Comparative Evaluation of Ethylene Glycol and Di-ethanolamine Modified African Pear Seed Oil as Pour Point Depressants for Waxy Crude Oil

ABSTRACT

The pour point depression of a Nigeria waxy crude oil was investigated using modified African pear seed oil. Waxy Crude oil sample collected from a marginal field in Delta state. African pear seeds sourced from Choba Port Harcourt were extracted from their oil content and the oil was modified using ethylene glycol and diethanolamine via the esterification and aminolysis reaction respectively. These modified products were applied as pour point depressants. The waxy crude oil was dosed with the modified African pear seed oil of concentrations 0.1ml, 0.2ml and 0.3 ml. The result showed a reduction in the pour point of the crude oil from; 21^{o}C to 14^{o}C and 21^{o}C to 13^{o}C for crude oils dosed with modified with ethylene glycol and diethanolamine respectively. The result also confirms that the concentration of the depressant does not affect the pour point. The modified product with diethanolamine was a better depressant compared to ethylene glycol modified products.

Keywords: modified; ethylene glycol; diethanolamine; depressant; esterification; aminolysis.

Introduction

Crude oil is a complex naturally occurring mixture containing mostly hydrocarbons with varying proportions of non-hydrocarbon constituents and traces of organometallic compounds. It is a non-renewable source of energy (Kelechukwu et al., 2010). The majority of the hydrocarbons contained in crude oil are structured in chains or rings and range in size from C1 to C60+. Crude oil may also contain oxygen, nitrogen, and sulfur molecules. In general, crude oil is composed of 85% carbon, 13% hydrogen, and 2% sulfur, nitrogen, and oxygen. Petroleum can be found in sedimentary rock formations all over the world (Khidr et al., 2015). Crude oil also contains several chemical fossils or biomarker molecules that are resistant to biodegradation and whose origin in crude oil is linked to organic molecules created by living organisms through transformation (Hao et al., 2019).

The relatively minor hydrocarbon liquids that are generated by most humic coals are characteristic of higher plant material (Davidson *et al*., 2004). Coal-sourced oils are generally dominated by cuticular-wax derived n-alkanes, although benzene, naphthalene, and phenanthrene and their alkyl derivatives are usually important. Small amounts of larger aromatic hydrocarbons formed from extensively fused benzenoid systems may also be present (White and Lee 1980). Such polycyclic aromatic hydrocarbons are also produced during combustion of oil and coal.

When the temperature falls below the wax appearance temperature WAT, wax crystallizes from the oil. With a lower temperature, wax crystals develop and agglomerate in oil, generating a vast three-dimensional network that alters oil flow behavior. Wax production raises oil viscosity, which increases the amount of energy required to pump the oil (Jinjun et al., 2013; Mansourpoor et al., 2019). Deposition of wax on the internal surface of tubings and pipelines, resulting in flow constriction and a high danger of oil gelation if the flow is briefly stopped, are further adverse effects of wax crystallization that can cause mechanical failure in production and transportation systems (Ajienka & Ikoku, 1990).

Following the continuous depletion of conventional oil reserves, the production of unconventional oils, such as waxy crude oils and heavy crude oils, increases. In fact, approximately 20% of the global oil reserves are of waxy crude oils, while heavy crude oils constitute about half of the recoverable oil reserves (Kumar et al., 2015).

The mechanical pigging method is also widely recognized for removing paraffin waxes, but it requires periodic production shutdowns; thus, resulting in a substantial economic predicament. Therefore, the pigging frequency must be greatly reduced to attain higher economic returns. Consequently, chemical methods, such as wax inhibitors (WIs) and pour point depressants (PPDs), are preferred (Wei, 2015).

