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Production and physico-chemical analysis of lubricant from castor beans

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Abstract

The large scale industrial production of lubricants is based on the use of fossil fuel. A journey has started towards the utilization of the renewable resources for lubricant production. The castor beans and Lubricant produced (LPN) were collected from Rubavu district (Nyamyumba). The production of lubricant LPKL (lubricant produced in KIST laboratory) and lubricants analysis were performed in KIST IV laboratory. The castor oil was extracted using hot extraction with water as a solvent and extracted oil was heated about at 450^{o}C to produce the lubricant. Physicochemical analysis of the produced lubricant was carried out: acid value, iodine value, saponification values and total acid number (TAN) were measured using titration method; viscosity, pH and refractive index were measured using viscometer, pH meter and refractometer respectively; water content and specific gravity was determined using gravimetric methods. According to results obtained, it was observed that viscosity; acid value, iodine value, pH, refractive index, water content and specific gravity of both LPN and LPKL are within the allowed limits. Saponification values of both LPN and LPKL were below the limit of 186-198 for vegetable oil designed for lubricating base oil, while TAN of LPKL exceeded the limit values. The lubricant production yield (LPKL) was 25%, which is less than 48% of castor oil content in castor seeds. The values obtained were compared with the commercial lubricant as reference. It can be concluded that when it is well purified castor oil can be utilized as engine lubricant. It was also observed that candles can be produced from the byproducts thus minimizing the waste generated.

Keywords: extraction, lubricant, viscosity, castor oil.

1. Introduction

Lubricant is motor oil or engine oil used for lubrication of various internal combustion engines. The main function is to lubricate moving parts; it also cleans, inhibits corrosion, improves sealing, and cools the engine by carrying heat away from moving parts (Klamman and Dieter, 1984). Majority of lubricants consumed worldwide are from petrochemical sources, coal and natural gases which are finite and will be exhausted in near future. The ever increasing oil demands, depleting oil reserves and negative environmental impacts of petro-fuel use have created a renewed interest in lubricants of biological origin (Azam et al., 2005) particularly lubricants from vegetable oils, to ensure energy security for a sustainable development.

Renewable resources such as vegetable oil and their derivatives are being considered as potential replacements for mineral oil in certain lubricant applications where immediate contact with the environment is anticipated. Worldwide major oil seed crops used for this purpose include sunflower, soybean, rapeseed, linseed, cottonseed, canola, castor oil beans etc. majority of which are edible in nature.

The castor oil plant, *Ricinus communis*, is a species of flowering plant in the spurge family, Euphorbiaceae (Kirk-Othmer, 1979). Castor seed is the source of castor oil. The seeds contain between 46% and 55% oil that is rich in triglycerides, mainly ricinolein (Ogunniyi.D.S. 2000). Castor seeds are poisonous to humans and animals because they contain ricin, ricinine and certain allergens that are toxic (Ogunniyi.D.S. 2006). Castor oil is a colourless to very pale yellow liquid with mild or no odour or taste. Its boiling point is 313 °C (595 F) and its density is 961 kg/m^3. Like other vegetable oils, castor oil is composed of mainly triglycerides which consist of three fatty acids and one molecule of glycerol. The fatty acids of this oil consist of approximately 80-90% ricinoleic acid,

$[(CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COO)_3(OC)_3H_5]$, 3-6% linoleic acid, 2-4% oleic acid, and 1-5% saturated fatty acids (Scholz et al; 2008).

Due to its high oxy-rich property it is valuable in the vehicle engine and gear box as a lubricant. The presence of ricinoleic acid, containing both a double bond and a hydroxyl group, impart increased lubricity to the castor oil and its derivatives as compared to other vegetable oils and makes of it a prime candidate as an additive for diesel fuel (Goodrum et al; 2005, Drown et al: 2001). Castor oil has excellent storage stability at room temperatures, but it polymerizes rapidly as the temperature goes up. As it polymerizes, it forms ever-heavier "oils" that are rich in esters. These esters do not even begin to decompose until the temperature hits about 650 degrees F (345° C). Castor oil forms huge molecular structures at these elevated temperatures - in other words, as the temperature goes up, the castor oil exposed to these temperatures responds by becoming an even better lubricant. (Scholz et al, 2008).

