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Comparative study of lube oils synthesized from chemically modified castor and soybean oils using additive

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Abstract

Petroleum-base-lube oils are non-biodegradable and their continuous use results in environmental pollution. Comparatively, vegetable oils are biodegradable, less toxic and renewable hence, their use as base stock for lubricant production will not only serve as viable alternatives but also help in avoiding environmental deterioration. This paper compares the properties of soybean and castor oils as potential sources for synthesizing bio-lubes when mixed separately with styrene as additive. Styrene was used because of its advantageous polymeric behavior. Samples of soybean and castor oils were mixed with different volumes of the additive at 50 °C. Fluid properties were determined with emphasis on viscosities of the oils. For the castor oil samples, their viscosities compare with those of standard oils at 40 °C and at 100 °C. These values show that soybean samples can replace base oils used in SAE15W - SAE20 monograde lubricant while castor oil samples can replace the SAE50 - SAE60 lubricants.

Keywords: Additive; Biodegradability; Comparative analysis; Vegetable oils; lube oil

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1. Introduction

A lubricant is a solid or fluid which helps to reduce wear and friction between moving parts. Lubricants usually comprise of 90 % base oil and 10 % additive. Other liquids like water can be used as lubricants to inhibit friction, wear and reduce heat between surfaces in motion or contact with each other [1]. The ability of lubricants to transport foreign substances away from surfaces in order to prevent clogging between the surfaces is known as lubricity. An estimated 37,300,000 tons of lubricants were used globally in the year 1999 [2]. In most machines, there is constant rubbing of surfaces resulting from moving, sliding and rolling of parts which pose resistance to movement. This resistance is otherwise known as friction. Friction leads to the release of large amounts of

energy in the form of heat which reduces the efficiency of the machine and can be minimized by introducing a substance of low shear strength between the surfaces [3]. The method used to reduce friction between surfaces through the introduction of a substance known as a lubricant is called Lubrication. The lubricant film can be a solid-liquid, liquid, liquid-liquid dispersion or rarely gas [4]. Examples of solid lubricants include graphite, molybdenum disulphide, tungsten disulphide and zinc oxide. They can withstand very high temperatures of about 650 °C. Solid lubricants can serve as additives to mineral oils and greases which help to improve their load-bearing capacities. Lubricants enable equipment to work for long with mild wear, reducing risk of damage and breakdowns that are most likely to occur. In addition, they help in decreasing wear and tear, surface deformation, and

loss of energy, maintenance cost and serves as a seal, corrosion resistor and coolant. Lube oils are used as lubricants because of their wide range of properties. According to Hwang and Erhan [5], three main types of lube oils include mineral, synthetic and vegetable oils. Mineral oils are formed by refining petroleum or crude oils while synthetic oils are produced from poly-alpha-olefins, which are hydrocarbon-based poly-glycols or ester oils. Mineral based oils have unique viscosities and can be blended to enhance their performance for certain operations. The use of benign technology for the conversion of petroleum-based products in forestry, farming, mining, and boating have resulted in the creation of products that are harmless to the environment [6]. The recent exploitation of vegetable oils for the production of biodiesel is due to the renewability and lesser pollution potential of the resulting diesel relative to conventional diesel. The paper of Lang et al. [7] asserts that emphasis has been on the use of oils of edible and non-edible oil seeds as blending materials for bio-lubes because of their rheological properties. According to Matthew and Siniawski [8], the high interest on lube oils in the automotive industry is as a result of their excellent lubricity, non-toxic nature and biodegradability. However, according to the paper, this will in turn increase the use of renewable resources and also cut down on the environmental and health impacts. Bio-lubricants are lubricants that quickly biodegrade and are not harmful to humans and aquatic life. Generally, vegetable oils are less harmful, renewable and will help to curb the over-dependence on unrefined petroleum oils [9]. Vegetable oils e.g. soybean, rapeseed (canola), sunflower, peanut, olive oil and others comprise mainly of triglyceride molecular structures and have disadvantages in their performances which include poor thermal, hydrolytic and oxidation stability but genetic improvements on their seeds have also helped to overcome some of the thermal and oxidative stability disadvantages, especially with soybean and canola oils. In the trans-esterification studies carried out by Chakrabarti and Ahmad [10] on the use of castor oil for biodiesel production, palmitic, stearic, oleic, ricinoleic, linoleic and linolenic acids were the acids identified in the castor oil while palmitic, stearic, oleic, linoleic and linolenic acids were those found in soybean oils. Fatty acid compositions for canola, corn and sunflower oils were also reported alongside their physico-chemical properties such as viscosity, sulfur content, density (at 15 and 20 °C), flashpoint, copper corrosion, cetane index, percent water and sediment. It is important to consider the environmental-friendliness of a lubricant based on the intended application as it relates to water, food insecurity/contamination and environmental pollution. Although, applications of bio-lubricants have mostly been restricted to use in situations where the lubricant ends up in the environment, this gives little or no concern as these lubricants are biodegradable. The

