PRODUCTION OF BIODEGRADABLE GREASE FROM ATILI (BLACKDATE) OIL

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ABSTRACT
The work was aimed at the production of biodegradable grease from Atili (Blackdate) Oil that will be environmentally friendly. The grease was produced by mixing and blending of the base oil (Atili oil) with a mixture of calcium hydroxide and the stearic acid at 90^{o}C which was then slowly heated to 190^{o}C for about three hours to obtain the desired product. Three sets of the grease were produced by varying the amount of thickener, the base oil, the stearic acid and the temperature of the reaction. The grease produced was then milled (pound) to obtain a smooth-textured product at room temperature. The tests carried out to analyze the grease produced were dropping point test, unworked and worked penetration test; and most importantly, the test for biodegradability known as BOD_5 test. Dropping point test was carried out to determine the temperature at which the grease sample began to drip. The consistency of the grease was measured using the worked and unworked penetration test. Finally, the Biochemical Oxygen Demand test or BOD_5 was carried out by measuring the amount of oxygen dissolved in a grease sample initially and after five days. The results showed that dropping point was 70^{o}C, 68^{o}C and 71^{o}C for sets 1, 2, and 3 samples respectively. The consistency values were 0.4 mm, 0.8 mm, and 0.3mm for sets 1, 2, and 3 samples respectively. The BOD was found to be 18.0 ppm, 16.8 ppm, and 18.0ppm for sets 1, 2, and 3 respectively. The grease produced was found to be more biodegradable than those made of mineral oil like Oando and Texaco grease which were 4.8ppm and 6.0ppm respectively. The consistency and dropping point of the grease was found to be dependent on the nature and amount of thickener used and also the viscosity of the base oil.

Keywords: *Grease, biodegradable, Atili oil, thickener, consistency, dropping point.*

1.0 INTRODUCTION

The search for biobased material as industrial and automotive lubricant has accelerated in recent years. This trend is primarily due to the nontoxic and biodegradable characteristics of vegetable oils that can substitute mineral oil as base fluid in grease making (Adhvaryu, et al, 2005). A grease generally can be seen as a lubricant of higher initial viscosity than oil, consisting originally of calcium, sodium or lithium soap emulsified with mineral oil. It is a substance (often a liquid) that is introduced between two moving surfaces to reduce friction and wear between them (Nailen, 2002). However, in spite of the numerous benefits obtainable from these greases, they still imposed a lot of environmental problems that need to be addressed. In recent times, much attention has been given to the production of greases that are environmentally friendly. These are the biodegradable greases suitable for industrial purposes that are made from the renewable resources of vegetable oils. Vegetable oils present a quick biodegradability, very desirable in applications where leaks and environmental contamination are difficult to be avoided like outboard 2-stroke engines, railway track greases and wire ropes (Lazaro and Aranda, 2014). Biodegradable grease provides an alternative to the costly disposal of petroleum products that are environmentally toxic (Anonymous, 2007). The biodegradability of greases essentially reflects the biodegradability of the base oils. It is one aspect of the necessary reductions of the toxic potential of greases (Nagendramma and Kumar, 2015). Vegetable oil-based greases are semi-solid colloidal dispersions of thickening agents (a metal soap) in a liquid lubricant matrix (vegetable oil). They are the preferred form of lubrication in hard-to-reach places in a mechanically rubbing or dynamic systems (Adhvaryu, et al 2005). It is a gel like structure formed when oil is trapped in the fiber network of specially made soap, during a process involving heating and cooling cycles. It can decompose and therefore environmentally friendly (Anonymous, 2007; Lazaro and Aranda, 2014)).

Grease is simply a lubricating fluid which has been gelled with a thickening agent. It is also essentially a two-phase system, a liquid-phase lubricant into which a solid-phase finely divided thickener is uniformly dispersed. The liquid is immobilized by the thickener dispersion that must remain relatively stable with respect to routine usage. Greases are composed of a lubricating fluid (base oil), a thickener, and usually performance enhancing additives (George, et al 2003, Nagendramma and Kumar, 2015; and Lazaro and Aranda, 2014).

