Original Research Article

Formulation of lubricant from calabash seed oil

.

ABSTRACT

The engine oil industry is faced with complex chemical reactions and difficult chemical engineering involved in the formulation of synthetic based engine oils, and therefore, the need to source for alternative base oils for engine oil formulation from vegetable oils has become urgent and inevitable. This research is aimed at formulation of lubricant using calabash seed oil (CSO). An experiment designed (Mixture Design Method using Minitab 17) was used to obtain the blend of CSO (28.75%), SN 500 (68.75%), and additive (2.50%) with improved physicochemical parameters. The lubricant obtained had kinematic viscosities 9.30±2.11 cSt (at 100^{o}C) and 53.11±1.03 cSt (at 40^{o}C), a viscosity index of 167±0.51, flash point of 240±2.01^{o}C, and pour point of -28±1.31^{o}C. The lubricant obtained in this research had quality parameters that are comparable to those of synthesised environmentally acceptable engine oils, and are within the standard for engine oils.

Keywords: Formulation, Environment, Lubricant, Calabash Seed Oil

1. INTRODUCTION

The engine oil industry is faced with numerous challenge such as renewability of the base oils [1-3], availability and accessibility of the products [1,4,5], compatibility of the products with modern machines and equipment [6], and environmental acceptability of the products [1,2,7].

Leaders in the engine oil industry have accepted the challenges and are formulating specialised products in conformity with the aformentioned challenge but the formulation processes are associated with costs because of the complex chemical reactions and difficult chemical engineering involved in the production of synthetic based engine oils [6].

The use of vegetable oils for the formulation of engine oil is associated with numerous advantages. Vegetable oils have high lubricity [2,4] owing to the polar group (esters) with long carbon chains [8,9], high viscosity indexes making them useful over a wide range of temperatures [2,10], they produce fewer emissions (due to higher boiling temperature range of esters) and have high valitilties and high flash points (because of their high molecular weight) [4,10] which makes them safe for transport and storage, and they are renewable, non-toxic, and ecofriendly [1,2,11].

The challenges inherent in the use of vegetable oils include poor low temperature stability [12] because of their high pour points (making them less applicable for any application at extreme cold temperatures), poor thermo-oxidative stability [2,4] owing to the degree of unsaturation of their molecular structures [7], relatively higher initial cost of production or processing [2,5] compared to mineral oils.

The use of vegetable oils for the production of environmetally acceptable engine oils is a promising development in addresing the drawbacks associated with the use of conventional mineral oils, the complex methods employed in the formulation of synthetic engine oils, and additionally, economic relevance in the local communities where vegetable oil crops are grown and processed [3-5,13-15].

This study is aimed at using calabash seed oil (CSO) for the formulation of lubricating engine oil.

2. METHODS

2.1 Sample Collection and Treatment

Calabash seeds (Appendix I) were obtained from Sokoto Metropolis, Sokoto State, North-western Nigeria, and authenticated by Botany Unit, Department of Biological Science, Faculty of Sciences, Usmanu Danfodiyo University, Sokoto. The seeds were dehulled, dried, ground into powder, and sieved to obtain a homogeneous powder. The powdered calabash seed (300.00 g) was weighed and preserved for oil extraction [7,16].

2.2 Oil Extraction

Soxhlet extractor (Figure 1) was employed in the extraction of calabash seed oil (CSO) with n-hexane (6:1 w/w% of solvent/sample) as the extracting solvent (in 500 cm^3 round-bottomed flask). The sample (50.00 g per each extraction) was placed in a thimble, while the n-hexane was heated gently (using a heating mantle). A reflux condenser was fitted (to cool the heated n-hexane), and the mixture was heated at 60^0C for 5 hours, while the condensed hot-solvent soaked the timble. The solvent siphoned into the flask when it reached the top of the siphon tube of the Soxhlet apparatus [5,7]. The oil was separated from the solvent with the aid of a rotory evaporator. The percentage yield of the CSO was calculated using equation 1:

$$\%\text{ Yield} = Weight\ of Oil(g) x\ 100\ /\ Weight\ of\ the\ Sample(g) \qquad \ldots\ldots\ldots\ldots 1$$

2.3 Lubricant Formulation

In order to achieve a better thermal and oxidative stability for the CSO [4,17], the CSO was blended with SN 500 mineral based oil and additive (poly alkylmethacrylate). A design of experiment (Mixture Design method of Minitab 17) was used to obtain the best blend with improved quality parameters from the raw CSO extract. The blend of CSO, SN 500, and additive was done in a conical flask at a temperature of 45^oC, and stirred at 600 rpm for 15 minutes, while a heating mantle equipped with a magnetic stirrer was used to achieve a homogeneous mixture [4,7].

