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EFFECT OF EPOXIDATION ON THE PHYSICOCHEMICAL PROPERTIES OF NEEM (*AZAADIRACHTA INDICA*) LEAF OIL FOR OIL AND GAS EXPLORATION

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Abstract

The study investigated the effect of epoxidation on the physicochemical properties of Neem (Azadirachta Indica) leaf oil for Oil and gas exploration. In this paper epoxidation method of Swern Daniel *of the Neem (Azadirachta Indica) leaf oil was employed upon which the effect of epoxidation of Carbon-Carbon double bond on physicochemical properties of Neem leaf oil with a view to employing it as base oil for drilling mud was examined. Neem leaf oil was Epoxidized and characterized for viscosity, acid value, peroxide value and iodine value. The results obtained show a decrease in viscosity at 40˚C, from 50 cSt to 37.5 cSt. The acid value and the iodine value were found to decrease from 1.45 mg/g.KOH and 94.4 weight respectively to 0.28 mg/g.KOH and 6.97 weight before and after epoxidation methods. The poor point was found to have acceptable values of 8ºC and 9ºC. These results appear to be encouraging for the formulation of thermally stable oil for high temperature and pressure drilling operations.*

Keyword: *Epoxidation, Drilling fluid, Neem oil, Acid value, Iodine value, oxidative stability*

1. Introduction

Oil based muds were initially developed to address the problems of reactive shale and high temperature wells, which water-based drilling mud (WBM) could not contain (Al-Yami *et. al*, 2018). OBMs are also better heat conductors for cooling and lubricating the drill bits. But the mineral oil based drilling fluids that are in vogue today are toxic, non-biodegradable, and non-renewable.As a result, an attempt was made to replace them with synthetic-based muds (SBM) which are less toxic but still are 5 times more expensive than conventional OBMs.These led to search for superior alternative fluids. Vegetable oils readily come to mind as they are non-toxic, biodegradable and renewable and cost only twice the price of WBM (Miles, 1998, Bhandarea, P. &Naik, G.R. (2015)). However, the direct use of vegetable oils to formulate drilling fluids has some limitations, some of which are poor flow property of oil at low temperatures; thermal instability and vulnerability to oxidation at high temperatures due to the presence of acyl groups and glycerol (Borugadda& Goud, 2016).They also have low electrical conductivity, typical of all oils (Mehdi, *et. al*. 2019).Chemical modification of the structure fatty acids in vegetable oils by epoxidation has been found to stabilize the oil against oxidation by saturating the carbon-carbon double bonds in the oil molecule (Onuh*et. al*.2017).But the application of vegetable oils in drilling fluids is limited beyond 120ºC due to their low thermo-oxidative stability. Alluring at, drilling mud popularly known as the drilling fluid, costs as much as $300 a barrel, about a quarter of total drilling costs for one well, according to Cecil-based Consol. Mud expenses alone could be as much as $150,000 per well, which requires about 500 barrels of mud on average but varies depending on how the shale formation reacts (Eman Ali Ateep, 2019).The African drilling and completion fluids market is gradually growing. Factors such as the increase in the number of drilling operations in African countries are expected to help drive the demand for drilling and completion fluids market. Additionally, the development of shale and deep-water and ultra-deep-water fields are expected to further drive the market for drilling and completion fluids. Drilling activities are increasing in African countries, especially Nigeria, Senegal, and mainly in Southern and Western Africa, owing to offshore oil & gas activities in these regions, where major projects have started. In Africa, wells are being drilled going farther away from land and into the sea and being drilled deeper than before, such as deepwater and ultra-deepwater projects. This has created ample opportunities for drilling and completion fluids in the region. Nigeria is expected to dominate the market over the period of 2023-2028 owing to its robust drilling activities in onshore and offshore regions (Lakrari, K., Moudane, M.E., Hassanain, I., Ellouzi, I. Kitane, S. and Belghiti, M.A.E. (2021)This can only be done with the aid of alternative renewable materials through chemical modification, the physico-chemical properties of the oil can be improved leading to higher performance in high temperature conditions(Onuh*et al*, 2017 & Tambuwal, F., R., · Oparanti, S., O., Ibrahim, A., · Umar, S., Amoka, A. A. 2021)**.** The various fatty acid content such as oleic and linoleum can be chemically altered to improve the oxidation stability and other physicochemical properties, and produce more desirable rheological properties in the oil (Miles, 1998). Epoxidation can enhance these properties (Sulaimon *et. al*., 2017).

