



Effect of Chemical Additives and Nanoparticles on Wax Deposition Tendency of Nigeria Waxy Crude Oil

Akinyemi O. P., Aborishade K. A., Ogun G. S.

Chemical Engineering Department, Lagos State University, Lagos, Nigeria
Corresponding author email: poakinyemi@yahoo.com

Abstract In the petroleum sector, still a serious concern is the deposition of paraffin wax in pipelines and well bores are not readily retrieved owing to its solidification over time. This is accountable for losses in output. This thesis intended to explore the Effect wax inhibitor and nanoparticles on wax deposition tendency of Nigeria crude oil. Waxy crude oil samples taken from Niger Delta area of Nigeria were analyzed to identify their wax deposition tendencies and the affects of the inhibitors on the wax deposition tendencies of the crude oil samples were assessed in cold finger test at room temperature and 40°C. The results obtained showed that all the inhibitors reduced the wax deposition tendencies of the crude oil samples appreciably in cold finger test. Castor seed oil CSO doped with 4 drops (0.2ml) gave optimum wax deposition tendencies of the waxy crude oils in cold finger tests. The paraffin inhibition efficiency (PIE) attained under this condition was maximum of 12.56% for the crude oil samples inhibitors with crude oil. Characterization of the samples confirmed that, sample B has the highest composition of hydrocarbon consisting majorly of compounds C₈-C₁₈ which clearly indicates that the sample crude may not deposit much wax because it contains majorly liquids. It was recommended more examination should be investigated with sample A, which was found to contains compounds from (C₁₈-C₃₈) which exist as solid, indicating high percentages of wax.

Keywords chemical additives, nanoparticles, wax deposition tendencies, paraffin inhibition efficiency

1. Introduction

Numerous challenges with production, transportation, and storage systems of crude oil have been ascribed to wax deposition. Its presence generates technical and economical concerns like increased surface roughness, larger pressure drops, and lower pipe inner diameter, which eventually reduces oil recovery. In the worst-case scenario and in conditions when the deposition is substantial, it may fully choke the pipeline system and lead to the field's abandonment [1].

For instance, the Staffa oil field in the UK, owned by Lasmo Oil Company, was one of the typical oil fields abandoned due to substantial and chronic wax deposition concerns; after four years of production, the oil field recorded over \$100,000,000 losses [2, 3]. When abandonment is not necessary, the deposit provides high-yield stress to enable flow to continue. This indicates that more pressure would be required for the system to function correctly after being restarted after a power outage [4].

Wax deposition may be managed and avoided by the use of a wide range of methods, some of which are thermal, others mechanical, chemical, and even biological in nature. Thermal methods typically include heating and oiling the well tube and flow lines. The mechanical methods often include the use of scrapers that are moved along wire lines, sucker rods, and work strings. Chemical methods include those that use solvents, dispersants, surfactants, or even modify the structure of wax crystals. In order to bio-produce surfactant and paraffin solvents, which are then employed to solubilize the paraffin fractions and prevent skin injury from



paraffin in the well bore, microbial approaches are used. Similar findings have been published by Banat *et al.* (2000) and Mahto *et al.* (2010) [5, 6]. Preventing the wax from waxy crude oil from precipitating requires a chemical process, where polymeric materials are added to or mixed with the crude oil to decrease the pour point and boost the crude oil's flow capacity at lower temperatures [6, 7].

Problems with wax deposition might halt production, lead to unsafe conditions, demand costly workovers, reduce output, and perhaps even cause irreparable damage that would call for the abandonment and replacement of equipment [8, 9]. Wax deposition has been seen in many elements of the production system, including the reservoir, wellbore, tubing, flow lines, and surface facilities. The Niger Delta industry has long suffered from problems related to wax deposition [10]. Paraffinic fractions, which are liquefied at room temperature, solidify at the cold seabed temperatures seen in deep water fields, causing wax layers to gradually develop in pipes and flowlines [11, 12].