The significance of WIs and PPDs has gained growing interest among academicians and industrial practitioners over the past decades (Woo et al., 1984). These chemical methods serve as a preventive measure, which forms a “kinetic barrier” and subsequently delays the precipitation of these waxes and the formation of hardened wax (Theyab & Diaz, 2016). These methods also aid in the removal of deposited wax. With that, the chemical methods are considered as significant practical applications to improve the flowability of waxy crude oils; thus, reducing the maintenance cost of these pipeline facilities. These widely used chemicals include ethylene vinyl acetate (EVA) copolymers, comb-type copolymers, nano-hybrid compounds, organic solvents, and surfactants, which were particularly explored in this paper. Accordingly, this paper explored several categories of WIs and PPDs as well as their purpose to prevent the formation of wax crystals and high pour points (PP). In addition, the mechanisms of WIs and PPDs in waxy crude oils, the factors that govern their efficiencies, and the summary of recent applications and challenges of using these compounds were also critically assessed (Wei, 2015).

The bio-based surfactants and natural surfactants are also widely studied as PPDs in petroleum flow assurance chemistry. In comparison to the classical surfactants, natural surfactants possess the following strengths: (1) lower toxicity; (2) biodegradable; (3) wide structural variety; (4) synthesized from inexpensive renewable materials; (5) stable in a wide range of pH (Oguntimein et al., 1993). Kumar et al. (2017) discovered that Sapindus mukorossi, as a natural surfactant, significantly reduced the viscosity by 80% when it was used as PPD on heavy crude oil.

Polyethylene glycol (PEG) esters have been used extensively to derivatize synthetic fatty acids, as well as linear and aromatic dicarboxylic acids, to lower the pour point of waxy gas oil and middle distillate fuel (Al-sabagh et al., 2007; Khidr et al., 2015).

It is thus clear that the avoidance or remediation of wax deposition is one key aspect of flow assurance. Many of these problems can be effectively resolved by the appropriate application of pour point depressing chemicals. Crude oil pour point depression is significant in eliminating paraffin wax deposition and is crucial for the assessment of flow behavior and storage of crude samples.

African pear

Safou (French), ube (Igbo), elemi (Yoruba), eben (Efik), and orumu (Benin) are all names for *Dacryodes Edulis* (African pear), which belongs to the *Burseraceae* family. They thrive in a wide range of climates and soil types, and they're found all over Africa. Cabinda, Cameroon, Congo (Brazzaville and Kinshasa), Gabon, Ghana, Equatorial Guinea, Nigeria, and Sao Tome are among the countries where they can be found. The trees are grown near homesteads in southeast Nigeria, and blossoming occurs from January to April. Between May and October is the main fruiting season. The fruits are boiled or roasted and eaten with corn in both rural and urban parts of Nigeria (Onuegbu et al., 2011). However, not much has been done in the characterization and refining of the seed oil.

This research is strictly laboratory work that undertakes the extraction and modification of *Dacryodes Edulis* (African pear) seed oil and the investigation of the modified African pear (*Dacryodes edulis*) seed oil as pour point depressants for Nigeria waxy crude oil. The plant seeds being considered are naturally non-edible seeds which may be regarded as agricultural wastes. This work is one of such attempts at using green substances as Pour Point depressants.

Methodology

The crude oil sample used for this study was collected from a Marginal field in Delta State Nigeria. The seed of *Dacryodes Edulis* (African pear) was obtained from Choba Area in Obio-Akpor Local Government of Rivers State. Seeds of *Dacryodes Edulis* 4kg were sundried and pulverized to a fine texture using an industrial blender. The physicochemical properties of the crude oil utilized in this research are provided in Table 1.

Table 1 Characterization of Crude Oil

S.NO.	Parameters	Unit	Value
1	specific gravity		0.883
2	API	^{0}	28.7
3	kinematic viscosity	Cst	2.09
4	pour point	^{0}C	21
5	wax content	%	29.5

Extraction of Dacryodes Edulis (African Pear) Seed Oil

3kg (3000g) of ground African pear (*Dacryodes edulis*) seed was measured using an analytical weighing balance into a container and soaked with 3.5 liters of n-hexane for 2 days. The container was covered and made airtight to avoid evaporation of n-hexane. Decantation was carried out followed by filtration. Distillation of the filtrate to recover the n-hexane was done at a temperature of 65^0C using Soxhlet (Onuegbu et al., 2011). The percentage yield of the oil was calculated thus:

$$\% \text{ yield } = \frac{\text{weight of extracted}}{\text{weight of sample used}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{eqn } 1$$