There is growing concern about the future availability of petroleum-based products as many products including lubricants are usually produced from carbon fuels which are expensive and non-renewable. In addition, millions of tons of lubricants are dumped into the environment through leakage, exhaust gas and careless disposal. Some of these wastes are resistant to biodegradation and are threats to the environment. Thus, there are two major issues confronting the lubricant industries today: the search for raw materials that are renewable and products that are biodegradable. For this reason Rwanda environmental policies emphasize on utilization of the limited resources to not only protect the environment or to save carbon based fuels but also to generate income and improve local technologies and job creation. The study was thus carried out to produce and characterize Lubricant from castor oil and to compare the properties of the produced lubricant to the commercial and international standards. It was also aimed at extracting castor oil using green chemistry instead of the conventional extraction using organic solvents.

2. Methods

All chemicals and reagents used were of Analytical grade and were purchased from Sigma Aldrich. The castor seeds were collected from Nyamyumba in Rubavu district.

Extraction of castor oil and lubricant production

The castor beans were cleaned by hand picking to remove some foreign materials and dirty through the process of clearing. The cleaned beans were sundried in the open, until the casing splits and sheds the seeds. The beans were further dried in the oven at 60°C for 7hrs to a constant weight in order to reduce its moisture content. The shell has been separated from the nibs (cotyledon) by using tray to blow away the cover in order to achieve very high yield through the process of winnowing.

After winnowing the size of nibs has been reduced by grinding them using mortar and pestle to crush the beans into a paste (cake) in order to weaken or rupture the cell walls to release castor fat for extraction. Water was added to the known weight sample and heating started at about 320^{o}C for four hours. The oil floated above water and then collected. The collected oil was dried in the oven to reduce the water content introduced during the collection of oil. It was then cooled in the desiccators and weighed again to determine the amount of oil extracted. The extracted oil was heated at about 450^{o}C and there was a change in colour of lubricant produced as noted in literature review. The obtained lubricant was then subjected to physico-chemical analysis.

Moisture content

The moisture content of both LPN and LPKL was determined by heating the lubricant in the oven at 120^{o}C. The lubricant was poured into a beaker of known mass (m_o), and then the beaker was weighed again to obtain (m_1), which was the mass of oil and beaker. The beaker containing the lubricant was then heated in the oven at 120^{o}C during approximately 7 hours.The beaker was cooled, and then reweighed and the mass m_2 was noted. The mass loss has been calculated (mass of water content) by subtracting m_2 from m_1. Finally the water content percentage was calculated in this way:

Water content %= $\frac{\mathrm{mH2O} \times 100}{\mathrm{m1} - \mathrm{m0}}$

Where: mH_2O is the mass of water obtained by subtracting m_2 from m_1.

Viscosity

In this test method, the oil was placed in a beaker, housed in an insulated block at a fixed temperature. A metal spindle was then rotated in the oil at a fixed rpm, and the torque required to rotate the spindle was measured. Based on the internal resistance to rotation provided by the shear stress of the oil, the oil's viscosity was determined. This procedure was repeated at different temperatures determine how viscosities of LPN, LPKL and CL change with temperature.

Refractive index

The instrument was calibrated with a glass prism of known refractive index or by using distilled water which has refractive index of 1.3330 at 20^{o}C and 1.3306 at 40 ^{o}C, the usual temperature of taking readings. Thereafter, few drops of the oil were transferred into the glass slide of the refractometer. Water at 30°C was circulated round the glass slide to keep its temperature uniform. Through the eyepiece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index.