A variety of wax prevention and removal strategies have been developed and assessed in laboratories and in the oil fields. Despite their advantages, certain treatments have an economic cost that affects CAPEX and OPEX in a number of ways. Capital cost reduction approaches such as installing subsea equipment and creating solid deposit avoidance solutions, such as chemical wax inhibitors, are examples. Furthermore, operational cost-cutting technologies such as chemical injection, heat procedures, pigging processes, and flow monitoring have been given consideration by some previous researchers [12, 13]. In many cases, none of the above techniques have been used as a stand-alone tool for the prevention and remediation of wax deposition. As a result, the purpose of this study is to investigate the impact of chemical additive from natural non-edible plant seed oil and nanoparticles of some oxides on the wax deposition tendencies of Nigerian waxy crude oil. The plant seeds oil used in this research comes from the Castor plant (*Ricinus communis*). The nanoparticles considered were Aluminium oxide and zinc oxide nanoparticles while xylene which has been a known solvent for paraffin was also considered for comparison,

2. Materials and Methods

2.1 Materials

The Castor seed oil was purchased from vendors at market in Epe, Lagos State-Nigeria. (xylene) used was analytical grade products of BDH Chemical Ltd, Poole England. The crude oil samples were obtained through the Nigeria Upstream Petroleum Regulatory Commission from major oil companies in the Niger Delta region of Nigeria.

The rheological property of waxy crude oil at different temperature was measured using Brooke field viscometer. The crude oil sample was doped with the different concentration of wax inhibitors. The cloud point or wax appearance temperature was determined by measuring viscosity over a range of temperature and taken to be a point at which a deflection in the slope occurs due to deviation from Newtonian behaviour as wax solids begin to form in the oil. The Brooke field viscometer was used for the determination of viscosity at 40°C temperature.

2.2 Methods

2.2.1 Sample preparation

The method employed in this study is adapted from [14] from the literature. Crude oil samples were reconditioned by heating them to a temperature of about 60°C for nearly 10h, with hand-rocking occasionally during heating in the laboratory prior to experiments to erase any previous history that might exist in such samples. Reconditioning the samples ensured that all pre-crystallized wax got redissolved into the oil, thereby erasing any thermal and shear history and producing homogenous samples for testing.

2.2.2 Characterization of crude oil samples

To characterised the crude oil samples their hydrocarbon composition were determined using Agilent Technologies 6890N gas chromatograph equipped with a flame ionization detector (FID) as described by [15]. The American Petroleum Institute gravity (APIg) and pour point of the crude oil samples were determined using ASTM D97 and ASTM D287 standard methods respectively. Brook-field rotational viscometer (Ndj-5S) was used to determine the viscosity of the crude oil sample at 30°C.



2.2.3 Wax deposition tendencies (Cold finger tests)

For non-flow of bulk crude oil condition, the wax deposition tendencies of the crude oil samples were determined using the procedure described by [16]. The cold finger test involved filling the apparatus with 50ml of the crude oil sample. During the depositional run, the bulk crude oil temperature was maintained at a temperature a little above its pour point (30°C for sample A, 40°C for sample B). The cold spot (cold finger) dipped in the bulk crude oil was maintained at 6°C in the test procedure for each sample to induce temperature gradient in the sample. Magnetic stirrer was used to induce mixing of the sample. After a deposition time of 60minutes, the cold finger was removed from the apparatus and the deposit weighed. The procedure was carried out with pure sample of crude oil and subsequently with sample treated the chemical additives. The chemical and Castor oil inhibitors used were doped at different concentration 0.05ml to 0.2ml (1-4 drops). The Paraffin-inhibition efficiency (PIE) of each of the inhibitor tested was determined by using equation (1):

$$PIE = \frac{W_p - W_a}{W_p} \times 100\% \quad (1)$$

where W_p = amount of paraffin deposition in pure sample, g

W_a = amount of paraffin deposition in sample with chemical additives g

3. Results

3.1 Results on Characterisation of crude oils samples

From the result hydrocarbon composition analysis, it was observed that sample B has the highest composition of hydrocarbon of (11.29%) nonane (C_9H_{20}). Nonane has the highest composition of paraffins in the sample while tricosane ($C_{23}H_{48}$) has the least composition (0.06%). The compounds C_8 - C_{18} has higher percentage composition compare to other hydrocarbon. This clearly indicates that the sample crude may not deposited much wax because it contains majorly liquids such as octane, dodecane and so on. Hence, few wax content present in the crude sample will be dissolved the solvent. The hydrocarbon with C_{20} - C_{48} exist as solid which were found in very minute amount in the characterized sample, this also proves that the sample is free of wax.

