crude oil and a greater prevention of wax deposition (Akinyemi *et al.*, 2018). When the quantity of CSO in the mix was favourably adjusted, the CSO-aluminum oxide blend produced a sizable amount of PIE in the sample. As opposed to other additives, this demonstrates that CSO has a high inhibitory efficiency in the sample.

Due to its high monounsaturated fatty acid content and beneficial components, the castor plant is one of the oil seeds with the highest oil content. Its fatty acid composition primarily consists of ricinoleic acid, with a small amount of stearic, palmitic, and oleic acids. According to reports, ricinoleic acid, a particularly hydroxylated and monounsaturated fatty acid, makes up around 90% of the total fatty acids in CSO-zinc oxide combination (Adeyanju *et al.*, 2013). Because CSO's ricinoleic acid is different from all other additions, it is desirable as a crude oil depressant.

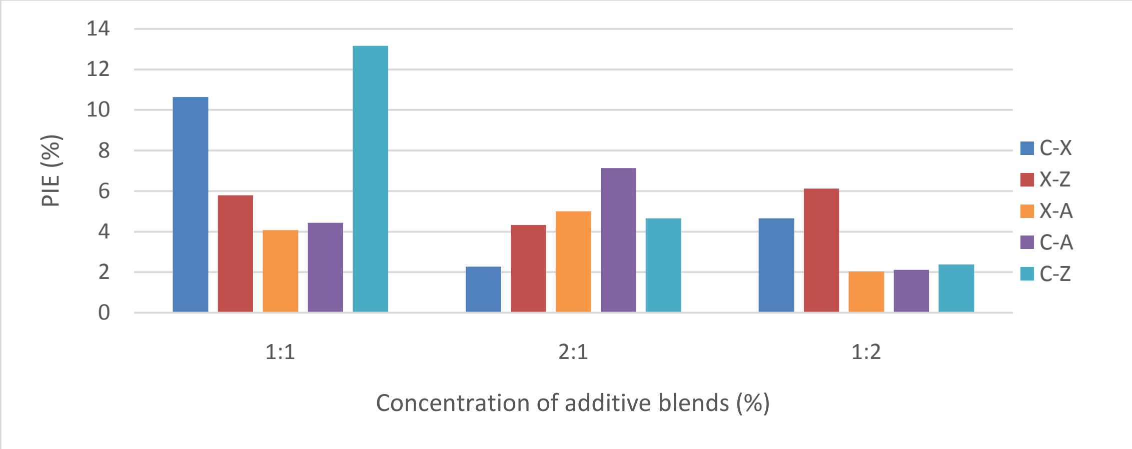

Figure 3: Optimum performance of additives on wax deposition tendencies of crude oil sample A at 40^{o}C

Triricinolein is the main triglyceride found in the oil. Castor oil contains a variety of minor biological substances, such as carotenoid, tocopherol, tocotrienol, phytosterol, phospholipid, phytochemical, and phenolic compounds. These substances give the waxy crude oil oxidation stability, anti-inflammatory effects, and antioxidant characteristics.

3.4 Effect of additives blends on wax deposition (Cold Finger tests) in sample B at 40^{o}C

Also form the results in sample B (Figure 4), blend of CSO-xylene at ratio (1:2) gave highest PIE of 7.32%, follow by the sample blend of CSO-xylene at equal proportion (1:1) with PIE of 6.38%. CSO-xylene concentration at (2:1) gave PIE value of (4.87). From Figure 4, it shows that the blend of CSO and xylene has more inhibitory efficiency as the blend of xylene-aluminium oxide result to appreciable amount of PIE.

3.5 Effect of cold finger temperature on wax deposition

Performance of additives on wax deposition tendencies of crude oil sample A at 40^{o}C shown in Figure 3 was observed to be higher than experiment conducted at lower temperature of 30^{o}C. Cold finger temperature has been identified as one of the most influential factors that affect the wax deposition (Akinyemi *et al.* 2018). The temperature difference between the bulk crude oil temperature and cold finger temperature, ΔT is calculated using the Eqn. (1).

$$\Delta T = T_o - T_c \qquad (1)$$

where T_o is the crude oil temperature in the vessel while T_c is the cold finger temperature. As the ΔT increases more wax deposits can be observed. T_o was constant at 30^{o}C while T_c has been varied from 30^{o}C to 40^{o}C.