Specific gravity

Density bottle was used to determine the density of the oil. A clean and dry bottle (pycnometer) of 25ml capacity was weighed (W_0) and then filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr) is:

Sp.gr $= \frac{(\mathrm{W1} - \mathrm{W0})}{\mathrm{W2} - \mathrm{W0}} = \frac{\text{Mass of the substance}}{\text{Mass of an equal volume of water}}$

Total suspended solids

A filter paper was weighed and filtration apparatus was assembled. Using distilled water, filter paper was wet on the funnel, and sample to be studied was stirred. 50ml of a sample was pipetted while stirring and filtered. After filtration the filter was washed three times and transferred to evaporating dish and dried. When the filter paper was dry, it was cooled, reweighed and results were recorded (the weight obtained for this time is that of a filter paper and suspended solids).

$$\text{mg Suspended Solids / L} = \frac{[(A-B)\times 10^3]}{\text{mL sample}}$$

Where:
A = weight of filter + dried residue, mg
B = weight of filter, mg

Flash and fire point

Pensky Marten's apparatus was used. Tetrachloromethane was used to clean all parts of the apparatus. The oil cup was filled with the test oil up to the mark. The lids were fixed on the top through which were inserted a thermometer and a stirrer ensuring that the flame exposure device is fixed on the top. The test flame was set alight and adjusted to about 4 mm in diameter.

The apparatus was heated as temperature of oil increased by 5 to 6^0 C per min. as stirrer was continuously rotated. At every 1^oC rise of temperature, the test flame was introduced into the oil vapor. This was done by operating the shutter. On moving knob of shutter, test flame was lowered in oil vapors through opening. When test flame caused a distinct flame in interior cup, the temperature was noted and represented the flash point. The oil was further heated at the rate of 1^oC/ min. and the flame test was continually applied as before. The temperature at which the vapors of the oil gave a clear and distinct blue flash for five seconds was recorded as the fire point of the oil (Vellguth G, 1983).

Total Acid Number (TAN)

10 g of sample was poured into a 200ml conical flask then, solvent (mixture of toluene: water:2-propanol) was added to make 100ml. The later solution was then titrated with potassium hydroxide 2-propanol until the appearance of pink color and the volume of titrant used was recorded. The blank test was also performed to obtain a blank level. TAN was calculated using the formula below:

$$\text{Total acid number (mg / g)} = \frac{(EPl-BLl)\times TF\times Cl\times Kl}{S}$$

EPl : Titration volume (mL)
BLl : Blank level (0.052mL)
TF : Factor of reagent (1.000)
Cl : Concentration conversion coefficient (5.611 g/mL) (Equivalent to potassium hydroxide in 1mL of 1mo1/L potassium hydroxide 2-propanol solution)
Kl : Unit conversion coefficient (1)
S : Sample size (g)

pH value

20ml of both LPN and LPKL were used for each experiment. The pH meter was calibrated by standardizing it's electrode with buffer 7 solution and then buffer 4 solution. The electrode was immersed into the sample and pH value recorded.

Peroxide value

To 1 g of the oil sample, 1 g of potassium iodide and 20 ml of solvent mixture (glacial acetic acid/chloroform, 2/1 by volume) was added and the mixture was boiled for one minute. The hot solution was poured into a flask containing 20 ml of 5% potassium iodide. A few drops of starch solution were added to the mixture and the latter was titrated with 0.025 N sodium thiosulphate and the peroxide value was determined as follows:

$$PV = \frac{SN10^3}{W}$$

Where:

S= ml of $Na_2S_2O_3$,

N= normality of $Na_2S_2O_3$,

W= weight of oil sample (g).

Iodine Value

0.4g of the sample was weighed into a conical flask and 20ml of tetrachloromethane was then added to dissolve the oil. Then 25ml of Dam's reagent were added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask vigorously swirled. The flask was placed in the dark for 2 hours 30 minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium-thiosulphate solutions until the yellow colour almost disappeared. Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) was given by the expression:

$$I.V = \frac{12.69C(V1-V2)}{M},$$

Where

C = Concentration of sodium thiosulphate used; V1 = Volume of sodium thiosulphate used for blank; V2 = Volume of sodium thiosulphate used for determination, M = Mass of the sample.