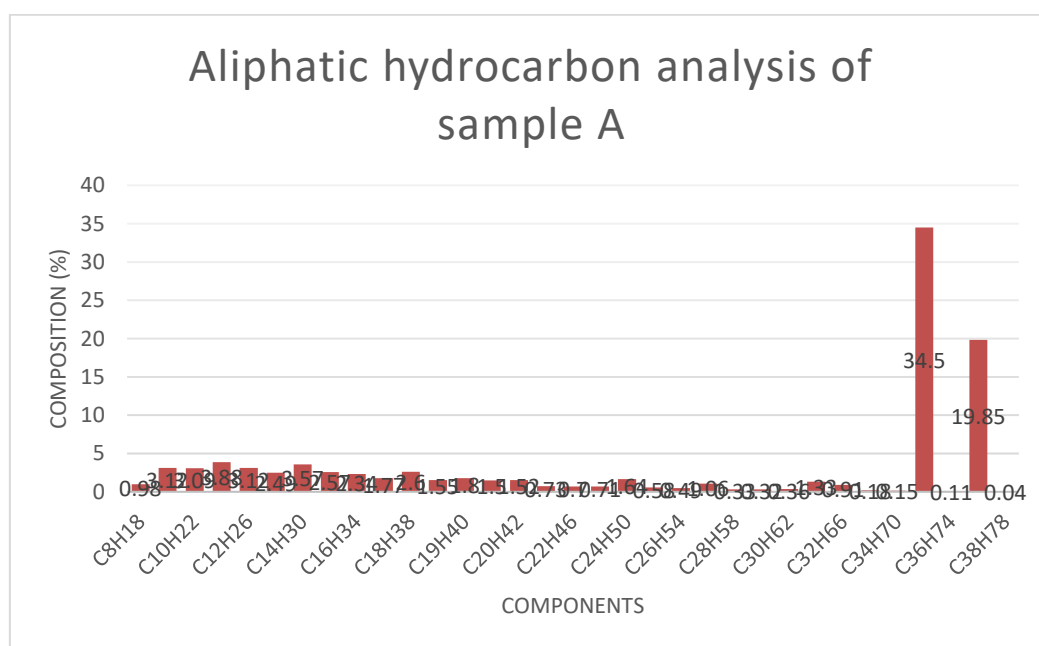


Figure 1: Hydrocarbon analysis on sample A



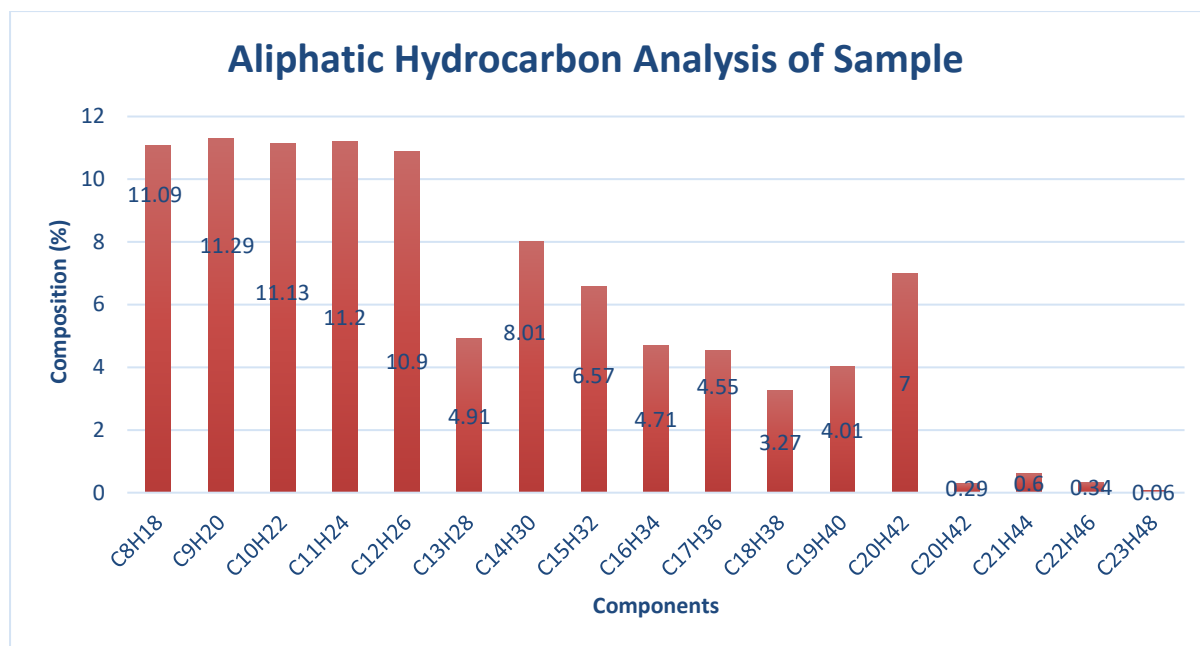


Figure 2: Hydrocarbon analysis on sample B

Pentatriacontane ($C_{35}H_{72}$) has the highest composition (34.5%) in sample A follow by Heptatriacontane ($C_{37}H_{76}$) 19.85%. Sample A contains compounds from (C_{18} - C_{38}) which exist as solid, this indicates Sample A crude will deposit much wax because it contains majorly solid. This might be due to the fact that sample A contains less proportion of wax inhibitor of castor oil and xylene.