two-stroke engine oils, chain saw lubricants and hydraulic oils are serviced with bio-lubricants while research on the use of bio-lubes in gasoline and diesel passenger car engines is still in progress [11]. Based on their applications, bio-lubricants can be sourced from vegetable oils or synthesized. Lubricants sourced from vegetable oils are usually meant for low temperature applications or in situations where oil stability is of less importance; however, this is not the case with synthesized oils as they possess better characteristics [12]. Synthetic esters are a class of bio-lubricants derivable from solid fats and waste materials such as tallow. Despite the similarity in biodegradability and low-toxicity of bio-lubricants and pure hydrocarbons, the type of additive employed during production determines the suitability or fitness of the oils to tests such as antifoam, antirust, oil stability etc. Options for trimming the additive-requirement for the formulation of lube oils with excellent properties were proposed by Tung et al. [13]. Hydrocarbon oils can be blended with long chain polymers and antioxidants like aminophenols, Gopalan et al. [3]. Common lubricants, with additives inclusive, have their origin in petroleum base oils. An additive is a substance mixed with a base oil in order to infuse additional characteristics. The end-quality of a lubricant rests majorly on the parent base oil and the additives employed in the production process. Most additives come in viscous forms/concentrated solutions which allow for proper mixing with the base oils. Additives are known for adding useful and new properties to the parent oil, enhancing the inherent characteristics of the lube oils as well as limiting the tendency for undesirable changes during the service life of the oil [14]. Producers of lube-oils may choose to adopt the same base oil with several additives for specific applications. The approximate w/w% additive in some lube oils is $\leq 5\%$ [2]. Some lubricants are stable under extreme conditions (i.e. high pressures, high temperatures and contamination) while others may not, this then informs the need to select additives based on their requirements [15]. For example, additives with antioxidant properties (organic amines and phenols) help to reduce the oxidative deterioration of base oils. Some are metal deactivators which provide a protective film-layer on metal surfaces when used [16]. The Society of Automotive Engineers (SAE) classification for automotive oils is based on viscosities with corresponding temperatures in the range of -5 °C to -40 °C (low temperatures) and 100 °C (high temperature) and low/high shear rates, hence, lube-oil for low temperature applications within the specifications of the 5 W grade, and below 100 °C i.e. say 30 °C, is assigned the code name SAE-5W30 which is characterized by its all-year-round-service application as a multi-grade or multi-viscous oil [17]. Petroleum-base oils are not environmentally friendly. They easily pollute the

environment, and have very low lubricity and low flash point when compared with other types of oils especially those derived from vegetable sources; unlike vegetable oils that have excellent lubricity, higher viscosity index, lower volatility and higher flash point, better skin compatibility, biodegradability and cost saving on account of the required maintenance. Hence, this research paper exploits the use of vegetable sources (edible oil and non-edible oil) to replace base oils as a key ingredient in the production of lubricants with essential qualities and properties as compared with standard monograde lubricants.

2. Methodology

Some equipment, raw materials used and the steps adopted in carrying out the work are reported in this section.

2.1 Materials and reagents

Castor and soybean oils from a local market in Sango Ota, Ogun state in Nigeria, 0.1 M (98 %) Sodium hydroxide - Nj08865 produced by J, T Baker USA, phenolphthalein Indicator (99.93 %) produced by J, T Baker USA, absolute Ethanol (99.99 %) produced by Fischer Scientific, UK, and benzene (99.7 %) produced by Sigma Aldrich Inc., Germany.

2.2 EQUIPMENT

(i) Calibrated Viscometer and Viscometer Bath

The ASTM IP, UBC, Size 4, No: 2118, PSL 1643/13, c = 0.4959, Ubbelohde and BS/U viscometer (made in England) SYD-265D-1, LiDA xmT-F 9000), No: 2014 - 7-765, 1800 W, 220 V was used to determine the kinematic viscosities of the 10 samples at two different temperatures; 40 °C and 100 °C. The equipment is coupled with a 50 Hz, 0.12 A, 1250 rpm, 0.5µF/450V YN60-06 motor.