Saponification Value

2g of the sample were approximately weighed into a 250ml conical flask then after, 25ml of 0.5N alcoholic potassium hydroxide was added. A reflux condenser was attached and the flask contents were heated on a boiling water bath for 1 hour with occasional shaking. While the solution was still hot, 3 drops of phenolphthalein indicator were added and the excess potassium hydroxide was titrated with the 0.5 N hydrochloric acid (V in ml of hydrochloric acid at end point represents S). The procedure was repeated but without sample (V in ml of hydrochloric acid at end point represents B).

The saponification number was calculated by using the following formula:

$$S.V = \frac{56.1(B-S)\times N \text{ of HCl}}{\text{Gram of Sample}},$$

Where B= the volume of the solution used for blank test; S= the volume of the solution used for determination; N = Actual normality of the HCl used.

Acid Value

5g oil sample was approximately weighed and dissolved in 50ml of the above prepared solution of ethanol-ether. 1ml of indicator was added and then the later solution was neutralized with sodium hydroxide titrant until pink coloration was observed.

A.V=(0.561×v of NaOH)/mass of sample

Statistical analysis

All measurements were done in seven replicates. Statistically significant differences between means was compared using one way ANOVA

3. Results

Table1: Yield

	m Sample	m LPKL in g	V LPKL in ml	yield in % m
E1	100.00	24.05	25.50	24.59
E2	200.00	49.96	53.00	24.98
E3	210.74	54.33	58.00	25.78
Mean of % yield in m				25.12±0.61

Table 2. Physical parameters

Parameter	Lubricant	Mean	Standards
Viscosity (cp)	LPN	515.7 ± 7.87^{a}	
	LPKL	548.6 ± 10.69^{b}	
	CL	461.4 ± 6.90^{c}	
Moisture content (% mass)	LPN	0.104 ± 0.004^{a}	
	LPKL	1.230 ± 0.33^{b}	
	CL	2.783 ± 0.08^{c}	
Specific gravity (g/ml)	LPN	$0.953\pm8E05^{a}$	0.80-0.97 g/ml as specified by ASTM.
	LPKL	0.959 ± 0.001^{b}	
	CL	0.887 ± 0.002^{c}	
TSS	LPN	2.037 ± 0.081^{a}	
	LPKL	2.151 ± 0.021^{b}	
	CL	1.782 ± 0.119^{c}	
Refractive index	LPN	1.477 ± 0.001^{a}	
	LPKL	1.490 ± 0.015^{b}	
	CL	1.456 ± 0.001^{c}	
Flash point (^{o}c)	LPN	191.7 ± 4.821^{a}	
	LPKL	214.4 ± 3.780^{b}	
	CL	182.7 ± 4.608^{c}	
Fire Point (^{o}c)	LPN	199.0 ± 4.690^{a}	
	LPKL	220.0 ± 3.162^{b}	
	CL	186.0 ± 3.512^{c}	

Mean values with the same letters within each parameter are not significantly different ($p>0.05$)

Table 3 Chemical parameters

Parameter	Lubricant	Mean	Standard
A.V: mgKOH/g	LPN	0.245±0.02^{a}	
	LPKL	1.271±0.02^{b}	
	CL	0.253±0.01^{a}	
S.V: mgKOH/g	LPN	171.5±1.06	186-198 (Blackbourn, J.H., et.al, 1983)
	LPKL	146.7±5.18	
	CL	-	-
pH	LPN	6.449±0.07^{a}	
	LPKL	6.437±0.06^{a}	Neutral ASTM
	CL	5.210±0.17^{b}	
TAN: mgKOH/g	LPN	0.504±0.04^{a}	
	LPKL	2.457±0.33^{b}	
	CL	0.493±0.06^{a}	
P.V	LPN	28.21±2.78^{a}	
	LPKL	25.36±2.67^{a}	
	CL	64.64±2.67^{b}	
I.V: g I_2/100g	LPN	114.7±2.50	
	LPKL	119.0±2	94-126 (Blackbourn, J.H., et.al, 1983)
	CL	-	-

Mean values with the same letters within each parameter are not significantly different (p>0.05)

Discussions

The results obtained from percentage yield (table1) show that 100g of castor beans give 24.78g of lubricant (24.78%). This percentage is small compared to the castor seed oil content given earlier ranging from 46% to 55%. The low percentage yield depends on various factors like extraction process, oil-water separation method, moisture content of the sample (castor seeds).

