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Modified and Unmodified *Jatropha Curcas* Seed Oils as Pour Point Depressants for a Nigerian Waxy Crude Oil

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ABSTRACT: Transportation of waxy crude oil faces great challenges in pipelines, however, pour-point depressant could be employed to improve flow properties of waxy crude oil by modifying the morphology and structure of wax crystals. In this paper, modified and unmodified jatropha curcas seed oils was used as a green pour point depressants to evaluate the flow properties of a Nigerian waxy crude oil. Jatropha curcas seed oil (49.5%) was extracted using petroleum ether and the oil was analyzed for oil quality parameters (acid value, iodine value, free fatty acid and saponification value) and subsequently modified using diethanolamine and ethylene glycol to give fatty amides and glycol esters with sulphamic acid (2% and 10% respectively) as catalysts. The modified products were characterized using Fourier transform infra-red (FT-IR) spectroscopy. The modified and unmodified Jatropha seed oils were used treat a Nigerian waxy crude oil to determine their effects on the pour point of the said crude oil. This was done by determining the viscosity and pour point of the crude oil before and after it is dosed with different concentrations of the modified and unmodified Jatropha oils. The results revealed the efficiency of the fatty amides to reduce the pour point and viscosity of the crude oil from 18^0C to 15^0C and from 3.49 cst. to 2.0 cst respectively. Both ethylene glycol-modified Jatropha seed oil and the unmodified Jatropha seed oil were able to also depress the pour point of the crude oil to the same degree showing that modification with ethylene glycol did not improve the ability of ordinary Jatropha seed oil to act as pour point depressant.

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Light crude oil like the Bonny light crude oil brand from Nigeria is very desirable. This is because they usually have low percentage of resins and very high percentage of hydrocarbons. This confers on them high API gravities thus attracting good prices in the oil market. Presence of long chain hydrocarbons otherwise known as waxes in crude oils gives rise to waxy crude oils. Flow assurance of waxy crude oil has been a major problem in the production and transportation of crude oil especially in cold region due to its high wax content (Ahmed, 2007; Achugasim et al., 2014). When the inner wall temperature falls below the wax appearance temperature and there is large temperature differential between the cold surface and wax solution, wax precipitates and deposits on the cold pipeline wall. (Singh *et al.*, 2000; Osuji *et al.* 2010). This occurrence disrupts the flow of crude oil, creating pressure abnormalities and causing artificial blockage leading to partial or total shutdown of production (Bern *et al.*, 1980). Wax precipitation is impacted by several factors such as temperature gradient, crude oil composition, flow rate, pipe wall temperature and crude oil temperature amongst others (Adeyanju *et al.*, 2016; Salam *et al.*, 2004). The approach of oil and gas industry in tackling this problem is through prevention and remediation. The formation of wax cannot be avoided in production but the rate of formation can be lowered using wax inhibitors and in turn delay the build-up of wax deposits (Pedersen *et al.*, 2003). In the removal of wax

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deposit, that is remediation one or combination of the following can be employed; mechanical, thermal insulation, pipeline heating and chemical method (Wei, 2015) (Guo *et al.,* 2004). Chemical method is usually used in the preventive manner where pour points depressants (PPDs) are majorly employed to manage the flow assurance problems (Uhde and Kopp, 1971). PPDs are materials that have similar chemical structure to the wax that is depositing. The mechanisms of dispersion include nucleation, adsorption, co-crystallization and improved wax dispersion (Fang *et al.,* 2012). Research on PPDs are now tilting towards the discovery of green and cost effective compounds depending on the crude oil in question. Recent studies have shown that some plant seed oils are effective natural PPDs. Example of such plant seeds include Jatropha curcas, castor, cashew, rubber and palm kernel seeds. Akinyemi *et al.* (2018) and Eke *et al.* (2019) amongst other scientists have shown their effectiveness on waxy Nigerian crude oils in improving their flow properties. The effectiveness of some of them are enhanced through modification. In this work we report the use of modified and unmodified Jathropha curcas seed oil as pour point depressants for a Nigerian waxy crude oil.

MATERIALS AND METHODS

Materials: The major materials used in this research include diethanolamine (Lobachemie chemicals), ethylene glycol, petroleum ether. Crude oil sample from a marginal field in Delta State, Nigeria. Jatropha curcas seed from Ibadan, South-west, Nigeria.

Methods: The seed was deshelled, dried in the oven at 100^0C for 1 hour to a constant weight and ground. 1kg of the ground seed was macerated with petroleum ether for 72 hours and multiple extractions was done. This afforded oil extract of 450g after the removal of the solvent. The extracted oil was subsequently analyzed for the following oil quality parameters; free fatty acid, acid value, saponification value, iodine value, moisture content, density and specific gravity.