(ii) Flash Point Tester

The SYD-3536 Cleveland-open-cup-tester was used to test for the flash points of the samples. It consists of a cup which holds samples as they rest on the heating coils; with an open flame passing across the cup, the temperature at which the vapour of the oil flashes was found.

2.3 EXPERIMENTAL PROCEDURE

12 different samples were used. The standard test methods and properties of a monograde SAE 40 lubricant were used as reference for this study.

2.3.1 Preparation of Lubricant Samples

The twelve samples were prepared by mixing 0, 10, 20, 30, 40 and 50 % of styrene as additive with 100, 90, 80, 70, 60 and 50 % of castor and soybean oils respectively. Each blend produced two samples; the blend was done at a temperature of 50 °C for 15 minutes. The volume of the mixture was 100ml. The samples of castor oil, soybean oil and the blends were then analyzed.

2.3.2 Sample Analysis

(i) Density test

The 50 ml empty specific gravity bottle was weighed and the mass was recorded, m_b . Each sample was poured into the 50 ml specific gravity bottle and the mass of the oil and the bottle was recorded, m_{bo} . The mass of oil ($m_o = m_{bo} - m_b$) was then obtained. The density was calculated by dividing the mass of the oil (m_o) by the volume of the specific gravity bottle (50 ml). The density of the samples were calculated using (1).

$$\rho = \frac{m}{v} \quad (1)$$

Where:

v = S.G. bottle (ml)

m_b = S.G. bottle (g)

m_{bo} = S.G. bottle (g) + oil (g)

m_o = Oil (g)

ρ_o = Density of oil (g/ml)

(ii) Determination of flash point

The samples were poured to reach the mark indicated on the Cleveland cup tester. The thermometer was placed into the cup. With the gas hose connected to the device, the device was switched on in order to supply the required heat through the coils underneath. The standard flashpoint for lubricants is above 200 °C; hence, as soon as the temperature was 200 °C the flame was ignited to determine the flashpoints of the oils. The temperatures at which the flame caused the vapors of the oils to flash were recorded as the flashpoints.

(iii) Viscosity test

The ASTM Ubbelohde and BS/U calibrated viscometers were used to estimate the kinematic viscosity of the oils. About 20ml of sample was poured into the first tube of the viscometer. The filled viscometer was then placed in the viscometer bath at a temperature of 40 °C. It was then left for about 15 mins so that the sample would attain the

temperature of 40 °C. A pipette filler/sucker was placed through the second tube, and then the third tube was closed while the liquid was sucked up into the ball part of the tube. The time it took for the liquid to move from the mark above the ball to the one below was recorded. The procedure was then repeated at 100 °C. The kinematic viscosities were calculated using (2).

$$v = c * t \tag{2}$$

Where:

v = Viscosity of the sample

c = Viscometer constant

t = Time taken

(iv) Determination of acid number

5.0 g each of the oil samples was weighed into 250 ml conical flasks 25 ml of absolute alcohol and 25 ml benzene were added to the oils in the flasks. The contents of the flasks were shaken well to dissolve. The contents were then titrated against 0.1 M Potassium hydroxide solution using phenolphthalein as indicator. The end point was the appearance of a pale pink permanent colour and the titre values were recorded. The acid values were calculated using (3)

$$A_v = \frac{X * M * 56.1}{W} \tag{3}$$

Where:

X = Volume of KOH required to neutralize the sample solution (ml)

M = Molarity of KOH (M)

W = Weight of oil used (g)

56.1 is the atomic weight of potassium hydroxide (KOH).

(v) Determination of pour point

This procedure was done manually; the samples were placed in a cooling system. At 30 minutes interval, the samples were brought out of the cooler and tilted to check their pour points. The temperatures of the samples were taken when the liquid seemed to stop flowing.

