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Production and Testing of Biodegradable Grease from Black-Date (*Canarium schweinfurthii)* Oil *(pp.223-233)*

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Abstract: This work focuses on the production and testing of biodegradable grease from Black-date oil. The production was carried out by extracting the oil from black-date seed with solvent extraction using n-hexane; hydrolyzing the oil extract as a mixture of the base oil, thickener (calcium hydroxide), stearic acid and additives to form solid grease. Tests were carried out to determine the quality of the biodegradable grease produced. Work ability, dropping point and biodegradability were also conducted. Oando and Texaco conventional greases were used as control and standards. The production condition, measurement standards and results were: water temperature for removing black-date flesh from the seed (60^0C -70^0C); and temperature for the productions of grease were 100^0C, 170^0C and 210^0C. The BOD test result were within the acceptable range of 4.0 – 8.0 and the cone penetration of grease (consistency) result was of the ASTM D217 – IP50 standard with the highest produced grease dropping point close to that of Oando grease. This work therefore has added to the list of feedstocks for bio-based lubricants which can be of use both in terrestrial and aquatic environments for industrial and other applications.

Key words: solvent extraction, feedstock, application, quality, lubricant, ASTM.

1 INTRODUCTION

The effect of friction on industrial equipments (machine parts) and on automobiles is a major problem confronting man. As a result, lubricants or greases made from petroleum products were initially developed to limit these dangerous situations. The need to develop as much as possible bio-based materials as industrial and automotive lubricants has increased in recent years. This trend is primarily due to the non-toxic and biodegradable characteristics of vegetable oils that can replace mineral oils as base fluids in grease making (Drake, 1991).

Biodegradable greases which are made from renewable resources vis a vis vegetable oils provide suitable alternative to the petroleum base greases that are environmentally toxic and non-biodegradable. Vegetable oil-based greases are semi-solid colloidal dispersions of thickening agents (a metal soap) in a liquid lubricant matrix (vegetable oil). The thrust therefore in the world of tribology today is the search for renewable, biodegradable high viscous oils that will satisfy the requirements of lubrication. Black-date oil can be one of such options in the search.

Black-date also known as *Canarium schweinfurthii* is found in the kingdom *plantae* (Dutta, 1979). Blackdate or *Atili* is an exotic tree introduced into Africa from Indonesia. It is acclimatized to West Africa and can be readily found in countries such as Angola, Cameroon, Ethiopia, Tanzania, Ghana, Guinea Bissau, Liberia, Mali, Senegal, Sierra Leone, Sudan, Togo, Uganda, Zambia and Nigeria (Evans, 2004).

In Nigeria, the trees are found mostly in Ibadan, Ijebu and Benin. They are equally common in the eastern part of the country. In the south, places like Calabar, Uyo are prominent. The north-central Nigeria is not left out. They include: Pankshin, Mangu, Barkin Ladi and Bokkos LGAs of Plateau state as well as Niger State. *Atili* or Black-date is the fruit of a perennial tree plant called *Atili* tree. It is called *ube okpoko* in Igbo and *Atili* in Hausa (Keay, 1964).

Black-date oils classified as vegetable oil is composed of triglycerides. The fatty acid composition of the black-date pulp oil is palmitic acid, stearic acid and palmitoleic acid. That of the seed oil and esters is oleic acid, linoleic acid, palmitic acid, stearic acid, linolenic acid and myristic acids (Igbum and Eloka-Eboka, 2011). It is hydrophobic in nature and in order to emulsify it in water for application purposes, it must be formulated with approximate surfactants (Ibrahim, 1998).

2 MATERIALS AND METHODS

2.1 Extraction of Base Oil

Samples of *Atili* seeds were washed and sundried for the purpose of removing dirt and afterwards transferred into a bowl. Warm water of about $60^oC - 70^oC$ in temperature was poured into it and covered with the lid which was allowed to stay for 10-15 minutes. Thereafter, the seeds were removed from the water and dehusked, separating the hard seeds from the mesocarp (soft fleshy part). The mesocarp were immersed into the normal Hexane solvent and allowed for several hours. The mesocarp from the solvent was further sent to the press to further extract the oil. The oil containing n-hexane was sent to a soxhlet extraction apparatus where the pure *atili* oil was collected in a round bottom flask and transferred to a bottle for the production of the grease. (See Plate 1.)