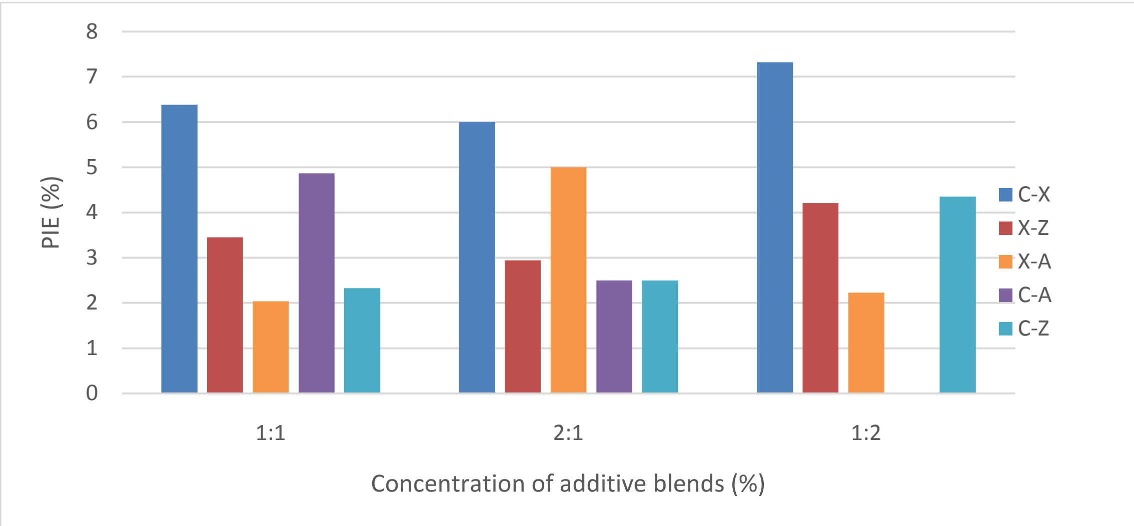

Figure 4.4: Optimum performance of additives on wax deposition tendencies of crude oil sample B at 40^{o}C

As the cold finger temperature rises as T increases, the wax deposit decreases while the PIE rises, which equates to a higher wax inhibition efficiency as illustrated in Figures 3 and 4. When nanoparticles are included, PIE improved. Therefore, the less wax forms, the smaller the T between the equipment surface and the bulk crude oil. In order to reduce the likelihood of wax deposition, operating temperature should be kept above the wax ambient temperature (WAT).

3.6 Characterization of aliphatic hydrocarbon on samples

In sample A, pentatriacontane ($C_{35}H_{72}$) has the greatest composition (34.5%), followed by heptatriacontane ($C_{37}H_{76}$), at 19.85% (Figure 5). Sample A contains solid-existing chemicals from (C_{18}-C_{38}), which means that Sample A crude will deposit a lot of wax at low temperatures since it is primarily solid. This may be because sample A has a lower concentration of the wax soluble component (lower hydrocarbons).

