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Tribological Study of Functional Fluids Based on Castor Oil

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Vegetable oil-based lubricants are environment-friendly options as against conventional lubricants. This paper discusses the synthesis as well as characterisation of esters from ricinoleic acid and sebacic acid whose main source is castor oil. Physicochemical properties, tribological study as well as oxidation study have been carried out for the esters. With the increase in ester chain length, extreme pressure properties, viscosity index and pour point has improved, whereas oxidation stability had a detrimental effect. The coefficient of friction for commercial base stocks was better than any of the studied esters.

Keywords: Biolubricants; Castor oil; wear test; Sebacic acid; Ricinoleic acid

I. INTRODUCTION

Environmentally friendly lubricants are becoming more popular, especially in locations where they may come into contact with water, food, or humans. Environment friendliness of lubricants has no clear definition that has been accepted globally. Local governments or policymakers define them. Biolubricants or environment-friendly lubricants are frequently, but not always, made from vegetable oils. Vegetable oils offer biodegradability and low toxicity. Biolubricants can also be synthetic esters that are partially obtained from natural products. Biolubricants can be manufactured from a wide range of natural sources, including animal fats. Although the market for natural esters is growing, research for the ester base oil, additive, and lubricant industries must continue to develop new as well as enhanced products that will be more widely approved by toxicologists, local governing bodies, and customers (Salimon, Salih & Yousif, 2010; Vidal Abarca Garrido *et. al.,* 2018; OSPAR Commission | Protecting and conserving the North-East Atlantic and its resources, 2021).

Hydrocarbon oils were unable to meet the needs of aviation engine oils and alkyl esters of aliphatic carboxylic acids were found to have favourable characteristics. Because of their strong dipole moments, carboxylic groups reduce the volatility and increase the flash point of lubricating oils, while also improving thermal stability (the bonds of the COO group are thermally more stable than the C–C bond), solvency, lubricity, and biodegradability; however, they harm lubricant hydrolytic stability and the reactivity with metals or alloys that contain copper or lead. Esters of branched primary alcohols with straight dicarboxylic acids and esters of straight primary alcohols with branched dicarboxylic acids have been discovered to be the most suitable lubricant components, as have their mixtures. The alcohols required for the manufacture of dicarboxylic acid ester oils can be synthesised by hydroformylation of olefins with hydrogen and carbon monoxide (Mang, 2007; Kodali, 2003; Kodali, 2002; Solanke & Gaval, 2020).

Castor oil is hydrolysed to produce Ricinoleic Acid (12-hydroxy-9-octadecenoic acid). It's a light-coloured liquid with a high ricinoleic content of around 90% (Mutlu & Meier, 2010). Sebacic acid is a dicarboxylic acid with the structure (HOOC) - $(CH_2)8$ - (HOOC) - $(CH_2)8$ - (HOOC) - $(CH_2)8$ - (HOOC) - (CH_2) (COOH). It's a white flake or powdered crystal in its purest form. Castor oil is a source of sebacic acid (Daulatabad, Desai & Hosamani, 1991; Stein, 1954; Borg, Lê, Lebrun & Pées, 2009; Solanke & Gaval, 2020). Butyl

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ricinoleate, methyl-acetyl ricinoleate, and some other esters of monohydric alcohols are usually made from methyl esters. They are used as plasticisers, in textile lubricating oils, etc. Dibasic esters like the 2-ethylhexyl ester of sebacic acid are very well-known jet engine lubricants (Migdal & Rowland, 2010; Solanke & Gaval, 2022).

Present research work deals with the preparation and characterisation of different esters of ricinoleic acid and sebacic acid with alcohols ranging from C4 to C8. Performance analyses of these esters in terms of tribological as well as physicochemical properties have been discussed in detail.

II. MATERIALS AND METHODS

A. Materials

Sebacic acid and Ricinoleic acid were procured from Ricinash Oil Mills Ltd., Mumbai. n-butanol, n-heptanol, n-octanol, 2-octanol, 2-ethylhexanol, and Sodium carbonate were procured from M/s S.D. Fine Chemical Ltd., Mumbai, India.

Catalyst p-toluene sulfonic acid was procured from M/s S. D. Fine Chemicals Ltd and solvent Toluene was procured from Thomas Baker Ltd.

B. Synthesis of Sebacic acid esters (Dibasic esters) and Ricinoleic acid Esters (Monobasic esters)

Sebacic acid and alcohol were weighed in 1:2 mole ratio in a three-neck flask. 1% by weight of a total reaction mixture of a catalyst was added. 150-200 ml of solvent (Toluene) was added.