2.2 Production of Grease

Three (3) sets of grease preparation were carried out with measurement from the extracted black-date oil, sodium hydroxide, stearic acid and calcium hydroxide. And the basis for the production was on two parameters which were percentage weight and temperature. The weight ratio of the base oil, calcium hydroxide, stearic acid and sodium hydroxide is 80:20:15:3 percent and each set were labeled samples 1, 2 and 3 respectively. Production set-up is as shown in Plate 2.

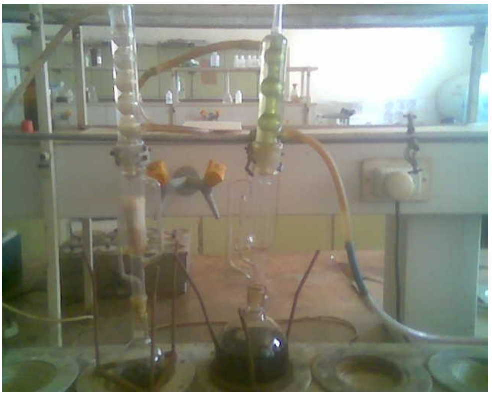


Plate 1: Soxhlet Extraction Apparatus with the extracted oil

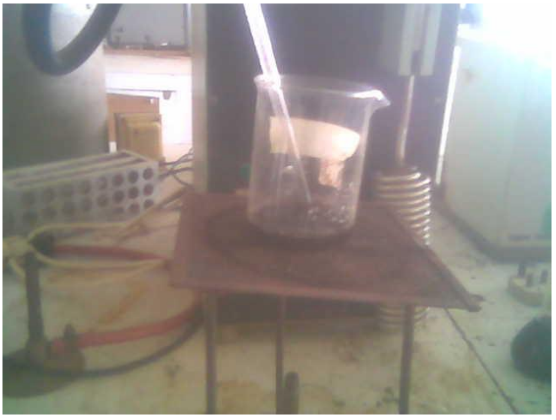


Plate 2: Grease production set-up

2.2.1 Sample 1

A mixture of calcium hydroxide Ca $(OH)_2$, stearic acid in the ratio 1:0.75 and the black-date oil which was thrice the combination of $Ca(OH)_2$ and stearic acid were mixed at the temperature of 100^{o}C in a glass reactor. The temperature was then raised to 200^{o}C and for 2 hours in the reactor with a continued stirring until soap foams were formed, when this was attained, the temperature was reduced to 160^{o}C for an additional amount of the base oil and additive to be added. The final mixture was allowed to cool to room temperature. The resulting mixture was roll-milled to obtain the grease. The initial temperature of 190^{o}C was attained so as to enable the base oil to be trapped in the fibre network of the soap.

2.2.2 Sample 2

The same weight measurement was carried out as in the first sample with little variation in the base oil and the temperature used. The mixing was done at the temperature of 110^{o}C and 210^{o}C for the cooking. The mixture was allowed to cool to 170^{o}C before the base oil and additive were added. The grease was obtained at room temperature.

2.2.3 Sample 3

The mixture of calcium hydroxide Ca $(OH)_2$ and stearic acid was in the ratio of 2:1 and the base oil was uniformly using a glass rod stirrer. The same reaction condition was maintained as in the first sample, with differences in the amount of the base oil and the additives used.

2.3 Grease characterization for performance

The experiments for the characterization of the performance of the grease were performed on the produced samples and two commercial samples made by Texaco and Oando Oil companies which were used as controls. The tests were carried out at the Petroleum Analysis Laboratory of the Petroleum and Natural Gas Processing Department (PNGPD) of Petroleum Training Institute, Effurun-Delta State of Nigeria.

2.3.1 Un-Worked Penetration Test

Three samples of the black-date grease and two samples of the controls (Texaco and Oando) were subjected to penetration test. They had their different penetration levels measured using penetrometer by filling in a standard grease cup, cylindrical in shape with 50ml capacity with a little disturbance, the surface was smoothened and placed on the penetrometer assembled and pressed for five seconds during which a special grease-cone on the assembly has its tip just touching the level of the grease surface at the start. The distance dropped for each sample were read from the dial indicator of the penetrometer and recorded.