The extraction method is a very important parameter which affects the yield. Many researchers use Soxhlet extraction method for extraction of vegetable oil. This method requires the use of organic solvents which are harmful to the environment. In this study, water was used as benign solvent as recommended for greener production.

Viscosity

Viscosity is one of the most important properties of lubricating oil. The formation of fluid film of lubricant between the friction surfaces and the generation of frictional heat under particular condition of load bearing speed and lubricant supply mostly depend upon the viscosity of lubricant and to some extent on its oiliness. From the literature review, it can be observed that the viscosity decrease with the rise in temperature as usual therefore variation of viscosity with respect to temperature found in lubricating oils LPN, LPKL and commercial lubricating). From the above data (table2), viscosity of lubricant produced from castor oil (LPKL and LPN) was found to be higher than that of CL. The oil viscosity depends on molecular structure and decreases with unsaturation of fatty acid (BL Burris, et al. 2007) and the difference in viscosity confirms the difference in molecular structure. The high viscosity indicates better lubricating property of LPKL and LPN based on viscosity.

Table 4 Change in viscosity with temperature

Temperature ^{O}C)	Viscosity (cp)		
	LPN	LPKL	CL
40	239	182	140
100	38	27	24

Table 4 above shows how viscosities of LPN, LPKL and CL change with temperature. Viscosities were measured at 40°C and 100°C as referenced in ASTM D2270 in determining viscosity index. Although the CL has the lower viscosity than LPN and LPKL at room temperature, it shows high viscosity index as its viscosity change with temperature is low. The high viscosity index of CL indicates its resistance to temperature which is the important characteristic of lubricating oils. Higher the V.I, lesser is the variation of viscosity with change in temperature. Thus, good lubricating oil should possess high V.I.

Moisture Content

Mean values of moisture content of both LPN and LPKL are below to that of commercial lubricant This indicates the better lubricating property of lubricant produced from castor oil based on moisture content. This high moisture content in CL was influenced by condensation effects and water uptake during storage (Thuneke and Kern, 2002).

Flash and fire point

Flash point of lubricant produced from castor oil (LPN and LPKL) is slightly higher than CL hence castor oil sustains more temperature compare to CL. Fire point of castor oil is also slightly higher than CL which means that castor oil is suitable at high temperature.

TSS and specific gravity

The results showed that the lubricants produced from castor oil (LPN and LPKL) have high specific gravity. Total suspended solids values of LPN and LPKL exceeded that of CL and the LPKL presented high TSS, this is probably caused by water-oil separation method during castor oil extraction where the oil was being collected above the water. Perhaps some residues were collected with oil. This TSS can be solved by a further purification of the lubricant before its utilization.

Acid value

A good lubricating oil should have a low acid value. High acid value indicates oxidation of oil which may lead to gum and sludge formation beside corrosion. Acid value of LPKL was found to be greater than LPN and CL but all are below the RK limit of 2 mg KOH/g. The high A.V of LPKL means that COOH group is higher in LPKL lower in LPN and CL.

Iodine value

Iodine value is intended as a measure of unsaturation and at times it is used as quick alternative to oxidation test of mineral oils. The higher the Iodine value, the higher the degree of unsaturation. When Iodine value is lower, it means that the double bond of the polyunsaturated fatty acid (PUFA) of the oil had been attacked and oxidation of the oil had taken place. Iodine value indicates drying quality of oil, the drying oil having higher iodine values. According to third global oil and fat business forum USA and Interfacing with the global oils and fat business by Ilija gawrilow iodine value designed for lubricating base oil is 94-126 (Blackbourn, J.H., et.al, 1983). Thus from above data, iodine values of both LPN and LKPL are within the range hence the lubricant from castor oil act as a good lubricant.