Characterization of Crude Oil Sample

Specific Gravity (ASTM D298-12b): The specific gravity of the crude oil sample was determined by hydrometer method and the API gravity (60^0F) was calculated using the expression.

$$\text{API Gravity} = \frac{141.5}{SpecificGravity} - 131.5$$

Viscosity (ASTM D445): The viscometer bath is set at 40^0C and a thermometer was inserted on the bath to take temperature of the bath fluid as a feedback reading. The sample was poured into a suitable viscometer U-tube, filled to mark and clamped. The setup was maintained at a bath temperature of 40^0C. Vacuum pump was used to suck the sample in the U-tube up to mark. The time taken for the sample to flow to the second mark of the viscometer was recorded. Viscosity was calculated by the kinetic viscosity V (unit is centistokes Cst or mm 2 /s) as

$$V = Ct$$

Where: V = Kinematic Viscosity, c = viscosity constant of the u-tube in mm^2/s^2; t = time (seconds)

Pour Point (ASTM D97-12): 40ml of crude oil sample was poured inside a test jar and sealed with a cork and a thermometer was inserted through the cork into the sample to monitor the temperature while avoiding shaking of the sample. The pour point machine was put on and allowed to run cold before putting the test jar into the machine. The sample was checked at interval to know if it has poured. The temperature of the sample was taken as it ceases to flow when the test jar was tilted.

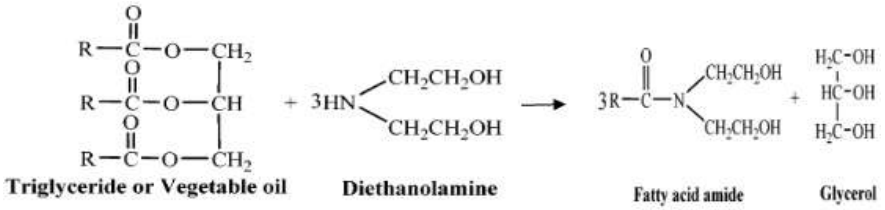
Water Content (ASTM D95-13e1, 2013): 100 ml of toluene and crude oil sample were mixed together in a 500 ml round bottom flask connected to a condenser and heated at 120^0C for 2 hours and the mixture of water and toluene was collected at the receiving end of the Dean and Stark apparatus. The volume of the resulting mixture was recorded and the volume of water was calculated by subtracting the initial volume of toluene from the resulting mixture volume.

Wax Content (Universal Oil Product 46-64 Method): 4g of the crude oil sample was mixed with 80 ml of n-pentane, mixture was stirred with a magnetic stirrer for 1 hour. 180 ml of acetone was mixed in a separate conical flask with 60 ml of n-pentane. The mixture of acetone/n-pentane was added to mixture of crude oil and n-pentane. The temperature of the mixture was reduced to -20^0C using a deep freezer for 24 hours. The solid substance formed was filtered and dissolved in 100 ml of n-hexane to remove asphaltene and the n-hexane was removed by heating the dissolved mixture in a fume cupboard at a temperature of 75^0C. The solid product was weighed and recorded.

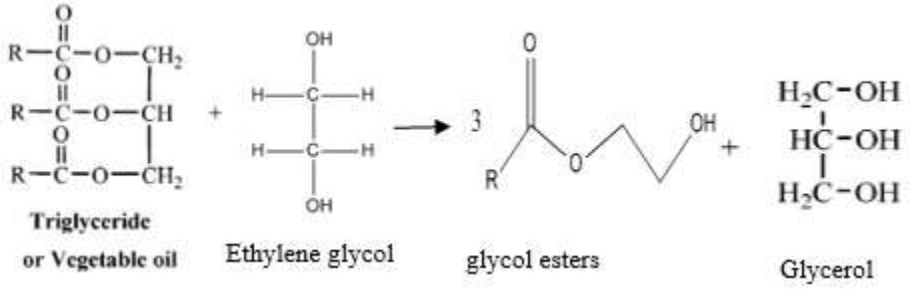
Modification of Jatropha Curcas Oil

Aminolysis: 50 g of the extracted oil was weighed into a 100 ml two neck round bottom flask and heated slightly. 36.17 g of Diethanolamine was measured into a beaker. The molar ratio of oil to DEA is 1: 6. Sulphamic acid, 2% by weight of the oil was added to the measured DEA and stirred. The mixture of sulphamic acid and DEA was added to the pre-headed

oil in the two neck round bottom flask and was refluxed for 1 hour at 110^{o}C in an oil bath. The resulting mixture was filtered through a filter cloth to remove the heterogeneous catalyst, sulphamic acid. 80ml of n-hexane was added to the filtrate and allowed to stand in a separating funnel for 24 hours for separation. The upper layer was washed with hot water till the solution is neutral. It was dried over sodium sulphate. The n-hexane was recovered by using a simple distillation method setting the temperature at 70^{0}C. The pure product formed was characterized with FT-IR analysis (Kumar *et al*., 2015).