2.4 Physicochemical Parameters of CSO and the Lubricant

The CSO extract and the formulated engine oil were analysed for their physicochemical properties as below (Appendix II):

2.4.1 Determination of Kinematic Viscosity

The oils were each poured into a viscometer tube and mounted upright in the viscometric bath which was maintained at 40 or 100°C. The oil in the tube was allowed to gain equilibrium for 15 minutes. When the equilibrium temperature was achieved, the oil level in the viscometer tube was adjusted using a suction pump to 7 mm above the upper mark of the viscometer tube. The time (***t***) taken for the oil to move from the upper mark to the lower mark of the viscometer tube was recorded [7]. The kinematic viscosity (KV) was obtained via equation 2:

$$KV\ (cSt) = \boldsymbol{C}\ (\mathrm{cSt\ s^{-1}})\ \boldsymbol{x}\ \boldsymbol{t}\ (\mathrm{s}) \quad \ldots\ldots 2$$

Where, **KV** is the kinematic viscosity; ***C*** is the calibration constant of the viscometer; ***t*** is the time.

2.4.2. Determination of Viscosity Index

Viscosity index (VI) of the oils were each obtained using values of kinematic viscosity obtained at 40 and 100°C with standard measurement table as determined by ASTM D-2270 method.

2.4.3. Determination of Pour Point

Pour point tester of accuracy of ±3°C was used to determine the pour points of the CSO and lubricating oil. The tester used methanol as the cooling solvent and has a minimun temperature of -68°C. The oil (45 cm^3) was poured into a test jar to the levelled mark. Then the tester was cooled to -37°C. While cooling the tester, the oil jar was heated to 45°C with the aid of a water bath. The oil jar was cooled with another water bath to a temperature of 27°C. When the pour point tester had reached -36°C, the oil jar was placed in a horizontal position in the hole at the top of the tester and the pour point temperature was taken after 5 seconds when the oil showed no movement [4].

2.4.4. Determination of Flash Point

The flash point of the CSO and lubricating oil were each determined by heating a cup holding the oil and moving a flame over the oil at regular temperature, starting with a temperature of 28°C below the expected flash point of the oil. The bulb of the thermoneter was immersed in the sample in order to allow monitoring and reading of the temperature at flash point. The flash occured in the cup containing the CSO when the temperature of the oil had reached its flash point [7].

2.4.5 Determination of Free Fatty Acid

The oil (2.00 g each of CSO and lubricating oil) was placed in a dry 250 cm^3 -conical flask. 50 cm^3 of ethanol and few drops (2-3) of phenolphthalein indicator were added. The mixture was heated at 60°C in a water bath for 10 minutes and then cooled. The mixture was titrated with 0.1 M KOH to the endpoint (with consistent shaking). A dark pink colour was observed and the volume of KOH used for the titration was recorded as the titre value [4]. The acid value and the free fatty acid value were calculated using equation 3 and 4:

$$\text{Acid value}\left(\frac{\text{mgKOH}}{\text{g sample}}\right) = \frac{\text{Volume KOH}(\text{cm}^3)\text{x N KOH}(\text{mmol/cm}^3)\text{x 56.1 (mg/mmol)}}{\text{sample weight (g)}} \quad \ldots\ldots\ldots\ldots 3$$

$$\text{Free Fatty Acid}\left(\frac{\text{mgKOH}}{\text{g sample}}\right) = 0.5 \text{ x Acid value} \quad \ldots\ldots\ldots\ldots 4$$

Where, **KOH** is potassium hydroxide; **N** is the molar concentration of KOH; and **56.10** is the molecular weight of KOH

3. RESULTS AND DISCUSSION

The formulated CSO lubricant with optimum physicochemical properties was obtained from the proportion with details as CSO (28.75% wt), SN 500 (68.75% wt), and additive (2.50% wt) (Table 1).