Esterification of African Pear (Dacryodes Edulis) Seed Oil with Ethylene Glycol

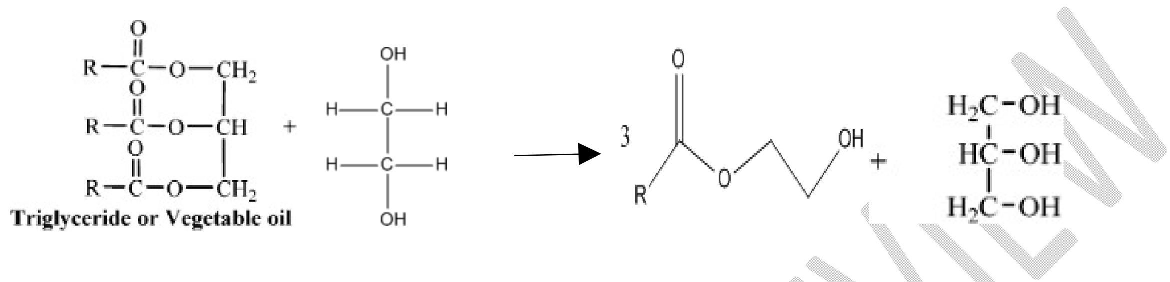
50g of the oil was measured into a 250ml round bottom flask and was heated to above 50^0C. 21g of Ethylene Glycol was measured into a beaker. Catalyst Sodium hydroxide, 10% by weight of the oil was added to the measured Ethylene glycol and was stirred. The mixture of Sodium hydroxide and Ethylene glycol was added to the pre-treated oil in the round bottom flask and refluxed for 1 hour at 60^0C in a magnetic stirrer keeping the agitation rate constant at 400rpm for oil to alcohol ratio of 1:4. The resulting mixture was poured into a separating funnel and allowed to stand overnight for separation after which two layers was observed. The lower glycerol layer was tapped off and the Ethylene glycol acetate layer was recovered. Ethylene glycol acetate was then heated on a heating mantle at 110^0 C to dry it.

Aminolysis of African Pear (Dacryodes Edulis) Seed Oil with Diethanolamine

50 g of the oil was weighed into a 100 ml round bottom flask and heated slightly to a temperature of 60^0C. 36 g of Diethanolamine was measured into a beaker. The molar ratio to; Diethanolamine is 1:6. Catalyst Sodium hydroxide, 2% by weight of the oil was added to the measured Diethanolamine and stirred. The mixture of sodium hydroxide and Diethanolamine was added to the pre-heated oil in the round bottom flask and was refluxed for 1 hour at 110^0C with a magnetic stirrer. The resulting mixture was poured into a separating funnel and allowed to stand overnight for the separation of Fatty acid amide after which two layers were observed. The

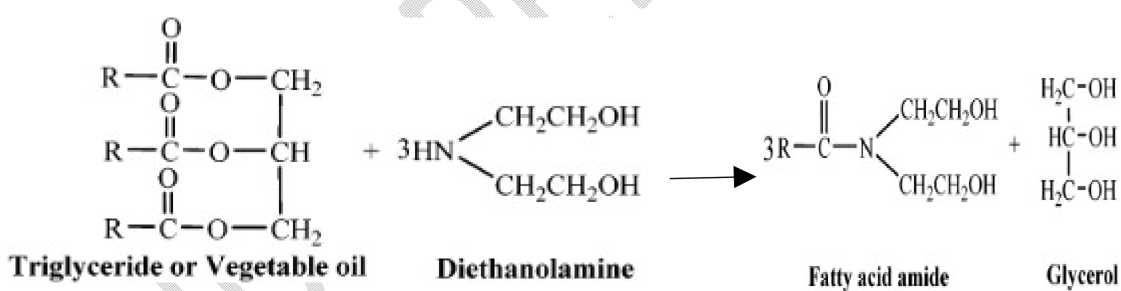
lower glycerol layer was tapped off and the Fatty acid amide layer was recovered. The Fatty acid amide was then heated on a heating mantle at 110^{0}C to dry it.