Esterification of Refined Jatropha curcas Oil with Ethylene Glycol: 50g of oil was weighed into a 100 ml two neck round bottom flask and was heated to above 50^{0}C. 21.35 g of Ethylene glycol was measured into a beaker. The molar ratio of oil to EG is 1: 1.4. Sulphamic acid, 10% by weight of the oil was added to the measured EG and stirred (Marcelo *et al.*, 2012). The mixture of sulphamic acid and EG was then added to the pre-heated oil in the two neck round-bottomed flask and refluxed for 8 hours at 160^{o}C in an oil bath. The resulting mixture was filtered through a filter cloth to remove the heterogeneous catalyst, sulphamic acid. The mixture was allowed to stand in a separating funnel for 24 hours. The upper layer was separated from glycerol and washed with hot water till the solution is neutral. It was dried over sodium sulphate and readied for FT-IR analysis (Marcelo *et al.*, 2012).



Application of Synthesized Pour Point Depressants on Waxy Crude oil: The *Jatropha curcas* oil and its derivatives were added to the waxy crude oil in different percentages of the volume of the waxy crude oil using a micro-syringe. The percentages range from 0.1 to 0.3% of the volume of the waxy crude oil. The effect of the PPDs on the pour point and viscosity of the crude oil was determined by measuring the viscosity and pour point of the crude oil before and after it dosing with different amounts of the PPDs.

RESULTS AND DISCUSSION

The extraction of *Jatropha curcas*oil using petroleum ether (Analytical grade) gave a pure light-yellow oil with a yield of 49.5 % which indicates that oil can be extracted from the seed at commercial quantities. This yield is low compared to other studies where n-hexane is used as the extracting solvent. According to Sepidar*et al.* (2009), n-hexane gives the maximum yield when compared with other solvent but the oil recovered is slightly yellow in colour which might cause problem in further biodiesel production. Thus, the pure light-yellow oil extracted using petroleum ether is more suitable for transesterification. The free fatty acid value of 5.338mgKOH/g gives an indication of the quality of fatty acids in the *Jatropha curcas* oil. It is also indicative of ease or otherwise of esterification. High acid value lowers the oxidative stability of the oil. The low moisture content shows that the likelihood of rancidity is low. Also, the low iodine value indicates low unsaturation in the fatty acid moieties of the oil which makes it less prone to oxidation and polymerization. The low saponification value indicates that the oil will not be suitable for the production of soap. The wax content of the crude oil sample is 29.5% which shows that it is a waxy crude oil. This is further supported by its API gravity of 30.6 (medium crude oil). The pour point of 18^{0}C and a viscosity of 3.49 cst indicate that the crude oil is prone to flow assurance problem. The results presented in

Table 1 and 2 makes the seed oil and crude oil suitable for pour point depression studies.

FT-IR Characterization of the Extracted Oil and Crude Oil: The FT-IR spectrum of the extracted *Jatropha curcas* oil, labeled Sample B is shown in Fig 1. The strong peak present at 1747.73 cm^{-1} confirms the presence of C=O stretching vibration of carbonyl group found in triglycerides. The peak at 2922.48 cm^{-1} confirmed the presence of antisymmetric stretching vibrations of C-H in CH_2 while the symmetric stretching vibrations of C-H in CH_3 are confirmed by the peak 2854.16 cm^{-1}. The presence of water molecules in the extracted *Jatropha curcas*oil is confirmed by the peak at 3470.81 cm^{-1} representing the stretching and bending vibration of O-H bonds of water molecules. The peak from 1400- 1200 cm^{-1} conforms with the stretching vibration of CH_2 and CH_3 aliphatic group of triglycerides. The peak at 1119.03 cm-1 conforms with the stretching vibration of C=O group of an ester. Fig 2 shows the FT-IR analysis of crude oil sample, sample A. The peak at 721.61cm^{-1} occurs due to the presence of long chain alkane group with more than seven carbon atoms in the crude oil sample. This peak points to the presence of paraffin or waxes in the crude oil sample.