Figure 1. Esterification Setup

Table 1. Stoichiometry of reactants for various Sebacic acid esters

Product	Reactants	Mol. Wt.	Moles	Weight	Water Obtained	A.V. of Product (before neutralisation)
Dibutyl sebacate	Sebacic acid	202.24	0.495	110	16.5	0.96
	Butanol	74	0.99	73.26		
Bis-(2-ethylhexyl) sebacate	Sebacic acid	202.24	0.495	110	16.69	1.61
	2-ethyl hexanol	130	0.99	128.7		
Diheptyl sebacate	Sebacic acid	202.24	0.495	110	16.68	1.04
	n-heptanol	115	0.99	113.85		
Dioctyl sebacate	Seabacic acid	202.24	0.495	110	16.33	2.26
	n-octanol	130	0.99	128.7		
Di-2-octyl sebacate	Sebacic acid	202.24	0.495	110	15	5.24
	2- octanol	130	0.99	128.7		

A magnetic needle was kept inside the flask. A temperature controller or a thermometer was inserted through one of the necks. Dean-Stark apparatus was attached over the flask. A reflux condenser is attached on top of that. This whole assembly was kept on a heating mantle-cum-magnetic stirrer for 3-4 hours at a temperature in the range of 125-130 °C. After the completion of the reaction, the product was checked for its acid value (which should be minimum) and a calculated amount of alkali, i.e., Sodium carbonate was added and stirred for some time. Hot water washings were given to this mixture to wash away soaps, if any, that were formed after neutralisation. Toluene was distilled off in the last step and the final product was obtained.

Table 2. Stoichiometry of reactants for various Ricinoleic acid esters

Product	**Reactants**	**Mol. Wt.**	**Moles**	**Weight**	**Water Obtained**	**A.V. of Product (before neutralisation)**
Butyl ricinoleate	Ricinoleic acid	298.48	0.268	80	4.54	0.98
	Butanol	73	0.268	19.56		
2-ethylhexyl ricinolete	Ricinoleic acid	298.48	0.268	80	4.45	1.01
	2-ethyl hexanol	130	0.268	34.84		
Octyl ricinoleate	Ricinoleic acid	298.48	0.268	80	4.41	0.73
	n-octanol	130	0.268	34.84		
2-octyl ricinoleate	Ricinoleic acid	298.48	0.268	80	4.4	0.86
	n-octanol	130	0.268	34.84		

The same procedure was followed as in the case of sebacic acid esters. Just the mole ratio of Ricinoleic acid to alcohol was taken as 1:1.

The experimental setup is shown in Figure 1.

C. Tribological Tests

1. Wear Scar

Wear scar is measured using Four-Ball Wear Test based on ASTM D-4172 standard. This test determines a lubricant's ability to prevent wear on metal rubbing surfaces. In the test lubricant bath three steel balls are placed and held next to one other forming a triangular pattern. Then the fourth ball is placed on the top with load and is rotated with a speed of 1200±60 RPM for one hour and the temperature is kept constant at 75±1 °C. After the test, wear scar diameters are measured on the lower three balls at the point of contact. The average of the three wear scar diameter is reported as result. Wear scar diameter is inversely proportional to wear protection provided by the lubricant.

2. Weld Load

This was determined by ASTM D2596. This test method distinguishes between lubricating greases with low, medium, and high levels of extreme-pressure qualities for specification reasons. The outcomes do not always correspond to the outcomes of service. It should be mentioned that lubricating greases with silicone or halogenated silicone as a fluid component, or a mixture of silicone fluid and petroleum oil, are not suitable for this technique of testing.

3. Coefficient of Friction

It was determined according to the ASTM D1894 method. The test is used to determine the kinetic and static resistance of one surface being dragged across another.

D. Pour Point

When the oil is cold for a long time, it will finally stop flowing out of the test tube when it is flipped upside down. The temperature has an inverse relationship with oil viscosity. The Pour Point is the temperature at which this happens. The experiments are carried out by cooling the oil and seeing what happens at what temperature.

Pour Point testing are lubricant quality checks that are done to evaluate new oils or when a wax problem is detected or suspected in the system.

Pour point detection test for Lubricants comes under ASTM D97**.**

E. Viscosity Index

Viscosity is determined by ASTM D445**.** Viscosity is a significant property of lubricants that is defined as a measurement of resistance to flow. Viscosity is measured in centiStokes (cSt). The viscosity of lubricating oils is usually measured at 40° C and for engine oils, at 100° C. Viscosity is the basis for the classification of lubricants. For example, an ISO VG 32 lubricant has a viscosity of 32 cSt at 40 °C with an allowed variation of about ± 10%. The viscosity of oils is inversely proportional to the temperature.

Increased viscosity is usually caused by lubricant oxidation and deterioration, as well as contamination by higher-grade oil. Contamination, either with gasoline in the case of engine oils or with product in the case of industrial oils, nearly invariably causes viscosity decreases. The viscosity index is a computed value that represents the rate at which the viscosity of a lubricant changes as it is heated. The lesser the change, the higher the Viscosity Index number. Viscosity Index is calculated using an API formula which requires viscosity of lubricant at temperatures 40 °C and 100 °C as input.

F. Flash Point

Flash point is determined by ASTM D92-05a. Under controlled laboratory circumstances, the specimen's potential to generate a combustible combination with air is measured. It is taken into account when determining a material's overall flammability risk. The term "flash point" is used to characterise flammable and combustible products in transportation and safety laws. The presence of highly volatile and flammable elements in a comparatively non-volatile or non-flammable material can be indicated by flash point. A manual Cleveland open cup apparatus or an automated Cleveland open cup apparatus can be used to measure the flash point. The flash point range for using the test method should be between 79°C (175°F) and 400°C (752°F) for all petroleum products except fuel oils.