An index for evaluating the internal resistance in the motion of engine oil is kinematic viscosity [18]. The higher the fluid's viscosity, the thicker it will be and more energy will be needed to move an object through it [19]. Kinematic viscosities of the lubricant were found to be 53.11±1.03 cSt at 40^{o}C and 9.30±2.11 cSt at 100^{o}C (Table 2) which are lower compared to the values for synthesised oil (Appendix III) but are within the standard for engine oils [7]. Thus, the lubricant is useful for engine oil application.

The effect of changing temperatures on the kinematic viscosity of lubricating fluid is called viscosity index (VI) and it is inversely proportional to temperature: a higher change in viscosity in response to temperature variation indicates small viscosity index [18,20]. The viscosity index of the lubricant was found to be 167±0.51 (Table 2) which is comparable to the available commercial lubricating oil. This shows that the lubricant will experience less change in its viscosities as a result of variations in temperatures during applications.

The value of flash point of the lubricant was found to be 240±2.0 ^{o}C (Table 2). Flash point is a useful lubricating oil property which suggests the minimum temperature at which the oil generates ignitable vapour [21], it determines lubricant's volatility and fire resistance [22].The high flash point of the produced lubricant suggests a higher and complex nature of its molecular structure, and hence, has low risk associated with vapourisation during transport and storage.

However, the pour point of the lubricant was found to be -28±1.31^{o}C (Table 2). According to Gobinda et al. [23], vegetable oil base stocks solidify at low temperatures making them less useful for some applications. Though the pour point of the lubricant is within the standard for engine oil [7], the produced lubricant would require a calculated amount of pour point depressant (PPD) for it to be applicable in extreme low temperature conditions as compared to synthesised engine oils. The PPDs will minimise the negative effects of precipitation at low temperatures during usage.

Free fatty acid component of crude vegetable oil is an important factor used to determine the food or oleochemical application of the vegetable oil; percentage free fatty acid greater than 5% suggests that the oil could be useful for the production of biodiesel, biolubricant, and bioplastics [24]. The free fatty acid value of the crude extract (1.06±12) decreases to 0.85±12 in the formulated lubricating oil (Table 2), this is due to the effect of additive in the formulated oil.

The result of the gas chromatography mass spectrum (GC-MS) of the extracted oil revealed the degree of unsaturation of the ester carbon atoms such as $C_{20}H_{36}O_4$, $C_{21}H_{38}O_4$, and $C_{23}H_{42}O_4$. The unsaturated nature of the oil extract is a factor that influence both the physical and chemical properties of the formulated lubricating oil [9,25,26]. Esters have been known for their lubricity and are good starting materials for the production of engine oils [26]. The presence of ester functionality was also confirmed by fourier transformed infra-red spectroscopy (FTIR) assay of the oil extract using sodium chloride plate [4] (Figure 2). Alkene stretching vibration, =CH, for the oil extract was observed at 3011 cm^{-1}, which suggests that the oil extract has methylene interrupted double bond in its molecule [27,28]. Similarly, the carbonyl functional group was observed at 1744 cm^{-1}, which suggests the presence of ester in the oil extract since there is no visible O-H absorption band (Figure 2).