Epoxides are of great industrial interest because they are intermediate compounds for the production of polymers, adhesives, resins, and other materials (Schneider, et. al., 2009).

This paper investigated the epoxidation of Neem leaf oil to develop an oil based drilling fluid that is electrically conductive for logging with resistivity imaging devices, and thermally stable for improved drilling operations.

2.0 MATERIALS AND METHODS

Glacial acetic acid, 100%; Aqueous hydrogen peroxide (~30wt %); Sulfuric acid; Diethyl ether; Ethanol; Ether, Phenolphthalein indicator; Potassium hydroxide (KOH); Chloro Potassium iodide; Starch indicator and sodium thiosulphate ($Na_2S_2O_3·H_2O$).

Samples procurement:

All chemicals were purchased from Padmavati Chemicals, Bangalore.Neem oil was extracted from fresh Neem leaves using Soxhlet extraction method, with hexane as solvent. Pre-treatment was carried out on samples prior to the extraction process for maximum yield and purity of the extracted oil. Mature Neem leaves were washed and subjected to Soxhlet extraction using hexane as solvent at a temperature range of 70-80 ^oC as shown in fig. 1. The following assays were conducted for test sample of Neem oil: This was carried out in accordance with American Standards for Testing of Materials (ASTM). 2003. D 3487, D3487, D2197-15, D924-92, D97, 57, D 93, 29, D 93.& IEC standard.

2.1 Extraction of Oil

All the experiments were conducted at Skanda Life Sciences Pvt. Ltd, Bangalore, India. Pre-treatment was carried out on samples prior to the extraction process for maximum yield and purity of the extracted oil. Mature Neem leaves were washed and sundried for 3 days and powdered.50g of the leaves were weighed and subjected to Soxhlet extraction using hexane as a solvent at a temperature range of 70-80 ^oC, as shown in fig. 1. The following assays were carried out for test sample of Neem oil:

2.2 Determination of Acid Value

To 25ml each of ethanol and ether, 5g of Neem oil was added and heated for 10 minutes. 1ml of phenolphthalein was added as indicator. The mixture was titrated with 0.5N potassium hydroxide until pink colour appears which persisted for 15 seconds. The entire procedure was repeated without the sample (blank). The acid value was calculated using the formula:

$$\text{Acid value } A_v = \frac{t_d \times n \times 56.1}{m} \quad (1)$$

whereb= titre value for blank; s= titre value with sample; n = normality of titrating solution; m = mass of sample, andt_d is the titre difference $b - s$.

2.1.2 Peroxide Value

30ml of glacial acetic acid-chloroform solution 5g of sample was added to 0.5ml of saturated potassium iodide solution was added and the contents swirled for exactly 1 minute. 30ml of distilled water was added and the contents shaken vigorously to liberate iodine from the chloroform layer 1ml of starch solution was added as indicator. The resulting mixture was titrated with 0.1N sodium thiosulphate until the blue-gray colour disappeared in the aqueous lay. The entire procedure was repeated without the sample (blank). The peroxide value was calculated using the formula as given for Acid value.

Figure 1: Extraction of oil Neem leaves using Soxhlet extraction method

2.1.4 Iodine Value

20ml of chloroform and 25ml of Wijs reagent were added to 0.2g of the oil. The resulting mixture was stirred and stored in a dark place at 25°C for 30 minutes.10ml of 30% potassium iodide was then added to the mixture as well as 100ml of distilled water. The mixture was titrated with 0.1N sodium thiosulphate until the yellow colour almost disappeared.1ml of starch solution was then added and the mixture was titrated further until the blue starch-iodine colour disappeared.The entire procedure was repeated without the sample (blank).The Iodine value was calculated using the formula below:

$$\text{Iodine value, } I_v = \frac{t_d \times 1.269}{\text{m}}$$

Where$t_d$and m are as defined in acid value above.