Black date oil is fragrant pleasant oil which is obtained from the outer layer of the fruit. The fatty acid compositions of the black date pulp oil are *palmitic* acid, *stearic* acid *palmitoleic* acid. That of the seed oil is oleic acid, *linoleic* acid, *palmitic* acid, *stearic* acid and traces of others (Ibrahim, 1998). Triglyceride vegetable oils include not only edible, but also inedible vegetable oil such as processed linseed oil, tung oil and castor oil used in lubricants, paints, cosmetics, pharmaceutical and other industrial purposes. The edible oil can be heated, and used to cook other foods. Oils that are suitable for this purpose must have a high flash point. Such oils include Canola oil, Sun flower oil, Peanut oil, Palm oil and Black date (*Canarium*

Schweinfurthii) oil (Vegetable-oil, 2008). In Nigeria the oil is sometimes prepared into a vegetable-butter and eaten as a substitute for Shea-butter (Vegetable-oil, 2008). The three forms of the oil (liquid, semi-liquid and solid) depend on the maturity of the plant.

The aim of this work is to produce biodegradable grease from Blackdate (Atili) oil that is environmentally friendly and to characterize it in terms of flow properties and consistency; and then to test it for biodegradability.

2.0 MATERIALS AND METHOD

2.1 Grease preparation

The grease was prepared in three different sets.

Set 1

A mixture of calcium hydroxide, stearic acid in the ratio 1: 0.75 and the Blackdate (Atili) oil (in equivalent weight ratio of the metal acid mixture) was uniformly mixed with a magnetic stirrer at 90^oC in a glass reactor according to Adhvaryu, et al 2005. The temperature was then slowly raised to 190^oC and maintained for 3 hours with the same stirring. After the cooking, the mixture was allowed to cool; and then at 150^oC according to Adhvaryu, et al 2005; an additional amount of the base oil (80wt% of the total reaction mixture) and additive-glycerol (5wt% of the total reaction mixture) was added. The final mixture was allowed to cool to room temperature to obtain the grease. The resulting grease was roll- milled to obtain the final product.

Set 2

Another mixture of calcium hydroxide, and stearic acid in the ratio 2:1 and the Blackdate (Atili) oil (in equivalent weight ratio of the metal acid mixture) was uniformly mixed with a magnetic stirrer. The same reaction condition was maintained as in the first set. The only difference is in the amount of the base oil (Blackdate oil) and the additive used. In this case the base oil used and the additive was 90wt% and 6wt% of the total reaction mixture respectively. The grease was obtained at room temperature.

Set 3

The same weight measurement was carried out as in the first set. The variation was in the temperature used. The mixing was done at 100^oC, and the cooking at 200^oC. The mixture was allowed to cool to 160^oC before the base oil and the additive were added. The grease was obtained at room temperature.

2.2 Grease characterization

Un-worked Penetration Test

The un-worked penetration was obtained when the penetration measurement was made on grease transferred from the original container to the standard grease worker cup, with only a minimum amount of disturbance. This test is used to indicate consistency variance in transferring grease from container to equipment.

Worked Penetration Test

This test method was measured after grease has been 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. The un-worked and worked penetration tests described above were used to determine the grease's consistency. The grease's consistency is its resistance to deformation by an applied force. A significant difference between unworked and worked penetration can indicate poor shear stability (George, et al 2003).

Dropping Point Test

Dropping point is an indication of the heat resistance of lubricating grease. It gives the temperature at which lubricating grease passes from a semi-solid to liquid state. The test was conducted to determine the temperature at which the lubricating grease will flow when heat is applied. The inside surfaces of the grease cup were coated with the grease to be tested. A thermometer was inserted into the cup and held in place so that the thermometer does not touch the grease. This assembly was placed inside a test tube. The test tube was lowered into the container which was filled with oil. Another thermometer was inserted into the oil. The oil was heated, while being stirred; at a rate of 8 to 12°F per minute until the temperature was approximately 30°F below the expected dropping point. The heat was reduced until the test tube temperature was 4°F or less than the oil temperature. The dropping point was the temperature recorded on the test tube thermometer when a drop of grease falls through the hole in the grease cup. This is called the ASTM D566 test method.