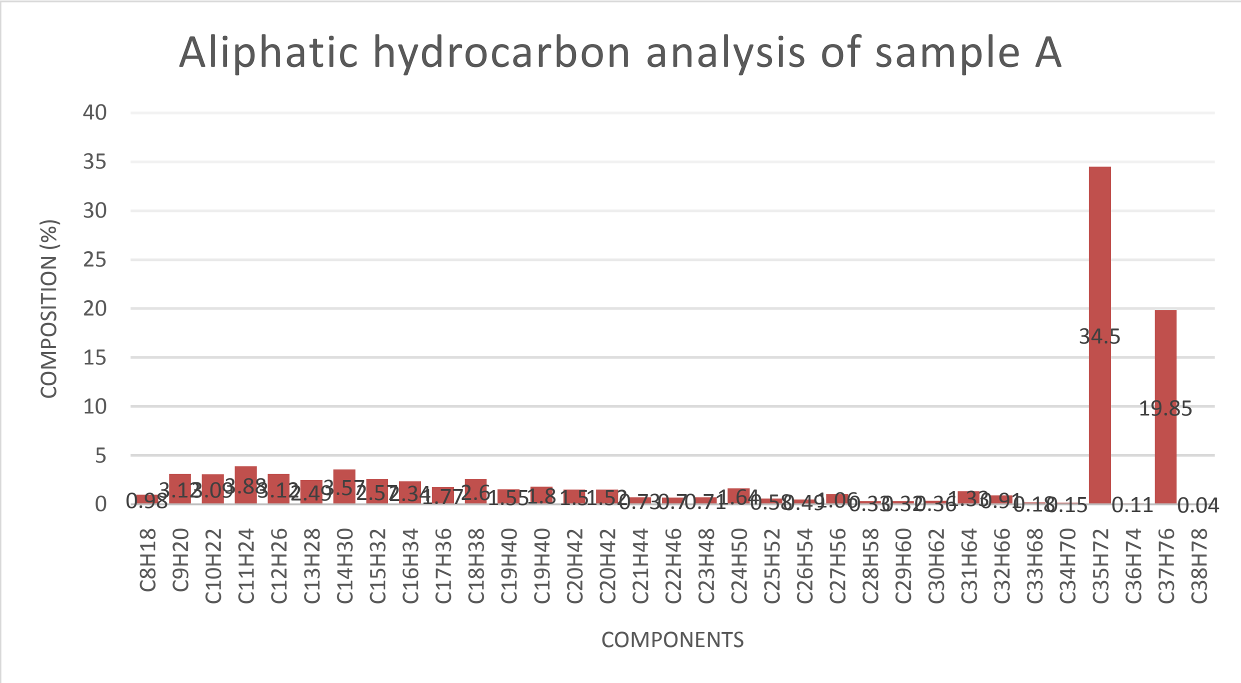

Figure 5: Hydrocarbon analysis on sample A

From Figure 6, sample B was found to have the greatest concentration of nonane hydrocarbons (11.29 %) (C_9H_{20}). In the sample, nonane has the highest paraffin content and tricosane ($C_{23}H_{48}$) has the lowest paraffin composition (0.06 %). Compared to other hydrocarbons, the molecules C_8 through C_{18} have a larger percentage composition. This demonstrates unequivocally that the sample crude may not have decanted much wax since it mostly comprises liquids like octane, undercane, dodecane, and so on. Therefore, the solvent will dissolve the small amount of wax that is present in the crude sample. The fact that relatively little amounts of solid hydrocarbons with the carbon atoms C_{20} to C_{48} were discovered in the described sample further establishes the absence of wax.

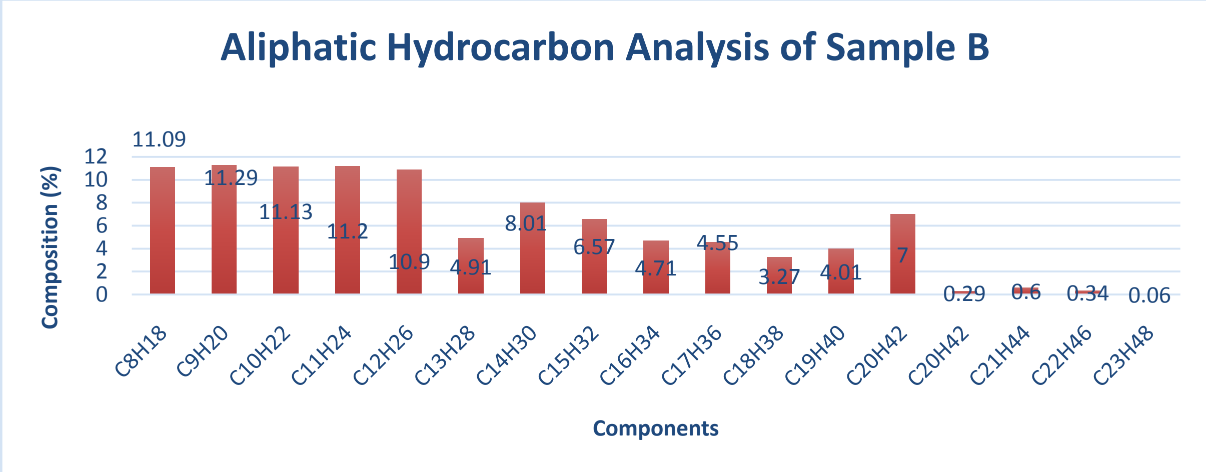

Figure 6: Hydrocarbon analysis on sample B

IV. Conclusion

One of the main issues facing the petroleum industry has been wax deposition. In this project, the effectiveness of a mixture of chemical additives (xylene, castor oil, and nanoparticles) as wax inhibitors and flow improvers in Nigeria's waxy crude oil was investigated. The effects of several blends, including plant seed oil, CSO-xylene blend, xylene-zinc oxide blend, xylene-aluminum oxide blend, and CSO-xylene-zinc oxide blend, on the wax deposition tendencies of waxy crude oil samples were examined at 30°C and 40°C using the cold finger test. The ratios of doping for the crude oil samples were 1:1, 2:1, and 1:2. The ratio of CSO to zinc oxide (2:1) produced the best performance for plant seed oil combination as a flow improver, with the maximum wax inhibition efficiency of 15.39 percent. This clearly shows that the oleic acid and ricin oleic acid molecules in CSO-zinc oxide bent molecules work in concert to offer a higher interaction with the high paraffin molecules of the crude oil, improving the prevention of wax deposition. Sample B has the highest composition of hydrocarbon in the sample that was described for aliphatic hydrocarbons, mostly composed of compounds C_8 to C_{18}, which have a greater percentage composition than other hydrocarbons. This demonstrates unequivocally that the sample crude may not have decanted much wax since it mostly comprises liquids like octane, undecane, dodecane, and so on. Therefore, the solvent will dissolve the small amount of wax that is present in the crude sample.

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