2.1.5 Specific Gravity

Empty specific gravity bottle weight was measured and recorded. It was then filled with 10ml of water and its mass measured and recorded. The specific gravity bottle was then filled individually with equal volume of each oil extract while its mass measured and recorded in each case. The specific gravity of individual oil extracts were calculated using the formula below

$$\text{Specific gravity} = \frac{W1 - W2}{W3 - W2},$$

Where, W1 = mass of specific gravity bottle + Oil extract

W2 = mass of empty specific gravity bottle

$W3$ = Mass of specific gravity bottle + Water

2.1.6 Dynamic Viscosity

Viscosity is an important fluid property when analysing liquid behaviour. Dynamic viscosity is a measure of the internal friction of the liquid when it is flowing. It is of paramount to ensure the viscosity of the oil to be as low as possible in order to elude affecting the cooling efficiency of oil transformers. Oils are the main class of lubricant, coolant and Insulant as well as the number of applications that the volume of Insulant used that seed-based oils composed of 80 to 90% oil. Due to their natural affinity for metal surfaces and their viscosity, Oil seep between the surfaces in relative motion and reduce friction, heat and wear because of their chemical inertness when subjected to electric fields. It is common to observe increases of viscosity with chemical modification causes lubrication effects instead thereby resulting decrease. Such a result could be of help in application relating to areas of heat extraction Bakak*et.al*. (2021).

2.3 Procedure for Epoxidation

The Epoxidation method of Swern, D.(2018) was used. Initially, 100ml of sample (Neem oil) was placed in a beaker and kept on a magnetic stirrer maintained at 2500 rpm to the reaction mixture, 0.02M of 100% acetic acid (126.3µl) and 2% sulfuric acid (576.3µl) were added, and the mixture with oil was stirred for 30 min. Hydrogen peroxide (450µl) in the ratio of (0.04M added drop-wise over 30 min and incubated at 60^0C for 4 hours. The reaction mixture was stirred continuously to avoid zones of high peroxide concentration that could lead to explosive mixtures. The collected samples were then extracted with diethyl ether and washed with water until they were acid free in accordance with IEC. The washed samples were analyzed further for the determination of acid value, iodine value and peroxide value of the Epoxidized Neem oil.

3.0 Results and Discussion

Table 1: Characterization of Neem Oil Pre- Epoxidation and Post- Epoxidation

Parameters	Pre-epoxidation Value	Post-epoxidation Value
Acid value	1.45	0.28
Viscosity	50.0	37.5
Iodine value	94.4	6.97
Peroxide value	34	28
Specific gravity	0.92	0.93

Table 2: Characterization of Thermal Properties

Parameters	Pre-epoxidation	Post-epoxidation
Flash point	255	250
Pour point	8	9
Fire point	265	261

3.1 Pre-Epoxidation:

Table 1indicates some of the physicochemical properties of Neem leaf oil.The oil yield was found to be 54.94% which is a good value in accordance with ASTM D3487 & ASTM D2197 standards. The yield indicates its suitability in the preparation of oleo chemicals for drilling fluid. The iodine value of 94.4 indicated that the oil is non-drying oil, consisting predominantly of polysaturated fatty acids, with a potential in production of lubricant. Acid value was found to be 1.45. Acid value of oil determines the extent to which the glycerides had been decomposed by lipase action. The decomposition is usually accelerated by heat and light during epoxidation.

The acids that are usually formed include free fatty acids, acid phosphate and amino acids. Free fatty acids are formed at a faster rate than the other acids. The peroxide value is the measure of oxidative rancidity of oil. Oxidative rancidity is the addition of oxygen across the double bonds in unsaturated fatty acids in the presence of enzyme or catalyst or certain chemical compounds. The odour and flavour attributed with rancidity are due to liberation or generation/formation of short chain carboxylic acids. High peroxide values are linked with high rate of rancidity. Variation of peroxide value could be as a result of the number of unsaturated fatty acid content, since the rate of oxidation of fats and oils increases with increasing level of unsaturation. The high peroxide value of 34 indicates it has viable oxidative rancidity but it decreased to 28 after epoxidation that shows it has poor oxidative stability at elevated temperatures.