2.3 Tests for biodegradability

25ml of the prepared grease was mixed with pond water which contains microorganisms in three incubation bottles. Two other incubation bottles were filled with 25ml mineral oil grease (Oando and Texaco) obtained from the market. 1ml each of iron (ii) chloride, calcium chloride, magnesium sulphate and phosphate buffer was mixed in 1 liter of distilled water. The water prepared was added to each of the five 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^oC for about 5 days after which the dissolved oxygen was recorded. The differences in the oxygen dissolved was then calculated and recorded. The Biodegadability of the grease produced or BOD_5 was calculated from the following relation (Rodger, et al, 2002).

[illegible]

where DO_i is the initial dissolve oxygen

DO_F is the final dissolve oxygen after five days and

P is a fraction given by P= volume of sample cm^3 /1000

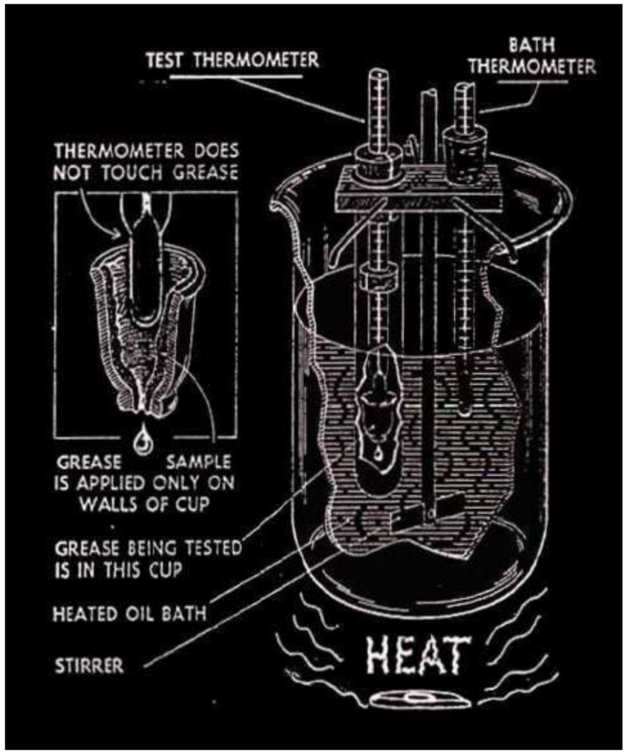

Figure 1 Dropping Point Determination Set-up.

3.0 RESULTS AND DISCUSSION

3.1 Results

3.1.1 Grease preparation

The preparation of the grease was done in three (3) different sets namely: set 1, set 2 and set 3. The same temperature condition was followed in the preparation of sets 1 and 2 but different weight measurement, while in sets 1 and 3, the same weight measurement was carried out but different temperature condition, set 3 being higher than set 1 by 10^oC in each case. Also set 2 and 3 were different in both temperature condition and weight measurement. This is shown in Table 1.

3.1.2 Biodegradability test

Biochemical Oxygen Demand (BOD_5) test values recorded at 20^oC in a cooled incubator for five days. The results obtained for this test were evaluated and recorded as shown in Table 2.

3.1.3 Consistency test (unworked and worked penetration)

The following results were obtained at the Department of Chemical Engineering, Ahmadu Bello University, Zaria and College of Engineering Kaduna Polytechnic. The two tests were conducted separately and the results obtained were recorded as shown in Table 3.

3.1.4 Dropping point test

The following values in Table 4 were obtained for dropping point test. The test was conducted in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

TABLE 1 VARIATION OF COMPOSITION AND TEMPERATURE IN GREASE PREPARATION

Grease set number	Set 1	Set 2	Set 3
Mass of base oil (Atili) used (g)	87	84	87
Mass of thickener ($Ca(OH)_2$ (g)	20	15	20
Mass of stearic acid (g)	15	10	15
Mass of additive (g)	3.25	3.6	none
Mixing temperature (^0C)	90	90	100
Maximum cooking temperature (^0C)	190	190	200
Temperature for addition of additive (^0C)	150	150	160
Cooking period (min)	180	180	200
Cooling temperature (^0C)	25	25	25