The results of the determination of the characteristic properties of the crude oil samples showed that sample A is lighter than sample B with sample A having the APIg of 31.5 (Table 1). However, the pour point and viscosity of sample B are higher than those of sample A.

Table 1: Characteristic properties of curde oil samples

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

3.2 Effects of the Chemical additives on the Paraffin Inhibition Efficiencies (PIE) of the crude oil samples

From the result obtained, the paraffin inhibition efficiency of the inhibitors on sample A at temperature of 30°C increases as the percentage of inhibitors increases shown in (Figure 3). However, as the inhibitors are doped further, the paraffin inhibition efficiency of sample A increases as well. From Figure 3, crude sample doped with castor seed oil CSO was found to have highest PIE value (6.32%). It was further observed as shown in Figure 3 that the xylene concentration of the sample also increased progressively when doped with the higher concentration of inhibitor. The xylene inhibited sample that gave the highest PIE value was found to be more dope of the mixture. Generally, it is confirmed that the addition of CSO and xylene inhibitors are able to enhance the PIE of all primary additives, but only if in a favourable concentration and load [14, 17].

Similarly, same trend was observed in the sample inhibited with zinc oxide. The PIE value increase progressively as the sample is being doped further. The same trend was observed in the sample test inhibited with aluminium oxide. The blend of doped aluminium oxide was found to be very low in PIE compare to samples inhibited with other additives.



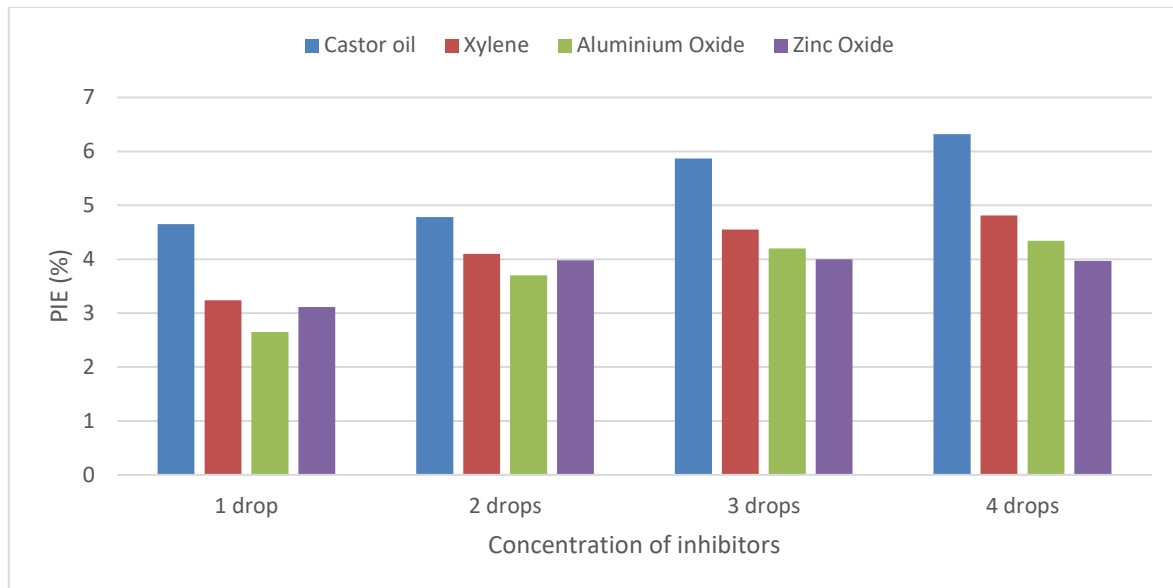


Figure 3: Performance of inhibitors on wax deposition tendencies of crude oil sample A at 30°C

From Figure 4, it was observed that the PIE value increases progressively when the inhibited samples are further doped. i.e., higher inhibitors concentration gives higher PIE value. Again, as reported in sample A, CSO gave the highest value PIE increased the wax inhibition efficiency of the seed oil on sample B at 30°C This may be attributed to the increment in the number of molecules of oleic acid and its derivatives in the blended mixture since the quantity of these molecules in CSO is high. However, it was observed that CSO doped with 4 drops gave the highest wax inhibition efficiency 6.1%.