Figure 1. A Set Up for the Extraction of CSO

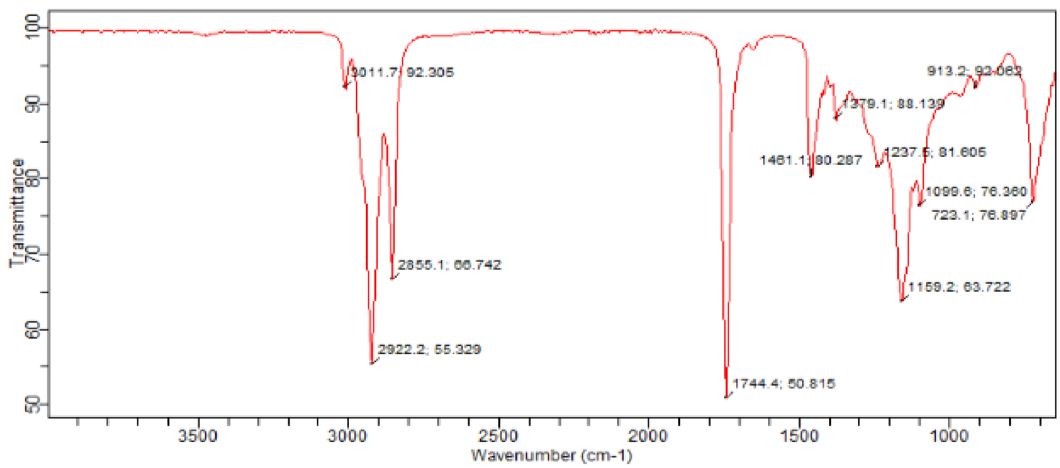

Figure 2. FTIR Spectrum for CSO Extract

Table 1. Optimised Blends for the Lubricant Formulation

Run Order	CSO	SN 500	Additive	KV @ 100^{0}C (cSt)	KV @ 40 ^{0}C (cSt)	VI	FP (^{o}C)	PP (^{o}C)
1	0.00	90.00	10.00	9.00	89.20	75	233	-10
2	68.75	23.75	7.50	8.02	34.43	219	146	-13
3	23.75	68.75	7.50	10.50	50.18	207	241	-19
4	90.00	0.00	10.00	8.11	20.44	270	153	-24
5	28.75	68.75	2.50	9.31	53.00	166	238	-28
6	68.75	28.75	2.50	7.70	41.30	163	144	-16
7	10.00	90.00	0.00	10.70	65.20	157	236	-14
8	28.75	68.75	2.50	9.30	53.11	167	240	-28
9	90.00	0.00	10.00	8.11	20.62	268	153	-23
10	23.75	68.75	7.50	10.51	50.13	208	241	-18
11	90.00	10.00	0.00	8.60	44.90	172	166	-28
12	68.75	28.75	2.50	7.60	41.90	155	145	-15
13	68.75	23.75	7.50	8.02	34.47	217	145	-13
14	47.50	47.50	5.00	9.59	49.32	183	232	-29
15	0.00	90.00	10.00	9.50	89.17	85	231	-11
16	90.00	10.00	0.00	8.60	44.90	174	164	-27
17	47.50	47.50	5.00	9.50	49.32	182	233	-28
18	10.00	90.00	0.00	10.70	65.20	156	236	-14

*Key: **CSO** = Calabash Seed Oil; **KV** = Kinematic Viscosity;*
***VI** = Viscosity Index; **FP** = Flash Point; **PP** = Pour Point*

Table 2. Physicochemical Properties of CSO and the Lubricant

Parameters	Units	CSO	Lubricant	Engine oil range*
Kinematic Viscosity @ 40^oC	cSt	21.78±1.22	53.11±1.03	> 28.80
Kinematic Viscosity @ 100^oC	cSt	6.55±1.01	9.30±2.11	> 4.10
Viscosity Index		266±2.11	167±0.51	> 90.00
Flash Point	^oC	145±1.01	240±2.01	> 150.00
Pour Point	^oC	-11±0.01	-28±1.31	< -5.00
Free Fatty Acid	mg KOH g^{-1}	1.06±12	0.85±12	-

*Key: **CSO** = Calabash Seed Oil; (**±**) = Mean Value Plus or Minus Standard Deviation (n = 3); (*****) = Owuna et al., 2018*

4. CONCLUSION

This research was undertaken in order to formulate engine oil from calabash seed oil. The results obtained showed that a blend of CSO with mineral based oil and additive gave a formulation of lubricant that has parameters that are within the standard for engine oils and are comparable to commercially available engine oils. The chemical assay of the calabash seed extract revealed ester functionality which makes the oil good base oil for the formulation or synthesis of lubricating oil. The lubricant can be used as substitute for any applications where synthesised engine oils are applicable if thermo-oxidative stability of the oil can be validated, and requisite (tailor-made) additive is incorporated in the formulation.