TABLE 2 BIOCHEMICAL OXYGEN DEMAND (BOD_5) TEST

Samples	Set 1	Set 2	Set 3	Oando	Texaco
Dissolve oxygen (DO_i) (ppm)	7.90	7.80	7.80	7.90	7.60
Dissolve oxygen after 5 days (DO_F) (ppm)	6.40	6.40	6.30	7.20	6.80
BOD_5 (ppm)	18.00	16.80	18.00	4.80	6.00

Table 3 Unworked and Worked Penetration Test

S/N	Test sample	Unworked penetration (mm)	Worked penetration (mm)	Difference (mm)
1	Set 1	28.2	28.6	0.4
2	Set 2	28.9	29.7	0.8
3	Set 3	27.8	28.1	0.3
4	Oando	33.3	33.9	0.6
5	Texaco	22.4	22.6	0.2

Table 4 Dropping Point Test

S/N	Test sample	Dropping point (°C)
1	Set 1	70
2	Set 2	68
3	Set 3	71
4	Oando	184
5	Texaco	198

3.2 Discussion

3.2.1 Grease preparation

In the preparation of the grease, it was noticed that the consistency of the mixing of the base oil (Blackdate Oil) and the soap thickener (calcium hydroxide) changed as the reaction progressed from melt (reaction of soap thickener and stearic acid) to syrup (mixture of soap thickener and stearic acid to base oil) to the formation of plastic-like particles. These particles were 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 (colour of the oil) to light brown as the final product.

The major component in the Base oil (Atili oil) used is triglycerides or triacylglycerol.

In the production process, the thickener and calcium hydroxide ($Ca(OH)_2$) were first reacted with stearic acid ($CH_3(CH_2)_{16}COOH$) to give a calcium stearate and water according to the reaction below:

$$Ca(OH)_2 + 2CH_3(CH_2)_{16}COOH \downarrow (CH_3(CH_2)_{16}COO)_2Ca + 2H_2O \quad (1)$$

This is the reaction for the formation of the soap fiber network that traps the oil and thickened it when heat is applied. It is expected that when the oil was added to the fiber network, a reaction should occur; but however, no further reaction should occur because the thickening process is only a physical process that leads to the formation of the grease. Hence the only reaction that occurs is the formation of the soap fiber network.

The production of the grease was as a result of physicochemical processes, with the aid of which the lubricating grease structure was constructed from the soap thickener molecules generated *in situ,* according to Kawamura (2011) which further explained the following: i-) In the reaction phase, the metal soap molecules were generated by the reaction of the soap thickener and the stearic acid. The metal soap thickener was present as fine crystals. ii-) In the structure formation phase which follows, the actual lubricating grease structure or lubricating grease matrix was generated by physicochemical processes. During this period, there was aggregation of thickener crystals generated in phase 1, the formation of soap micelles by intercalation and adsorption of base oil molecules, the commencement of melting of the soap micelles (heating above the melting point of the soap molecules), and finally the recrystallization of the soap molecules (control cooling). iii-) In the mechanical phase, additives and additional amount of the base oil was added for fine adjustment of the end consistency.

It is also important to mention that the ratio of the thickener to base oil used affected the thickness of the grease. This was demonstrated in set 2 which had less mass of the thickener compared to others. The thickness of the grease was also found to depend on the cooking temperature. The thickness was found to increase with increase in cooking temperature, but this could be negligible compared to the amount of thickener used. The thickener used in the production of these greases is a material that, in combination with the selected oil (mineral, vegetable, synthetic) will produce the solid to semifluid structure.

The additives used also play important roles in the lubricating grease which includes enhancing the existing desirable properties (heat resistance), suppressing the existing undesirable properties (evaporation loss), and imparting new properties (extreme pressure resistance). The additives used in this lubricating grease include glycerol and sodium hydroxide. Each of the samples of lubricating grease produced was heated to a temperature of 190—200°C, below which the desired product cannot be obtained.