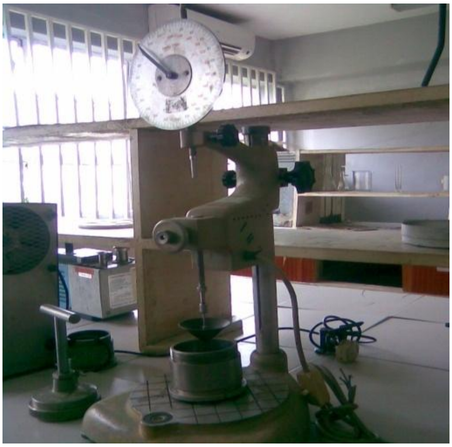
2.3.2 Worked Penetration Test

The worked penetration test was carried out in the same manner with that of the Un-worked penetration test but the difference was that the grease samples were worked for 60 double strokes in the standard grease worker cup. In this method, the disturbance of the grease was standardized by the prescribed working process and is more reliable than Un-worked penetration test because the grease has been subjected to a work load of double strokes over a wide range of temperatures.

The Un-worked and the worked penetration test describe above were used to determine the grease consistency and the grease consistency is its resistance to deformation by an applied force. A significant difference between un-worked and worked penetration can indicate poor shear stability.

2.3.3 Dropping Point test

Samples of grease were collected and filled into the shouldering ring. ASTM thermometer was used with ball-centering guides in position; the bath was filled with freshly boiled distilled water to a depth of not less than 102 mm and not more than 108mm (the use of freshly boiled distilled water was to prevent air bubble from forming on the specimen). And the test container was placed on the ice water and taken to heating machine in which heat was applied in a manner that the liquid temperature was raised to 5^{o}C, the rate of temperature rise dropping point of 80^{o}C and the rate of rise fall, within which the specimen surrounding the ball touches the bottom plate and the temperature at the spot was recorded from the thermometer. This is the dropping point.



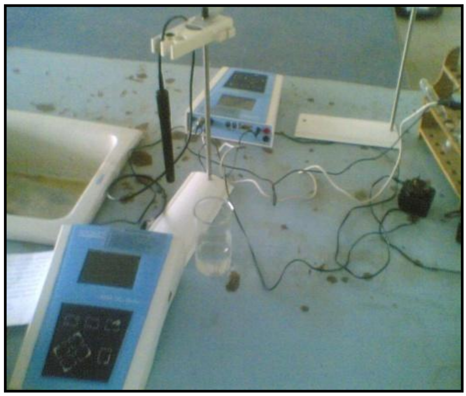


Plate 3: A Penetrometer **Plate 4: BOD Test Apparatus**

Dropping point is an indication of the heat resistance of lubricating grease and this gives the temperature at which grease passes from semi-solid to liquid state, the test was conducted to know the temperature at which grease will flow when heat is applied to it.

2.3.4 Test for Biodegradability

Biochemical oxygen demand (BOD) is the amount of oxygen used by microorganism as they decompose the organic matter in a given sample over a period of time and at a particular temperature. For this test, the standard period and temperature required were five days and 20^{o}C respectively. 20ml of the produced grease labeled 1, 2 and 3 were mixed with pond water which contains microorganisms in incubation bottles each and this bottles do not allowed the passage of light through it. Two other incubation bottles were also filled with 20ml of mineral grease (Controls); 1ml each of iron (ii) chloride, phosphate buffer, calcium chloride and magnesium sulphate were mixed in 1 liter of distilled water.

The dilute water prepared was added to each of the incubation bottles for about two hours at room temperature from which the dissolved oxygen was measured using an oxygen meter. The incubation bottles were kept at the same temperature of 20^{o}C for five (5) days after which the dissolved oxygen was recorded. The differences in the oxygen dissolved was calculated and recorded. The biodegradability of the grease produced was calculated using the formula below:

$$BOD = \frac{DO_i - DO_f}{p} X \frac{300}{1000} \qquad (1)$$

Where DO_i = the initial dissolve oxygen
DO_f = the final dissolve oxygen after five days;

P = the fraction given by

$$\frac{\text{volume of sample } (cm^3)}{1000} \qquad (2)$$

3 EXPERIMENTAL RESULTS

3.1 Grease Production

The summary of the grease produced with the various percentage compositions of the base oil (black-date oil), calcium hydroxide, stearic acid and sodium hydroxide is as shown in Table 1 and the formulation of these raw materials with their respective temperature conditions to produce grease samples as labeled from sample 1 to 3.