The proposed reaction chemical equation for both modifications is presented below.



Ethylene glycol glycol esters Glycerol

Esterification of *Dacryodes Edulis* (African pear) seed oil with ethylene glycol in the presence of NaOH catalyst. R groups can be linear, branched, or cyclic rings (Arisa 2008)



Aminolysis of *Dacryodes Edulis* (African pear) seed oil with Diethanolamine in the presence of NaOH catalyst. R groups can be linear, branched, or cyclic rings (Arisa, 2008)

Determination of Oil Quality Parameters of the Extracted Oil

Saponification Value

0.5g of the oil sample was weighed into a conical flask. 50mls of 0.5N ethanolic solution of potassium hydroxide was added and the solution was refluxed to ensure perfect dissolution. The solution was allowed to cool. 3 drops of phenolphthalein were added. The solution was titrated with 0.5N HCl until the pink color of the indicator disappeared (V1). A blank (V2) was carried out as well.

Thus, the saponification value was calculated using this equation:

$$\text{Saponification Value} = \frac{56.1 \times (V2 - V1) \times 0.5}{\text{weight of sample}} \ldots\ldots\ldots \text{eqn. 2}$$

Iodine Value

0.5g of the oil sample was weighed into a conical flask. 15ml of chloroform was added after which 25ml of Wiji solution (mixture of iodine, acetic acid and chloroform) was added and covered slightly using a foil and masking tape. The resulting solution was placed in the dark for 30 minutes. 20ml of potassium iodide was added followed by 150ml of distilled water. The solution turned red. 5ml of 1% starch indicator was added which turned the solution blue black. The whole solution was titrated with 0.1N sodium thiosulphate till the end point was achieved (V1). A blank (V2) was carried out too starting with 15ml of chloroform. The solution turned to blue black precipitate and then to colourless. Iodine value was calculated using Equation 3

$$\text{Iodine Value} = \frac{12.69 \times (V2 - V1) \times \text{Normality of the titrant}}{\text{weight of sample}} \ldots\ldots\ldots \text{eqn 3}$$

Free Fatty Acid (FFA)

0.5g of the sample was weighed into a dry beaker and 20ml of ethanol was added to it. 3 drops of phenolphthalein indicator were added and shaken. The solution was titrated with 0.1N sodium hydroxide until a pink coloration was observed.

$$\% \text{ FFA} = \frac{\text{titre value} \times 0.0282 \times 10}{\text{weight of sample used}} \ldots\ldots\ldots\ldots \text{eqn. 4}$$

Acid Value

2 g of the sample was weighed into a dry beaker, 25 ml of chloroform, and 25 ml of ethanol was added and mixed. 2 drops of phenolphthalein were added to the resulting mixture. The mixture was titrated with 0.1N NaOH to the endpoint of which a dark pink color was observed.

$$\text{Acid value} = \frac{\text{titre value} \times \text{normality of the base} \times 56.1}{\text{weight of sample used}} \ldots\ldots\ldots \text{eqn 5}$$

Application of The Modified And Unmodified African Pear (*Dacryodes Edulis*) Seed Oil on the Waxy Crude Oil

The African pear (*Dacryodes Edulis*) seed oil derivatives were added to the waxy crude oil in different concentrations using a micro-syringe. The concentration ranges from 0.1 ml to 0.3 ml to 20 ml of the waxy crude oil. The mixture was allowed to stand for one hour and collected for physiochemical analysis.