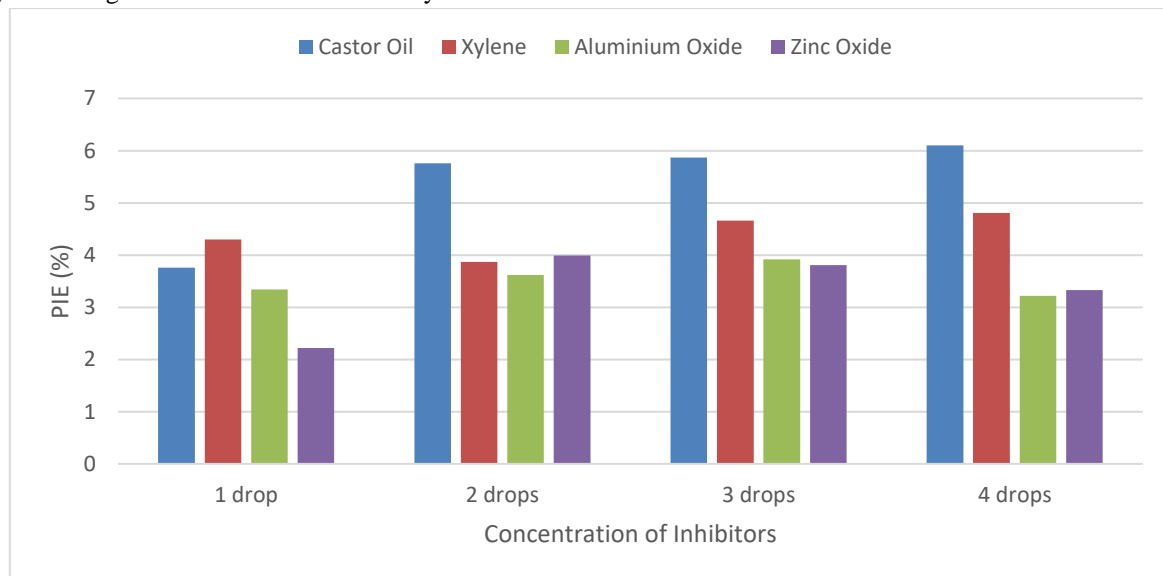


Figure 4: Performance of additives on wax deposition tendencies of crude oil sample B at 30°C

Optimum PIE value of 9.76 % was observed in sample A inhibited with CSO inhibitor at 40°C (Figure 5). Increased in the wax inhibition efficiency of the seed oil may be attributed to the increment in the number of molecules of oleic acid and its derivatives in the inhibitor since the quantity of these molecules in CSO is high. However, when the concentration of CSO was decreased, the PIE values reduce. Same result was observed in sample doped with xylene.