3. Results and discussion

Table 1: Volume of Vegetable oil to volume of additive

Basis of oil blend: 100ml

Vegetable oil Sample	Volume (ml) of Oil Sample	Volume (ml) of additive	Sample No
Soybean oil	50	50	1
	60	40	2
	70	30	3
	80	20	4
	90	10	5
	100	0	6
Castor oil	50	50	7
	60	40	8
	70	30	9
	80	20	10
	90	10	11
	100	0	12

TABLE 2: Density of the samples

Sample No	Oil (g)	Oil density (g/ml)
1	48.50	0.972
2	48.50	0.972
3	48.45	0.969
4	48.25	0.965
5	48.10	0.962
6	45.80	0.916
7	51.25	1.025
8	50.95	1.019
9	50.45	1.009
10	50.20	1.004
11	48.20	0.964
12	47.95	0.959

For the analyses, 12 samples were used; samples 1 – 6 being soybean oil and samples 7 – 12 being castor oil. Table 1 shows the various blends obtained for the vegetable oils. In Table 2, the measured mass of soybean

oil is seen to decrease with decreasing density of oil i.e. since mass is the product of volume and density hence, mass is proportional to density. For samples 1-6 (soybean oil), the mass of soybean oil is 48.50 g each for samples 1 and 2, 48.5 g for sample 3, 48.25 g for sample 4, it is 48.10 g for sample 5 and 45.8 g for sample 6; the corresponding densities are 0.972, 0.972, 0.969, 0.965, 0.962 and 0.916 g/ml respectively. For castor oil, the measured mass and densities are 51.2 g, 1.025 gm/l, 50.95g, 1.019 gm/l, 50.45g, 1.009 mg/l, 50.20 g, 1.004 gm/l, 48.2 g, 0.964 mg/l and 47.5 g, 0.959 gm/l for samples 7 – 12 respectively. The results agree with reports of soya bean oil 0.916-0.922 g/ml as given by Gonzalez [12], while those of castor oil agree with results of ASTM specification (i.e. 0.957-0.968 g/ml) for quality castor oil as reported by Akpan et al. [18]. In Table 3, samples 1 and 2 have equal pour points of -8 °C each. For samples 3, 4, 5 and 6, the pour points are -10, -11, -14 and -16 °C respectively showing a decreasing order of pour points. Taking a close look at Table 3 again, one can infer that the higher the mass of oil, the higher is its density and hence the higher its pour point and vice-versa. For the castor oil samples i.e. samples 7 – 12, the pour points of the samples are 3, 2.2, 2 -2, -1 and -2 °C respectively which is indicative of decreasing densities of the oil which varies from 51.25 - 47.95 gm/l for the samples respectively but the value is same for samples 10 and 12 even with their different densities. However, this implies that the density of castor oil has no direct relationship with its pour point, but this is not the case for soybean oil where densities increase with pour point; the lowest pour points for the soybean and castor oils were -16 °C and -2 °C respectively. The pour points of the soybean oil samples are lower because they contained more unsaturated fatty acids while those of the castor oil are higher because they contained more saturated fatty acids which corroborates the findings of Erhan and Pertz [19]; this can be further confirmed by the results of the acid tests (Table 3). For the soybean and castor oil samples, the pour point increased as the volume of additive increased because according to Rudnick [20], the exact mechanism for lowering the pour point of the modified vegetable oils by conventional pour point depressant has not been well established and this is due to the presence of wax which is infused by the additive in the vegetable oils and is responsible for the high pour points in mineral oils. In Table 3, for soybean oil, flash points were seen to decrease for all samples from 340 °C for sample 1 to 300 °C for sample 6. Castor oil samples showed variation from 227 to 250 °C. Considering their corresponding flash points, one would see a direct variation of both parameters i.e. a decrease in flash point corresponds to a decrease in pour point for all samples of vegetable oils. From the results, an increasing trend was observed for the estimated acid numbers for samples 1 - 6; same applies to samples 7 - 12. Hence, it can be deduced that the higher the pour

and flash points of the soybean and castor oils, the lower is the acid number and vice-versa.

TABLE 3: Pour point, flashpoint and acid number of the oils

Lube oil sample	Pour point (°C)	Flash point (°C)	Acid number (mg KOH/g oil)
1	-8	340	0.301
2	-8	335	0.514
3	-10	326	0.763
4	-11	318	0.978
5	-14	307	1.264
6	-16	300	2.346
7	3	277	0.184
8	2.2	276	0.191
9	2	263	0.209
10	-2	261	0.217
11	-1	256	0.224
12	-2	250	1.101

The acid values shown in Table 3 for the soybean and castor oils were in the range of 0.301- 2.346 mg KOH/g soybean oil and 0.184 - 1.101 mg KOH/g castor oil respectively which fall within the range found in literature i.e. which are in the range of 0.4 – 4 for both oils [21]. The results also reveal that unsaturated fatty acids are more in lube oils produced from soy bean oil than lube oils sourced from castor oil.