Results and Discussion

The physicochemical characteristics of the *Dacryodes Edulis* seed modified with Diethanolamine are shown in Table 2. The extracted *Dacryodes Edulis* seed oil has a fairly high FFA value of 2.5%, and if the oil is used to make lubricant, the finished product is likely to have a high saponification value, which could result in foam formation. The unmodified oil has an FFA value of (2.5%), but when it is modified with diethanolamine, the FFA value drops to (1.1 %), and the saponification value increases from 94.3 to 121.6 mgKOH/g. This is a result of the refined nature of the oil, as investigated by a study by Mohamed et al (2017). The yield decreased from 67% to 40% when this oil was used for transesterification to create fatty acid amide because it was challenging to separate the glycerol from its byproduct. The oil or fat used in alkaline transesterification reactions should contain not more than 1% free fatty acids (FFAs), which is equivalent to 2 mg KOH/g triglyceride, according to Machado et al. (2001). If the FFA level is higher than this threshold, saponification interferes with the ester's ability to separate from glycerine and lowers the yield and rate of fatty acid amide from being produced. But when the oil was modified with Diethanolamine, the acid value dropped from (5.4 mgKOH/g) to (1.5 mgKOH/g). It has been suggested that acidity below 1 mg KOH/g triglyceride, or a 0.5% FFA content, is appropriate for the production of biodiesel (Chala et al., 2014). The iodine value is used to determine how unsaturated fat or oil is. Iodine content in *Dacryodes Edulis* seed oil increased from 30.65 to 40.78 g/iodine/100g when modified with diethanolamine. The lower iodine value of D. *Dacryodes Edulis* seed oil indicates the presence of fewer unsaturated C=C bonds, whereas modified oil with diethanolamine will have more of these bonds, according to the iodine value from the result.

Effect of Dacryodes Edulis Seed Oil and Its Derivatives on the Crude Oil Sample

The pour point of the crude with and without pour point depressant is presented in Table 3. *Dacryodes Edulis* (African pear) seed oil modified with ethylene glycol (Esterification) showed a significant reduction in the pour point of the crude oil sample from 21^0C to 14^0C. This reduction could be attributed to a change in the functional group leading to a lower free fatty acid and acid level. The pour point of the crude oil sample shows a significant decrease from 21^0C to 14^0C due to the change in the structure and characteristics of the *Dacryodes Edulis* (African pear) seed oil as shown in Table 2.

Dacryodes Edulis (African pear) seed oil modified with Ethanolamine (Aminolysis) showed a greater significant decrease in the pour point of the crude oil sample from 21^0C to 13^0C compared with that modified with ethylene glycol. This could be attributed to the change in the structure and characteristics as shown in Table 2. This could be because of a much lower acid value and a higher saponification value.

Table 2 Characterization of *Dacryodes Edulis* Seed Oil (modified and unmodified)

S.No.	Parameters	Unit	Unmodified oil	modified with Ethylene glycol	modified with Diethanolamine
1	% FFA	%	2.5	1	1.1
2	acid value	mgKOH/g	5.4	1.89	1.5
3	saponification value	mgKOH/g	94.3	94.9	121.6
4	iodine value	g/iodine/100g	30.65	40.78	60.6
5	yield	%	67	40	45

Table 3 Effect of *Dacryodes Edulis* (African pear) seed oil Modified and Unmodified on the pour point of a waxy crude oil sample

Concentration of additive (ml)	Pour point of crude oil dosed with modified *Dacryodes Edulis* seed oil	
	modified with ethylene glycol	**modified with ethanolamine**
0.1	14^0C	13^0C
0.2	14^0C	13^0C
0.3	14^0C	13^0C

Conclusion

This work has demonstrated that *Dacryodes Edulis* seed oil is promising and efficient in depressing the pour point of a waxy Nigeria crude oil. The performance of *Dacryodes Edulis* seed oil is enhanced when modified with ethylene glycol and Ethanolamine

Based on the results obtained from this work, the following recommendations are suggested

More research should be done on other modifications of African pear (*dacryodes edulis*) seed oil, to evaluate their performance as PPD. The mechanism of interaction between the PPDs and the oil molecules should be studied using optical microscopy. The rheology of the dosed crude oil should be studied vis-à-vis the ordinary oil.

This study has shown that African pear (*dacryodes edulis*) seed oil, a relatively cheap and eco-friendly natural product has the quality of being an effective pour point depressant when modified with ethylene glycol and diaethanolamine. It also confirms that the concentration of the depressant does not affect the pour point of waxy crude oil.

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