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Environmentally Friendly Lubricating Oil Candidate

Aykut Özgülsün and Filiz Karaosmanoğlu*

Istanbul Technical University, Department of Chemical Engineering, 80626 Maslak, Istanbul-Turkey, E-mail: filiz@itu.edu.tr

Abstract

Synthetic lubricating oils based on renewable sources, excluding petroleum, have a great importance among all of the lubricating oil alternatives that are included in the research field about clean and environmentally friendly lubricating oil technologies. One of the environmentally friendly lubricating oils is a vegetable oil-based product. In this study, the esterification product of oleic acid with a fraction of molasses fusel oil as a lubricating oil candidate was determined according to the American Society for Testing and Materials (ASTM) standard tests. The results indicate that the ester product can be used as an environmental friendly lubricating oil or lubricating oil additive.

Index Entries: Oleic acid; fusel oil; transesterification; lubricating oil; vegetable oil-based lubricating oil; environmental friendly lubricating oil; lubricating oil properties.

Introduction

Prior to the early 19th century, the main lubricants were natural esters contained in animal fats such as sperm oil and lard oil, or in vegetable oils such as rapeseed and castor oil. During World War II, a range of synthetic oils was developed. Among these, esters of long-chain alcohols and acids proved to be excellent for low-temperature lubricants. Following World War II, the further development of esters was closely linked to that of the aviation gas turbine. In the early 1960s, neopolyol esters were used in this application because of their low volatility, high flash points and good thermal stabilities. Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils, and grease formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance. The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and

*Author to whom all correspondence and reprint requests should be addressed.

raise the flash point. This is owing to strong dipole moment, called the London forces, binding the lubricant together. The presence of the ester group also affects other properties such as:

1. Thermal stability;
2. Hydrolytic stability;
3. Solvency;
4. Lubricity; and
5. Biodegradability.

A wide variety of raw materials can be used for the preparation of ester type based fluids and this can affect a number of lubricant properties including:

1. Viscosity;
2. Flow properties;
3. Lubricity;
4. Thermal stability;
5. Hydrolytic stability;
6. Solvency; and
7. Biodegradability *(1)*.

The ester types used as lubricating oil are diesters, phtlates, trimellitates, C_{36} dimer esters, polyols, polyoleates, and fatty-acid esters. Fatty-acid esters have importance in the environmentally friendly lubricating oil alternatives.

An environmentally acceptable lubricating product could be defined as a material that when used would maximize protection or minimize pollution of air, water, soil, and sediment. At the same time, it should minimize health and safety hazards to humans, animals, and plants during the process of production, use or accidental misuse, and disposal or recycling. There are three categories for environmentally acceptable lubricating products: primary, secondary, and tertiary. Tertiary products are produced from recycled components. Examples are rerefined motor oils, recycled paper, and recycled aluminum cans. Secondary products are those that help minimize the pollution generated by machinery and vehicles; they are really variations of conventional products. Examples of secondary products are energy-conserving motor oils, fill for life lubricants, fuel-economy lubricants, and emissions friendly diesel fuel formulations. The last category of environmentally acceptable products is primary products; which offers the greatest challenge technically. These nontoxic and biodegradable products should cause little if any harm when released into the environment. Environmentally acceptable lubricants fit into this category, with examples being vegetable oil-based lubricants and water-based, metalworking fluids.

There is an interest in environmentally acceptable lubricants because of the amount of lubricant that currently is dumped into the environment. Of the 1305 million gallons of lubricant used in the European Community in 1990, 174 million gallons, or 13%, disappeared into the environment. Approximately 32% of the 1351 million gallons of lubricating oil that is generated in the United States is either put in landfills or dumped.

Using vegetable oil-based fluids (natural oleochemicals) for environmentally acceptable lubricants has many advantages. It is nontoxic, it is biodegradable, it is a renewable resource, and, as was shown, it has a reasonable cost when compared to synthetic fluids *(2)*.

Fatty-acid esters are a natural oleochemicals and can be used many industrial purposes. Oleic acid (cis-9-octadecenoic acid) is one of the most important fatty acid. Oleic acid generally considered to be the predominant fatty acid in nature. It comprises 50% or more of the total acids of many fats; few fats are known to contains less than 10% of this acid *(3)*. Esters are one of the most important derivatives of oleic acid. Oleic acid, esters of oleic acid and various derivatives of oleic acid can be used as a lubricating oil. There are lots of patents about this subject *(4–8)*.

In this study, the esterification product of oleic acid with a fraction of molasses fusel oil as a lubricating oil candidate is investigated and this product is presented to the literature for the first time. There is no article or data about using the ester of fusel oil as a lubricating oil in the literature, and only one patent where in fusel oil was investigated as a lubricating oil. In this Japanese patent, fusel oil has been used as a lubricant for low-temperature press molding of aluminium alloys *(9)*.