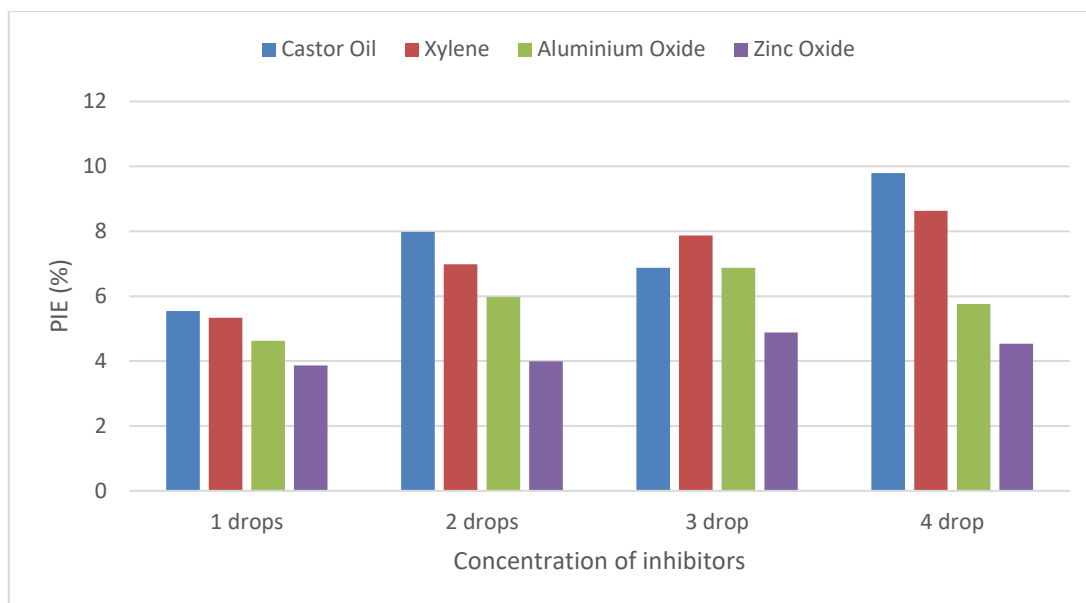


Figure 5: Performance of inhibitors on wax deposition tendencies of crude oil sample A at 40°C

It was observed that the PIE values of sample B at 40°C were very high when compared with other samples mixed (Figure 6). The least PIE value was found to be 4.34% (sample doped with zinc oxide inhibitors), while CSO gave the optimum value of PIE of (12.56%). It was also observed that CSO has the highest value of PIE at all concentration. This show that CSO has the highest wax inhibition efficiency at optimum temperature of to 30°C. This was closely followed by xylene inhibitor.

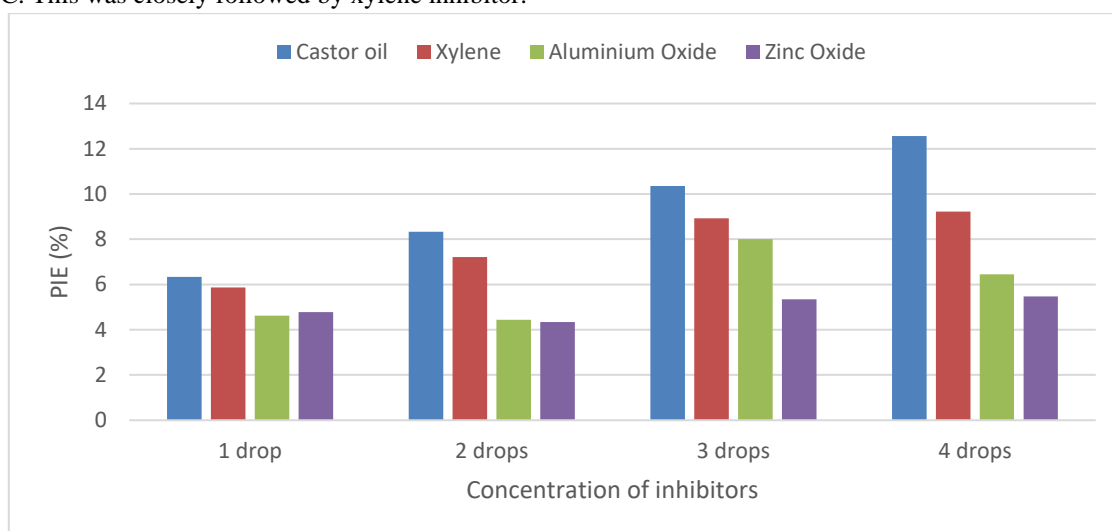


Figure 6: Performance of inhibitors on wax deposition tendencies of crude oil sample B at 40°C

4. Conclusion

The impacts of plant seed oil CSO, xylene, aluminium oxide nanoparticles, and zinc oxide nanoparticles as wax inhibitors on the wax deposition tendencies of waxy crude oil samples were investigated under temperatures of 30°C and at 40°C. The inhibitor CSO doped with (4 drops) result displayed the highest wax inhibition efficiency of 12.56% which gave the optimum performance for plant seed oil inhibitor as flow improver. This clearly indicates that, there is a synergy between the oleic acid molecules and the ricin oleic acid in CSO molecules in presenting a greater interaction with the high paraffin molecules of the crude oil thereby increasing the inhibition of wax deposition. In the sample characterized for aliphatic hydrocarbon, sample F has the highest composition of hydrocarbon consisting majorly of compounds C₈-C₁₈ which has higher percentage composition compare to other hydrocarbons. This clearly indicates that the sample crude may not deposited much wax



because it contains majorly liquids such as octane, undercane, dodecane and so on. Hence, few wax content present in the crude sample will be dissolved the solvent.

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