3.2 Post-Epoxidation

The results in table 1 for the epoxidation of *Neem (Azadirachta Indicia)* leaf oil indicates the viscosity of the oil was found to be 50.0cSt and it decreases to 37.5cStafter Epoxidation of the oil. This is an indication that the oil extracted was of high degree of purity. The acid value of epoxidized oil of 0.28 is lower than that of the extracted oil of 1.45. This could be attributable to structural modification formed during epoxidation (Tambuwal, F., R.*et al*., 2021),since acid value is found to decrease with free fatty acid and structural modification. The iodine value of 6.97 of the epoxidized oil is lower than that of the extracted oil of 94.4. The specific gravity also increases from 0.92 to 0.93,this could be attached to decrease in the degree of unsaturation, cause by epoxidation (Bhandarea, P. &Naik, G.R. 2015).

Table 2 indicates that Neem oil has high flash and fire points similar to most of vegetable oils. It falls in the category of high temperature oil. The high flash and fire points of the oil may be attributed to the high number of saturated fatty acids in the oil. Meanwhile, the flash point of the oil sample was observed to have decreased from 255°C before epoxidation to 250°C after epoxidation, while fire point decreased from 265°C to 261°C. The decrease in these values was most likely as a result of structural modification owing to Epoxidation (Ado M., & Tambuwal, F., R. 2018). On the other hand, the pour point of Neem increased from 8°C to 9°C as shown in table 2.

3.4 Fourier transform infrared spectroscopy (FTIR) Analysis

The FTIR spectra of Neem oil and Epoxidized Neem oil samples are shown in figures 3 and 4.