G. Oxidation Stability

ASTM D943 is followed to determine the oxidation stability of the lubricant.

III. RESULTS AND DISCUSSION

Table 1 and 2 shows various ricinoleate and sebacate ester products obtained by reacting ricinoleic acid and sebacic acid with different alcohols. For the reaction of ricinoleate and sebacate ester products, different molar ratios of alcohol were taken because ricinoleic acid is a monobasic acid and sebacic acid is a dibasic acid. Also, different alcohols were taken for the reaction with ricinoleic acid and sebacic acid in order to find out the effect of alcohol types used on the end products performance in terms of physicochemical properties, tribological performances, and oxidation stability. Table 3 shows the performance evaluation of both ricinoleate and sebacate esters as lubricant base stock. Various tribological properties of the products as well as commercial mineral oil base stocks, i.e., 150N and 500N are determined and they are compared. Table 4 contains the data on the oxidation stability of all the esters. The acid value and viscosity values are determined before and after the oxidation stability test. It is observed that acid values have drastically changed in the cases of Butyl Ricinoleate, Diheptyl Sebacate, and Bis-(2EH)-sebacate. Viscosity values also got increased after the oxidation stability test.

Table 3 gives an idea about the rest of the tribological properties of the same esters. Weld load values are comparatively good in the case of ricinoleate esters than that in sebacate esters. Wear scar values are less in the cases of Octyl Ricinoleate, Bis-(2EH)-sebacate, and 2-EH-ricinoleate. The lowest Pour point values are shown by 2-ethylhexyl esters. These values are better than commercial mineral oil base stock pour point values. The coefficient of friction is lower in the case of mineral oil base stock. Flash point values are higher in the case of sebacate esters. The viscosity index is higher for all the esters specially 2-ethylhexyl esters.

Table 3. Performance Evaluation of Esters

Name of Ester	**Fourball Tester**		**Pour Pt.**	**Coefficient of friction**	**Flash point**	**Viscosity**		**V.I.**
	Weld Load (kg)	**Wear Scar (mm)**	**(°C)**		**(°C)**	**40 °C**	**100 °C**	
Dibutyl sebacate	165	0.988	-20	0.268	167	17.692	3.986	123.86
Butyl ricinoleate	210	0.745	-22	0.214	162	20.178	4.6462	154.56
Diheptyl sebacate	210	1.074	-9	0.28	183	6.587	2.1036	122.49
Dioctyl sebacate	180	0.859	-10	0.23	210	5.8801	2.0027	146
Octyl ricinoleate	195	0.78	-18	0.189	194	9.7614	2.9025	160.11
2-octyl ricinoleate	225	0.927	-28	0.187	202	14.87	3.878	164.45
Bis-(2-EH)-sebacate	165	0.762	-31	0.21	215	7.2014	2.5196	189.21
2-EH- ricinoleate	225	0.745	-32	0.19	210	10.06	3.1396	197.77
150N	165	0.68	-26	0.13	320	17.992	4.325	155.71
500N	195	0.62	-22	0.11	356	69.677	9.84	122.8

Note: - Di-2-octyl sebacate formed is in solid form.

Table 4. Oxidation stability study

Name of Sample	**Oxidation Stability**					
	Before			**After**		
	A.V.	**Viscosity (CSt)**		**A.V.**	**Viscosity (CSt)**	
		40 °C	**100 °C**		**40 °C**	**100 °C**
Dibutyl sebacate	1.085	17.692	3.986	9.627	20.127	5.231
Butyl ricinoleate	3.759	20.178	4.6462	53.18	22.303	4.9993
Diheptyl sebacate	3.67	6.587	2.1036	20.35	10.256	2.50132
Dioctyl sebacate	4.085	5.8801	2.0027	12.93	6.5966	2.2568
Octyl ricinoleate	3.843	9.7614	2.9025	6.299	11.5298	3.2844
2-octyl ricinoleate	3.341	14.87	3.878	5.8407	23.03	5.4731
Bis-(2-EH)-sebacate	3.85	7.2014	2.5196	9.53	7.1438	3.1567
2-EH- ricinoleate	3.821	10.06	3.1396	12.012	11.818	5.23

IV. CONCLUSION

From the experimental results it can be concluded that as the chain length of alcohols, as well as fatty acids, has increased, their ability to withstand load under certain pressure and temperature is also seen to be increased. 2-ethyl hexyl ester of ricinoleic acid shows the highest values of weld load.

Also, an increase in ester chain length has resulted in improved low-temperature properties of the synthesised esters as they form a steric barrier surrounding the molecules, inhibiting crystallisation, thus lowering the pour point. The reverse is the case for oxidation stability, as chain length increases, oxidation stability goes on reducing. The coefficient of friction is less in the case of all the esters as compared to the commercial base stock. Higher molar weight and modified molecular structure have resulted in improved VI of esters.

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