In Table 4, for soybean oil at 40 °C, the kinematic viscosities i.e. the ratio of viscosity of soybean oil to its density showed significant reduction for samples 1 – 6 with values ranging between 125.13 and 33.4 mm²/s. The same trend was observed for castor oils (samples 7 – 12), where the reduction is from 450.92 – 240.56 mm²/s. For the soybean oil at 100 °C the measured kinematic viscosities for samples 1 – 6 range from 12.8 – 7.92 mm²/s whereas, it is in the range of 47.7 – 19.5 mm²/s for samples 7 – 12. Hence, soy or castor oil-base lube oils with higher kinematic viscosities tend to have higher viscosities and vice-versa; this assertion also spans from the fact that kinematic viscosity is the ratio of viscosity to density. At 100 °C, the viscosities of vegetable oils tested were seen to be lower than the oil viscosities measured at 40 °C. Figures 1 and 2 show variation of densities of both oil samples with different volumes of additive and the variation of kinematic viscosities with separate volumes

of additives respectively. The increasing trend for both profiles shows the effect of additives in lube oils produced from vegetable oils. This simply implies that increased volume of additives improved the viscosities of the oils. Considering the effect of temperature, generally, one would expect that oil viscosities at higher temperatures will be lower than oil viscosities at lower temperatures and as explained earlier, kinematic viscosity is directly proportional to viscosity. The kinematic viscosity plot against viscosities for both vegetable oils at 40 °C and 100 °C for the given volumes of additive shows this trend. The findings agree with the findings of Udeagbara et al. [22].

TABLE 4: Kinematic viscosities of the oils @ 40°C and 100°C

Lube oil Sample	Kinematic viscosity at 40°C (mm ² /s)	Kinematic viscosity at 100°C (mm ² /s)
1	125.13	12.8
2	105.4	11.34
3	98.2	10.22
4	70.5	8.8
5	50.16	8.3
6	33.4	7.92
7	450.92	47.7
8	421.72	40.7
9	371.01	35.2
10	298.38	30.1
11	274.52	24.4
12	240.56	19.5

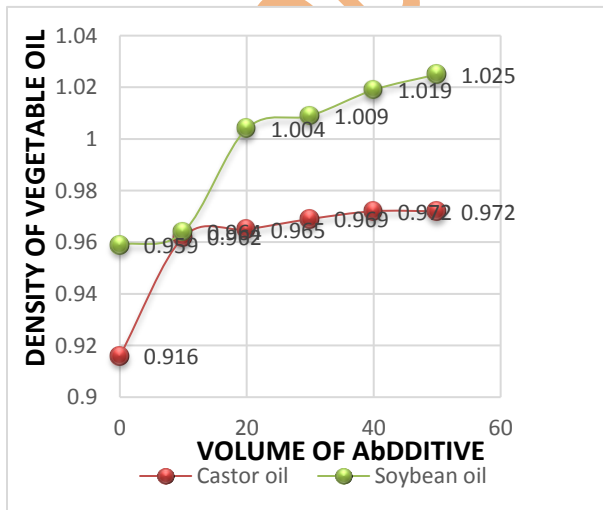


Figure 1: Variation of densities of castor and soybean oil samples with volume of additives

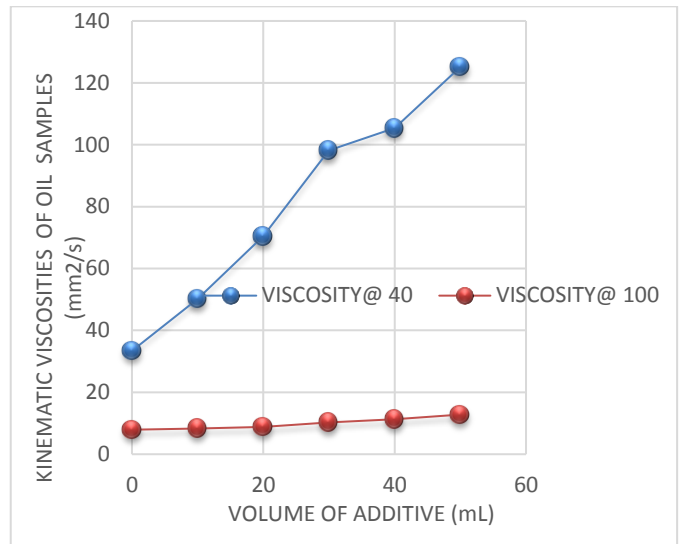


Figure 2: Profile of viscosities of the oil samples with given volumes of additive

Table 5a: Standards for monograde SAE 40, SAE 30 and SAE 50 diesel engine oils

Property	SAE 40	SAE 30	SAE 50
Density at 15°C, g/ml	0.9573	0.9279	0.903
Kinematic Viscosity at 40°C, mm ² /s	154	112.4	273.7
Viscosity at 100°C mm ² /s	14.5	12	19
Flash Point, °C	240	240	240
Pour Point °C	-27	-30	-24

Adopted from [23].