Table 1. Physicochemical properties of extracted *Jatropha curcas* oil

Parameters	Results
Free Fatty Acid (%)	5.338
Acid Value ($mgKOHg^{-1}$)	10.68
Density (g/cm^3)	0.9048
Specific Gravity	0.9158
Iodine Value (g of iodine/100g	92.10
Moisture Content (%)	1
Saponification (mgKOHg-1)	157
Yield (%)	49.5

Table 2: Physicochemical properties of crude oil sample

Parameters	Results
Specific Gravity	0.873
API gravity	30.6
Kinematic Viscosity@40^0C	3.49 cst
Water Content	5%
Wax Content	29.5%
Pour Point	18^0C

FT-IR Characterization of the Modified Jatropha Oil: The FT-IR spectrum of extracted *Jatropha curcas* oil and the esterified *Jatropha curcas* oil are alike with little differences. These differences or little shift in the peaks of the samples implies that a chemical reaction has occurred. Also, there are disappearance of some bands and appearance of new ones which evidently confirm the conversion of the triglyceride. The appearance of the peak 1744.37cm^{-1} represents the vibration of C=O of gylcol ester which confirmed that transesterification of the *Jatropha curcas* oil has taken place. The peak at 1621.71 cm^{-1} represent the stretching vibration of C=O of amide. This confirmed that aminolysis of the *Jatropha curcas*oil has taken place.