Saponification value

The animal oil and vegetable oil undergoes saponification but mineral oil does not. Further most of the animal oil and vegetable oil possesses their own characteristic saponification value. Hence determination of saponification value helps to ascertain the presence of fixed oil in lubricant. According to third global oil and fat business forum USA and Interfacing with the global oils and fat business by Ilija gawrilow saponification value of vegetable oil designed for lubricating base oil is 186-198. Only saponification values of both LPN and LPKL were measured and the results obtained were below the above limit. It may be due to experimental error range that can be attributed to the presence of some impurities and other component of the oil mixture.

pH

pH value of the CL is slightly acidic but about neutral in case of lubricant produced from castor oil. The pH of CL obtained was 5.21, 6.43 for LPKL and 6.44 for LPN. The low value in pH of CL means that CL contains materials which when mixed with water supply hydrogen ions to the water phase, slightly higher or lower pH values may be encountered depending on those materials (additives), which are present. All these values are within the range given by ASTM standards for lubricating oils.

Conclusions

The percentage oil content of castor seed was found to be 25% using hot extraction and water as solvent. A satisfactory yield can be achieved using machine extraction with pressure and water as solvent which is greener. From the results obtained after the physical and chemical analysis of the purified lubricant produced from castor oil it can be concluded that the castor oil is utilizable for lubricant production. More studies should be carried out on the byproducts of the castor oil extraction because it was been realized that the candles could be produced from the byproducts in order to avoid the waste generation. Other physico-chemical parameters such as total base number, cloud point, pour point, sulfur content, adhesiveness and volatility should also be carried out.

References

ASTM D, 664-95 *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration*

Azam, M.M,Waris, A. and Nahar, N. M. 2005.Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass and Bioenergy* **29**:293-302.

Blackbourn, J.H. (1983).Performance of Lubricating Oils in Vegetable Oil Ester-Fuelled Diesel Engines, *SAE Technical Papers 83135*

BL Burris; B Bosel; GR Bourne; WG Sawyer, *Journal of macromolecular materials and engineering*, 2007, 292, 387-402

Drown, D. C., Harper, K.; Frame, E.2001, Screening Vegetable Oil Alcohol Esters as Fuel Lubricity Enhancers. *J. Am. Oil Chem. Soc*, **78**, 579.

Goodrum, J. W., Geller, D. P. 2005, Influence of Fatty Acid Methyl Ester from Hydroxylated Vegetable Oils on Diesel Fuel Lubricity. *Bioresour.Technol*, **96**, 851.

Kirk-Othmer, 1979. Encyclopedia of Chemical Technology, vol, 5. John Wiley & Sons, New York.

Klamman, M.K and Dieter, H. *Lubricants and Related Products*, Verlag Chemie, 1984.

Ogunniyi, D.S., Njikang, G.N., 2000. Preparation and evaluation of alkyd resin from castor oil. *Pak. J. Sci. Ind. Res*. **43**, 378–380.

Ogunniyi, D.S., Fakayejo, W.R.O, Ola, A, 2006.Preparation and properties of polyurethanes from toluene diisoyanate and mixtures of castor oil and polyol. *Iranian Polym. J*. **5**, 56–59.

Scholz, V,Nogueira da. Silva, J. 2008, Prospects and Risks of the Use of Castor Oil as a Fuel. *Biomass Bioenergy*, **32** (2), 95.

Thuneke, K. und Kern, C. 2002: Pflanzenölbetriebene Bloc kheizkraft-werke – Teil 1. "Materialien 171", Hrsg.: Bayerisches Staatsministerium für Landes entwicklung und Umweltfragen (StMLU).

Vellguth G, Performance of vegetable oils and their monoesters as fuels for diesel engines SAE paper no. 831358, 1983.