REFERENCES

1. Naima, K. and Liazid, A. Waste oils as alternative fuel for diesel engine: A review. Journal of Petroleum Technology and Alternative Fuels. (2013);4:30-43.
2. Ocholi, O., Menkiti, M., Auta, M. and Ezemagu, I. Optimization of the operational parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology. Egyptian Journal of Petroleum. (2017);27:265-275.

3. Jagadeesh, K. M., Satish, V. K., Venkatesh, K. and Kathyayini, N. Evironmentally Friendly Functional Fluids from Renewable and Sustainable Sources – A Review. Renewable and Sustainable Energy Reviews. (2018);18:1787-1801.
4. Dabai, M. U., Owuna, F. J., Sokoto, M. A. and Abubakar, A. L. Assessment of Quality Parameters of Ecofriendly Biolubricant from Waste Cooking Palm Oil. Asian Journal of Applied Chemistry Research. (2018);1:1-11.
5. Muhammad, C., Usman, Z. and Agada, F. Biodiesel Production from Ceiba pentandra Seed Oil Using CaO Derived from Snail Shell as Catalyst. Petroleum Science and Engineering. (2018);2:7-16.
6. Mobarak, H. M., Niza, M. E., Masjuki, H. H., Kalam, M. A., Al Mahmud, K. A .H., Habibullah, M. and Ashraful, A. M. The Prospects of Biolubricants as Alternative in Automotive Applications. Renewable and Sustainable Energy Reviews. (2014);33:34-43.
7. Owuna, F. J., Dabai, M. U., Sokoto, M. A., Muhammad, C., and Abubakar, A. L. Use of Lagenaria siceraria Seed Oil for the Production of Environmentally Friendly Biolubricant. American Journal of Applied and Industrial Chemistry. (2018);2:1-7.
8. Tirth, M., Panchal, A. P., Chauhan, D. D., Merlin, T. and Jigar, V. P. A Methodological Review of Bio-lubricants from Vegetable Oil Based Resources. Renewable and Sustainable Energy Reviews. (2017); 70:65-70.
9. Aloko, S., Azubuike, C. P. and Hebert, A. B. C. Physicochemical Properties and Lubricant Potentials of Blighia Sapida Sapridaceaceae Seed Oil in Solid Dosage Formulations. Tropical Journal of Pharmaceutical Research. (2017);16:305-311.
10. Anjana, S. and Preeti, S. Vegetable oils as Lube Bastocks: A Review. African Journal of Biotechnology. (2013);12:880-891.
11. Ozioko, F. U. Synthesis and Study of Properties of Biolubricant Based on Moringa Oleifera Oil for Industrial Application. AU Journal of Technology. (2017);17:137-142.
12. Panchal, T., Chauhan, D., Thomas, M. and Patel, J. Synthesis and Characterization of Biolubricants from Tobacco Seeds Oil. Research Journal of Agriculture and Environmental Management. (2013);3:97-105.
13. Abadi, B. and Shimels, A. A Review on Potential and Status of Biofuel Production in Ethiopia. Journal of Plant Sciences. (2017);5:82-89.
14. Adolf, O., Akwasi, A., Gyang, N. O., Amoa, C. A. and Akorfa, A. A. Comparative Assessment of some Physico-chemical Properties of Seed Oils of Parkia biglobosa and Monodora myristica with some Commercial Oils. African Journal of Food Science. (2018);12:1-5.
15. Anuchaya, D., Vijay, K. D., and Dhanapati, D. Evaluation of the effectiveness of potato peel extract a a natural antioxidant on biodiesel oxidation stability. Industrial Crops & Products. (2018);123:454-460.
16. Mukhtar, M., Muhammad, C., Dabai, M. U. and Muhammad, M. Ethanolysis of Calabash (Langeneria sinceraria) Seed Oil for the Production of Biodiesel. American Journal of Energy Engineering. (2014);2:141-145.
17. Jeevan, T. P. and Jayaram, S. R. Experimental Investigation on the Performance of Vegetable Oil Based Cutting Fluids in Drilling AISI 304L Using Taguchi Technique. Tribology Online. (2018);13:50-56.
18. Ratchadaporn. I., Natthawud, D., Churat, T., Jutaporn, C. and Rameshpraba Ramaraj. An Experimental Investigation of Palm Oil as an Environment Friendly Biolubricant. The 22nd Tri-U International Joint Seminar and Symposium, Jangsu University, China, October18 - October 23. (2015);2015:1-4.
19. Jumat, S., Bashar, M. A., Rahimi, M. Y. and Nadia, S. Synthesis, Reactivity and Application Studies for Different Biolubricants. *Chemistry Central Journal*. (2014);8:8-16.