The results in Tables 5a and b compare favourably with the properties of standard monograde lubricants. Comparing the properties in Tables 1–4 with corresponding properties in Tables 5a and 5b for the standard grade oils, results of the soybean and castor oils although a bit higher than those of the standard grade oils, can be used as replacement for petroleum base oil as base stock for lubricant production. Comparing the various densities of both samples, all the soybean samples passed the density test whereas for the castor oil, only samples

11 and 12 passed the test while samples 7, 8, 9 and 10 are higher (i.e. > 0.99 g/ml) than the density standard making the samples too viscous to be used in any engine. For the viscosities of the soybean samples, samples 4 and 5 can be used for systems that do not require too much pressure due to their low viscosities while samples 1, 2 and 3 can be used as proper monograde diesel engine oils based on their viscosities.

Considering the viscosities of the castor oil samples, samples 7, 8, 9 and 10 should not be used as monograde lubricants because of their very high viscosities which are not appropriate for a 4-stroke diesel engine while the castor oil samples 11 and 12 have relatively good viscosities. For flashpoints, the soybean and castor oil samples in Table 4 have relatively higher flashpoints compared to the base oil monograde lubricant (Tables 5a and b) which is very impressive, also the total acid numbers which are higher for the soybean oil samples than for castor oils shows that the additive can help to minimize the amount of acids in a vegetable oil making it useful for lubricant production, since higher volumes of additives corresponds to lower flash points for both oils. The mixture of castor oil and additive required to produce a proper lubricant (i.e. by volume basis) should be restricted to a range of 100 – 90 ml of castor oil to a range of 0 – 10 ml of the additive because of the viscous nature of the castor oil and additive else the mixture becomes too thick and may not pass the standard tests for monograde oils.

Table 5b: Standards for monograde SAE 40, SAE 30 and SAE 50 diesel engine oils

Typical Properties	SAE30	SAE 40	SAE 50
SAE Grade	30	40	50
@40c, cSt (mm ² /s)	90	148	200
@100c,cSt (mm ² /s)	10.5	14.5	18
Viscosity Index	97	97	96
Pour Point °c	-23	-20	-20
Flash Point °c	210	210	213

Adopted from [24].

TABLE 6: SAE J300- AUTOMOTIVE ENGINE OIL CLASSIFICATIONS

SAE viscosity grades	Kinematic viscosity(mm ² /s) at 100 °c, minimum	Kinematic viscosity(mm ² /s) at 100 °C maximum
15W	5.6	---
20W	5.6	---
25W	9.3	---
20	5.6	<9.3
30	9.3	<12.5
40	12.5	<16.3
50	16.3	<21.9
60	21.9	<26.1

Source: [25] <http://www.synlube.com/viscosit.htm>

Table 6 shows the standard maximum and minimum properties of diesel oil SAE J300 at 100 °C. Comparing the viscosities of the samples of the soybean and castor oils to the range of viscosities for the different types of SAE oils in Table 6 to the results in Table 3.4, the soybean oil samples 1-6 can be used as monograde SAE 15W-SAE 40 oils because their kinematic viscosities fall in the range of the kinematic viscosities for the standard oils while the castor oil samples 10 and 11 can be used as monograde SAE 50 and SAE 60 as their kinematic viscosities are higher and are consistent with the viscosities of those of SAE 50 and SAE 60 oils.

Conclusion

Soybean and castor oil samples 11 and 12 can serve as base stock for monograde lubricant. The additive (styrene) improved the properties of the oils. Viscosities of the soybean samples at 100 °C were from 7.92-12.8 mm²/s hence, are suitable for use at winter and summer. Viscosities of samples 11 and 12 range from 19.5-24.4 mm²/s and are suitable for use at summer. Densities of the soybean oil are in the range of 0.916 - 0.972 g/ml while those of samples 7-10 slightly exceeded the specification (0.99 g/ml). Flash points for all samples ranged between 250 – 340 °C making them safer to handle than petroleum base lubricant oils.

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