Table 1: Variation of composition and temperature of the produced grease

Grease sample	**Sample1**	**Sample 2**	**Sample 3**
Mass of base oil (P) (g)	75	72	70
Mass of thickener ($Ca(OH)_2$ used (Q) (g)	17.24	17.24	9.3
Mass of stearic acid used (R) (g)	12.9	12.9	4.7
Mass of additive (S) (g)	2.8	2.8	2.8
Mixing temperature (^{O}C)	100	110	100
Maximum Reaction temperature (^{O}C)	200	210	200
Temperature for addition of additives (^{O}C)	160	160	160
Cooling period (minutes)	120	120	120
Reaction temperature(^{O}C)	25	25	25
Percentage ratio of P: (Q + R +S)	75:33	72:33	70:17

3.2 Consistency Test (Un-Worked and Worked Penetration)

The summary of the un-worked and worked penetration values of the five (5) grease sample is as shown in Table 2.

Table 2: Consistency/Penetration tests

S/N	Test sample	Un-worked penetration (0.1 mm)	Worked penetration (0.1mm)	Difference (0.1mm)
1	Sample 1	169	200	31
2	Sample 2	180	198	18
3	Sample 3	190	205	15
4	Texaco (Control)	220	230	10
5	Oando (Control)	288	290	2

Table 3: NLGI Grade

NLGI Grade	Worked penetration after 60 strokes at 25^{o}C (0.1mm)	Appearance
000	445 – 475	Fluid
00	400 – 430	Fluid
0	355 – 385	Very soft
1	310 – 340	Soft
2	265 – 295	Moderately soft
3	220 – 250	Semi – fluid
4	175 – 205	Semi - hard
5	130 – 160	hard
6	85 – 115	Very hard

3.3 Dropping Point Test

The summary for the dropping point test values of the grease in degree Celsius (^{O}C) of sample 1 – 3 and controls are as shown in the Table 3.

Table 4: Dropping point values

S/N	Test Sample	Dropping Point (^{O}C)
1	Sample 1	90
2	Sample 2	87
3	Sample 3	160
4	Control (Texaco)	198
5	Control (Oando)	184

3.4 Biodegradability Test

Biochemical oxygen demand (BOD_5) test values recorded at 20^{o}C in a cooled incubator for five days. The results obtained for this test were evaluated and recorded in part per million (ppm) after two hours and five days respectively are as shown in Table 4.

Table 5 showing the results carried out for BOD_5 test

Sample	Sample 1	Sample 2	Sample 3	Control(T)	Control(O)
Dissolved oxygen (DOi) (ppm)	7.60	7.50	7.50	7.50	7.80
Dissolved oxygen after 5 days (DO_f) (ppm)	6.20	6.20	6.10	7.0hh0	7.40
BOD_5 (ppm)	21.00	19.50	21.00	7.50	6.0

4 ANALYSIS OF RESULTS

During the grease production/preparation it was observed that at the mixture of base oil, thickener (calcium hydroxide) and stearic acid and continuous stirring in the reactor, the product changed as the reaction progresses from melt to syrup to the formation of plastic-like particles which later changed to hard lumpy larger particles and finally into particles having fine beach sand-like consistency as a result of pounding. The colour of the product also changed from dark green to light brown and some yellow signifying the reaction and formation of the final product.

Furthermore, the ratio of base oil to calcium hydroxide (thickener) matters a lot because the higher the quantities of the thickener or close to the amount of the base oil, the more difficult will be the formation of grease. Grease formulations are mainly due to the composition and chemo-physical properties of the base oil with particular reference to viscosity especially in relation to temperature (Olisakwe, 2011). In the production process, the thickener of the grease was found to increase in cooking temperature; but this could be negligible compared to the amount of thickener used. The additives used functioned in many ways such as enhancing the existing desirable properties (heat resistance), suppressing the existing undesirable properties (evaporation loss), and imparting new properties (extreme pressure resistance).