20. Ebtisam, K. H., Elmelawu, M. S., Salah, A. K. and Elbasuny, N. M. Manufacture of Environment Friendly Biolubricants from Vegetable Oils. Egyptian Journal of Petroleum. (2017);26:53-59.
21. Janes, A. and Chaineaux, J. Experimental Determination of Flash Points of Flammable Liquid Aqueous Solutions. Chemical Engineering Transactions. (2013);31:943-948.
22. Ghazi, T., Gunam, R. M. F. M. and Idris, A. Production of an Improved BiobasedLubricant from Jatropha curcas as Renewable Source. *Proceedings of the Third International Symposium on Energy from Biomass and Waste,* Venice, Italy: CISA, Environmental Sanitary Engineering Centre. (2010):1-11.
23. Gobinda, K., Pranab, G. and Bragendra, K. S. Chemically Modified Vegetable Oils to Prepare Green Lubricants. Lubricants. (2017);44:1-17.
24. Japir, A. A.-W., Salmon, S., Derawi, D., Bahadi, M., Al-Shuja'a, S. and Yusop, M. Physicochemical Characteristics of High Free Acid Crude Palm Oil. Oilseeds & Fats Crops and Lipids. (2017);24:1-9.
25. Ogunbusola, E. M., Fagbemi, T. N. and Osundahunsi, O. I. Fatty Acid Characterisation, Sterol Composition and Spectroscopic Analysis of Selected Cucurbitaceae Seed Oils. International Food Research Journal. (2017);24:696-702.
26. Dhia, F. A. and Sawsan, A. A. Fatty Acids Composition by GC-MS and Most Important Physical Chemicals Parameters of Seed Oil Pomogranate and Grape Seeds. Journal of Biology, Agriculture and Healthcare. (2016);6:25-32.
27. Aliyu, A. W., Richard, U. U. and Ibrahim G. W. Physico-chemical and GC-MS Analysis of Calabash (Lagenaria siceraria) Seed Oil . International Journal of Biochemistry Research & Review. (2016);14: 1-7.
28. Omahu, O. J. and Omale, A. C. Physicochemical Properties and Fatty Acid Composition of Castor Bean Ricinus communis L. Seed Oil. American Journal of Applied and Industrial Chemistry. (2017);3:1-4.

DEFINITIONS

ASTM = American Society for Testing and Materials
CSO = Calabash Seed Oil
FTIR = Fourier Transform Infra-Red Spectroscopy
GC-MS = Gas Chromatograpy Mass Spectroscopy
HTHS = High Temperature High Shear
mg/l = Milligram per Litre
mPa = Millipascal
SEA = Society of Automotive Engineers
Wt% = Weight Percent

APPENDIX

Appendix I: Calabash Fruit (A) and Dehulled Seeds (B)

A **B**

Appendix II: Analyses of Oils in Progress OVH Energies & Marketing, Kaduna, Nigeria

Appendix III: Fully Synthesised Mobil 1 5W-30 Oil (Mobil) Technical Data Sheet

Typical Properties

Mobil 1 5W-30	
SAE Grade	5W-30
Viscosity @ 100ºC, cSt (ASTM D445)	11.0
Viscosity, @ 40ºC, cSt (ASTM D445)	61.7
Viscosity Index	172
Sulfated Ash, wt% (ASTM D874)	0.8
HTHS Viscosity, mPa•s @ 150ºC (ASTM D4683)	3.1
Pour Point, ºC (ASTM D97)	-42
Flash Point, ºC (ASTM D92)	230
Density @15.6 ºC, mg/l (ASTM D4052)	0.855

Source: http://mobil.moovelub.com/sites/default/files/mobil_1_5w-30.pdf