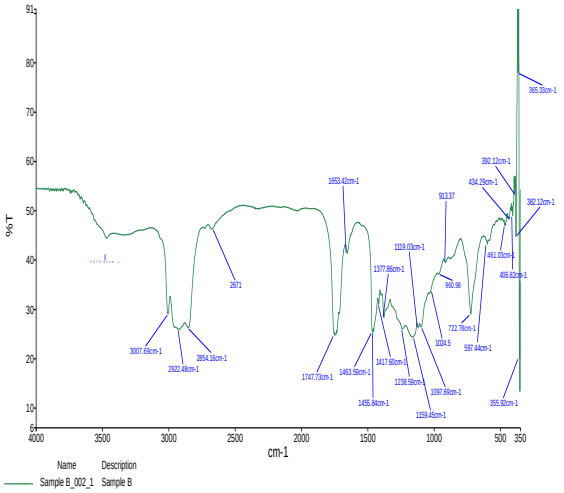


Fig 1: FT-IR spectrum of extracted *Jatropha curcas* oil

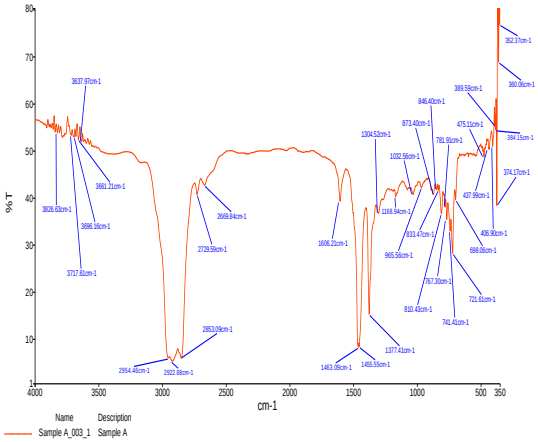


Fig 2: FT-IR spectrum of crude oil sample

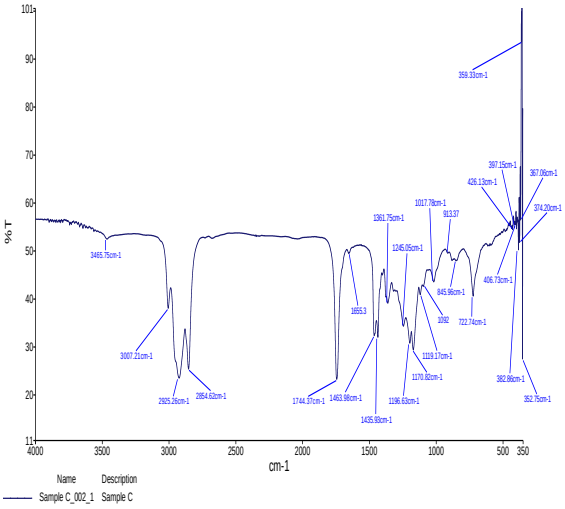


Fig 3 FT-IR spectrum of *Jatropha curcas* oil modified with Ethylene Glycol

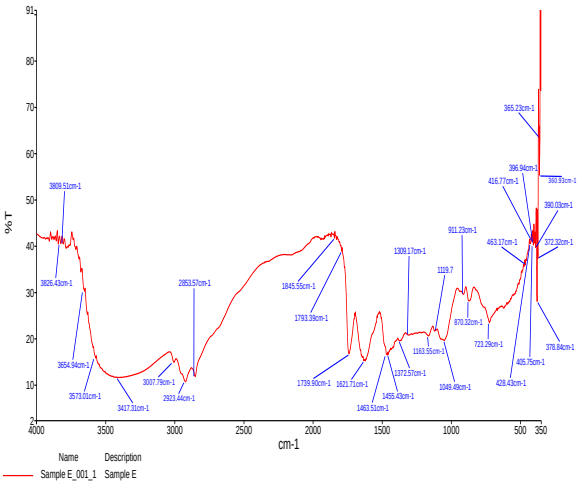


Fig 4: FT-IR spectrum of *Jatropha curcas*oil modified with Diethanolamine

Pour Point: The pour point of the crude oil sample without the additive is 18^0C while the viscosity at 40^0C is 3.49cst. On addition of the extracted *Jatropha curcas* oil, there was a slight decrease in the pour point of the crude oil sample at 0.1% dosage. Increase in dosage of the pour point depressants did not have any further effect on the pour point of the crude oil. Although the viscosity of the crude oil increases as the dosage of *Jatropha curcas* increased. This effect confirms that the extracted *Jatropha curcas* oil is in itself a flow improver and pour point depressant. Table 3 shows the result of the pour point and viscosity of crude oil dosed with *Jatropha curcas* oil. On addition of the transesterified *Jatropha curcas* oil to the crude oil the pour point depressed and peaked at 0.2% dosage to give a pour point of 15^0c and viscosity of 2.21cst. Table 4 shows the result of the viscosity and pour point of the crude oil dosed with *Jatropha curcas* oil modified with ethylene glycol. On addition of the *Jatropha curcas* oil modified with DEA, the effect optimized with 0.2% dosage to give a pour point of 15^0C and viscosity of 2.00cst. Table 5 shows the result of the pour point and viscosity of the sample crude oil when esterified *Jatropha curcas* oil is added. The *Jatropha curcas* oil modified with DEA proves more effective than others at reducing the viscosity of the crude oil sample. In terms of pour point both the unmodified *Jatropha curcas*oil and modified *Jatropha curcas* oil with DEA reduced the pour point at 0.1% dosage, making it more effective than the modified *Jatropha curcas* oil with ethylene glycol.

Table 3: Effect of the *Jatropha curcas* oil on the pour point and viscosity of the crude oil at various doses

Dosage (%)	Pour Point (^{0}C) (Before dosage)	Pour Point (^{0}C) (After dosage)	Viscosity @40^0c (cst) (Before dosage)	Viscosity @40^0c (cst) (After dosage)
0.0	18	-	3.49	-
0.1	-	15	-	2.37
0.2	-	15	-	2.19
0.3	-	15	-	2.18

Table 4: Effect of the *Jatropha curcas* oil modified with ethylene glycol on the pour point and viscosity of the crude oil at various doses

Dosage (%)	Pour Point (^{0}C) (Before dosage)	Pour Point (^{0}C) (After dosage)	Viscosity @40^0c (cst) (Before dosage)	Viscosity @40^0c (cst) (After dosage)
0.0	18	-	3.49	-
0.1	-	18	-	2.37
0.2	-	15	-	2.21
0.3	-	15	-	2.61

Table 5: Effect of the *Jatropha curcas* oil modified with diethanolamine on the pour point and viscosity of the crude oil at various doses

Dosage (%)	Pour Point (^{0}C) (Before dosage)	Pour Point (^{0}C) (After dosage)	Viscosity @40^0c (cst) (Before dosage)	Viscosity @40^0c (cst) (After dosage)
0.0	18	-	3.49	-
0.1	-	15	-	2.05
0.2	-	15	-	2.00
0.3	-	15	-	2.05

Conclusion: The modification of *Jatropha curcas*oil using ethylene glycol and diethanolamine was confirmed and the modified *Jatropha curcas* oils were able to improve the flow properties of the crude oil sample with wax content of 29.5%, kinematic viscosity of 3.49cst and pour point of 18^0 C. The efficiency of the modified *Jatropha curcas* oil as pour point depressants for the crude oil samples was optimized with 0.2% dosage of diethanolamine to give a reduction in the initial pour point of the crude oil from 18^0C to 15^0C and viscosity from 3.49 cst to 2.00 cst.

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