For the grease consistency test, both the prepared one and that of the controls (Oando and Texaco) were measured using the parameters of the un-worked and the worked penetration test and there was significant difference between them. A significant difference between un-worked and worked penetration if any indicates poor shear stability. Grease consistency is the resistance to deformation by an applied force; this depends on the type and amount of thickener used and the viscosity of the base oil. This is confirmable in Table 2 which shows the values (in mm) obtained from the un-worked and worked penetration tests as compared to the amount of thickener in Table 1 for each sample.
Even though the same amount of thickener was used in some of the samples, it still shows variation in penetration values. And this can be likened to the difference in the quantity of additives used. So, it can be deduced from the consistency test result that greases with higher penetration values will have poor shear stability and hence low consistency than those with lower penetration. The grease samples used as controls (Oando and Texaco) have higher and lower penetration values respectively. The result shows that the quantity of thickener used for Texaco is higher than that of Oando grease.
Therefore, when considering the value of the worked penetration levels, the three prepared grease samples are classified as semi hard type of grease as classified during production in Table 3 according to the National Lubricating Grease Institute (NLGI).Table 3 highlighted the NLGI grades and the worked penetration ranges.

Dropping point test is of importance for grease properties because it gives a general indication of the temperature at which lubricating grease changes from semi – solid to liquid state under specific test conditions. It is also an indication of the heat of resistance of lubricating grease. As lubricating grease temperature increases (heat generation), penetration increases until the lubricating grease liquefies and the desired consistency is lost. This dropping point is the temperature at which the lubricating grease becomes fluid enough to drip. The dropping point indicates the upper temperature limit at this lubricating grease retains its structure, not the maximum temperature at which grease may be used. Dropping point depends to a large extent on the type of thickener used.

It was observed that the lubricating grease produced which was made of calcium soup thickener, has dropping point of 87^oC – 160^oC which differs from the values obtained for the commercial grease (controls) - 184^oC and 198^oC. This variation may be accounted for as a result of the mentioned factor(s).

First of all after the production of the lubricating grease, the final product was supposed to be roll-milled which will help in breaking the hard lumpy structures into fine particles that will enhance mixing and blending within the molecules of the lubricating grease. And hence increases the intermolecular forces and temperatures but this milled was not done due to lack of roll-mill but was smashed manually and this led to low dropping point in some of the samples.

Secondly when the grease was produced, it was supposed to be under continuous heating and stirring for homogeneity at maximum cooling temperature. This could not be achieved due to lack of a magnetic stirrer. This gave rise to irregular and interrupted stirring over temperature and time for intermittent temperature measurements

BOD test is one of the key tests which this work is based and aimed at. It is the biodegradability of the grease produced which is of interest. The BOD test is a chemical procedure for determining the action(s) of microorganisms including bacteria in using up the oxygen in a body of water. This experiment is the easiest environmental procedure to determine the extent to which oxygen within a sample can support microbial life or can be used up.

The BOD test results in Table 5 shows that the oxygen consumption after five (5) days was greater in ppm than that of two (2) hours and the grease produced has greater tendency of degradation far more than that of petroleum products (Controls) which does not show much significant environmental friendliness of the grease produced.

5 CONCLUSION

It is evidenced from the data obtained from this research work that the aim of producing a biodegradable grease and some characteristics was met and it can be concluded that the vegetable oil (black-date oil) used is a good renewable source for biodegradable grease production and three (3) samples were successfully produced with different compositions of the base oil, thickener, additives and also under different conditions while the grease produced after being subjected to the necessary tests (especially bodegradation) was far better than commercial grease used as controls. Also the fact that the dropping point of grease depends largely on the composition and consistency of stirring as shown in the result (Table 4) which ranged from 87^0C to 160^0C for the grease produced and 184^0C and 198^0C for the commercial grease and this biodegradable grease corresponded with the National Lubricating Grease Institute (NLGI) grade specification of the United state of America. Finally, the limitations identified were due to lack of efficient magnetic stirrer, roll-mill and the finance to carry out some further tests such of wear, viscosity and so on but however these are recommended for further research works.

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