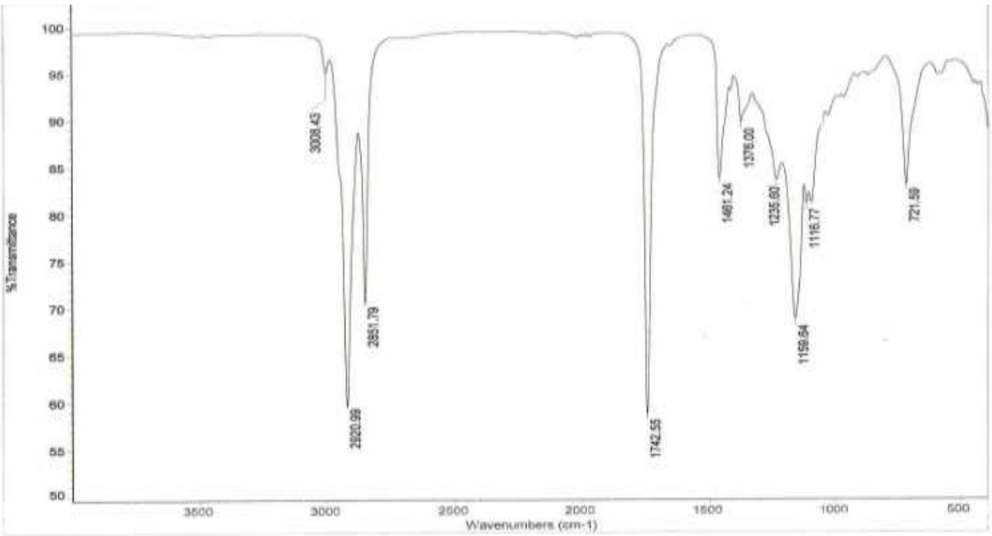

Figure 3: FTIR Spectra of Neem Oil

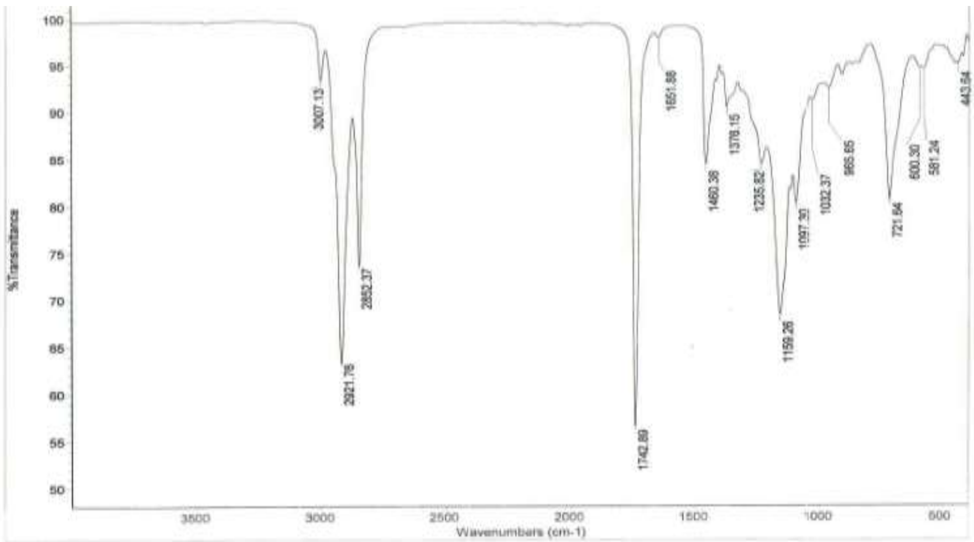

Figure 4: FTIR Spectra of Epoxidized Neem Oil

Table 3: FTIR Results for Neem Oil and Epoxidized Neem Oil

Frequency (cm^{-1}) Literature	**Assignment and Mode of Vibration**	**Frequency (cm^{-1}) of Neem Oil**	**Frequency (cm^{-1}) ofEpoxidized Neem oil**	**Functional Group**
3100-3000	=C-H Stretching vibration	3008.43	3007.13	Aromatics
3000-2850	C-H asymmetric stretching vibration of CH_2	2920.99 2851.79	2921.76 2852.37	Alkanes
1750-1735	Overtone of C=O, stretching vibration	1742.55	1742.89	Esters
1470-1450	C-H scissoring vibration of CH_2 and CH_3 and symmetric bending vibration of CH_3	1461.24	1460.38	Alkanes
1320-1000	C-O Ring stretching of the vibration of the C-C, contraction of C-O	1159.64	1159.26	Alcohol, carboxylic acid, Esters
900-675	C-H asymmetric ring stretching vibration of the C-C during the contraction of the C-O, C-H rocking vibration of CH_2 Epoxy functional group.	721.59	721.64	Aromatics

As seen from the figures 3 and 4, the spectra of the two oil samples were observed to have similar peaks. The assignment of the peaks and mode of vibration that led to produce the peaks were depicted in figures 3&4 for the two samples under study. A vibration frequency was observed at 3008.43 cm^{-1} and 3007.43 cm^{-1} for Neem oil and Epoxidized Neem oil respectively which is a characteristic of C-H for aromatics. The vibration frequency at 2920.99 cm^{-1}, 2851.79 cm^{-1} for Neem oil and 2921.76 cm^{-1}, 2852.37 $cm^{-1}$for the Epoxidized Neem oil were seen and that seemingly characterized to be alkanes functional group. The medium and strong peaks within the range of 1470-1450cm^{-1} and 1320-1000cm^{-1} are alkyl esters of long chain fatty acids, but distortion and rapid movement of the alkylate group was observed between 1460.38cm^{-1} to 1159.26cm^{-1} for the sample as ring-opening relieves the strain in the ring for Epoxidized Neem oil and at the same time grafts the side hydrocarbon chains that led the fatty acid to be closely packed, and subsequent grafting of molecular side chains to the epoxy group. At vibration frequency of 721.64cm^{-1}, a peak of Epoxidized ester occurs that indicated the effect of chemical modification (epoxidation) on green plant for proper utilization.

4. Conclusion

Neem oil was epoxidized and characterized for viscosity, acid value, peroxide value, iodine value as well as Fourier transform infrared spectroscopy (FTIR) was carried out. The results obtained show a decrease in viscosity at 40˚C, from 50 cSt to 37.5 cSt. The acid value and the iodine value were found to decrease from 1.45 mg/g.KOH and 94.4 respectively to 0.28 mg/g.KOH and 6.97 before and after epoxidation. The pour point was found to have acceptable values of 8ºC and 9ºC. The epoxidation of Neem oil has desirable effects onflash and fire points, though the values decreased from 255°C to 250° C and 265°C to 261°C respectively.A vibration frequency was observed at 3008.43 cm^{-1} for Neem oil. It was also observed that, at vibration frequency of 721.64cm^{-1}, a peak of Epoxidized ester occurred.These results appear to be encouraging for the formulation of thermally stable oil for high temperature and pressure drilling operations.

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