3.2.2 Biodegradability (biochemical oxygen demand)

Biochemical Oxygen Demand (BOD) is a chemical procedure for determining how fast biological organisms use up oxygen in a body of water. It is a common, environmental procedure for determining the extent to which oxygen within a sample can support microbial life. From the biodegradability test conducted, Table 2, it is obvious that the oxygen consumption for the grease produced from vegetable oil is more than that made of mineral oil (Oando and Texaco). From the table it can be deduced that the rate of oxygen consumption for the grease produced is about three times greater than those obtained from the market (mineral oil). It also implies that if the grease produced is disposed to the environment, for instance and it takes two months to biodegrade, the other grease made of mineral oil will take six months or more. Therefore, the grease produced is said to be environmentally friendly due to its nontoxicity and biodegradability.

3.3.3 Consistency test (ASTM D217)

The grease's consistency is its resistance to deformation by an applied force. Lubricating grease consistency depends on the type and amount of thickener used and the viscosity of its base oil (Booser, et al 2008). The consistency of the lubricating grease produced was measured in terms of worked and unworked penetration test. A significant difference between unworked and worked penetration can indicate poor shear stability (George, et al 2003).

The unworked and worked penetration values of the grease produced varies according to the amount of thickener used. For sets 1 and 3, which have the same amount of thickener, the two tests shows a significant difference as shown in Table 3. The two results were expected to be the same based on the amount of thickener used, but there was a deviation. It was discovered that the penetration of set 1 was higher than set 3. For set 1, an additive was used while in set 3 none was used. According to Adhvaryu, et al 2005, the presence of additive in grease gives soap with looser network and larger fiber structure than similar grease with no additive. For this reason, the penetration values of set 1 with additive should be higher than those of set 3 without additive. The unworked and worked penetration values for set 2 was greater than set 1 and 3, this is true because the amount of thickener used in set 2 was less than that of set 1 and 3. From the differences in the unworked and worked penetration, Table 3 above, it can be deduced that greases with higher penetration values will have poor shear stability and hence low consistency than those with lower penetration. The grease obtained from the market that is Oando and Texaco, have higher and lower penetration values respectively. This implies that the amount of thickener used for Oando is lower than that of Texaco.

3.3.4 Dropping point (ASTM D566)

The lubricating grease produced which was made of calcium soap thickener, has dropping points of 70°C, 68°C and 71°C which shows a little deviation from typical values of calcium soap greases. This deviation may be accounted for as a result of these factors: i) After the production of the lubricating grease, the final product was supposed to be roll-milled. This roll milling helps in breaking the hard lumpy structure into fine particles that enhance mixing and blending within the molecules of the lubricating grease. The smaller the particles, the closer they are to one another and the stronger the intermolecular forces between them, which will lead to increase in temperature. But the lubricating grease produced, was not milled due to lack of roll-mill to carry out the process, but pounded manually to break the lumps. As a result, there was no proper mixing or blending of the molecules and hence low dropping point; and ii) During production of the grease the heating and stirring was supposed to be continuous until the maximum cooking temperature is reached. But stirring was stopped at intervals in order to measure the temperature of the reacting mixture which was regulated to maintain the maximum temperature needed. Also the mechanical stirrer used was not strong enough to continue stirring until the cooking period of three hours is reached, but however stopped at a point where the grease became too thick. All these factors hinder the proper mixing of the grease which might have affected the dropping point. This effect would have been minimized by increasing the cooking period of the grease as shown by grease of set 3 which has a dropping point of 71°C as expected of grease made from calcium thickener.

4.0 CONCLUSION

The following conclusion can be drawn from the work: Production of biodegradable grease using Atili (Blackdate) Oil was carried out. The production at the laboratory scale was done in three different sets namely set 1, 2, and 3. The 3 sets produced differ either in the amount of thickener to the base oil used or in the cooking temperature. A test was conducted to measure the biodegradability of the grease produced which was far more biodegradable than those made of mineral oil obtained from the market (Oando and Texaco). The dropping point of the grease produced was also determined to be 70 °C, 68 °C and 71°C for set 1, 2, and 3 respectively. The consistency of the grease was determined in terms of unworked and worked penetration. The difference between the two results indicated the hardness of the grease which is a function of the thickener used.

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