Materials and Methods

The oleic acid was obtained from MERT Chemicals Co. (Istanbul-Turkey). Molasses fusel oil was obtained Turkish Sugar Factories Inc. The fraction of molasses fusel oil has been prepared under the conditions that Karaosmanoğlu et al. have suggested *(10)*. Fusel oil was distilled in a Normschliff Gerätebau fractional distillation unit, and the higher boiling fraction (above 120°C and 75% v/v of fusel oil) of fusel oil containing 0.1% (v/v) water was used as the reactant in the esterification reaction. Other reagents were analytical grade from Carlo-Erba products. The esterification reaction of oleic acid-fraction of molasses fusel oil and refinement of the ester product were performed according to the results of MSc thesis of A. Özgülsün *(11)*. The lubricating properties of the ester product were determined according to the ASTM (American Society for Testing and Materials) test methods (*see* Table 1). The ASTM tests were performed in MOBIL-Turkey Laboratory. Composition of the ester product was investigated by thin-layer chromatography/flame ionization detector (TLC/FID) latroscan TH-10 MK IV analyser *(12)*.

Preparation of the Esterification Product of the Oleic Acid With Fraction of the Molasses Fusel Oil

The esterification reaction conditions were chosen as follows: Duration, 1 h; temperature, 90 ± 1°C; acid/alcohol molar ratio, 1/2; catalyst, H_2SO_4; and amount of catalyst, 1.25% by the weight of the acid *(11)*.

Table 1
The Lubricating Properties of the Ester Product

Properties	ASTM method no.	Ester product
Appearance	—	Bright, clear, and yellow
Color	D1500	2.5
Density, 15°C, kg/m^3	D1298	870.9
Flash point, °C	D92	190.0
Pour point, °C	D97	–21.0
Viscosity index	D2270	204.9
Carbon residue, w/w %	D189	0.06
Copper corrosion, 50°C, 3 h	D130	No. 1a
Total acid number	D664	7.38
Composition, w/w %		
Oleat esters of fraction of molasses fusel oil	TLC/FID combine method	97.3
Oleic acid	TLC/FID combine method	2.7

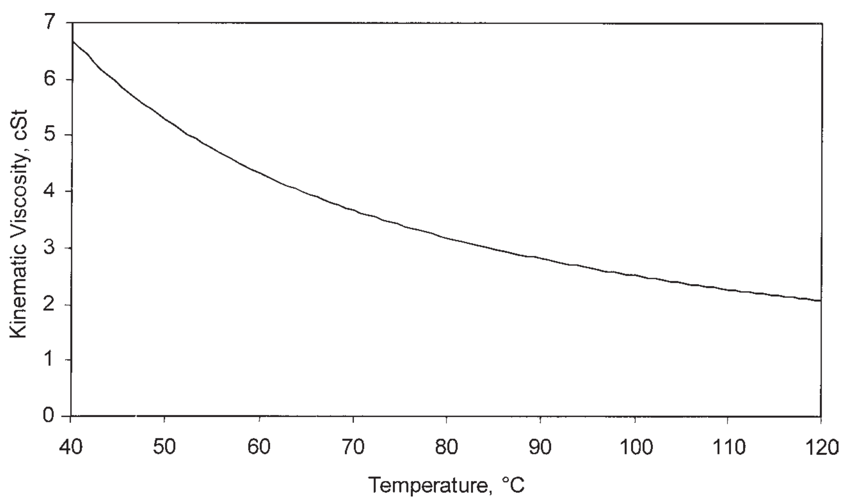

Fig. 1. The variation of ester product viscosity at different temperatures.

Esterification reaction were performed in a 3-necked flask equipped with a reflux condenser. Refinement of the ester product was done by washing with distilled water and drying over sodium sulfate *(11)*.

Results and Discussion

The lubricating properties of the ester product are given in Table 1. The variation of ester product viscosity at different temperatures is shown in Fig. 1. The high flash point (above 120°C) is an advantage that ensures security during storage, transportation, and usage. The very low pour point of ester product is an advantage for use in cold climates and in cold processes. The viscosity index of ester product is also very high. It means that viscosity of ester product does not change too much with temperature; a property that is one of the most important that lubricating oils should have. The ester product contains very low carbon residue. The low carbon residue value indicates that ester product will show very limited coking in thermal effects.

The total acid number of ester product is 7.38. The product contains fusel oil fraction of 97.3% and oleic acid of 2.7%. Oleic acid provides positive properties. It can reduce the wear rate, and can be used in cold conditions and in vapor phase lubrication. Therefore, it has not been necessary to separate oleic acid from ester product with an additional refinement process.

The comparison of the properties of ester type synthetic lubricating oils and the properties of ester product are shown in Table 2. The viscosity of ester product is very close to the viscosity of diesters and polyols. The other properties of ester product show harmony with the properties of ester type lubricating oils. The ester product can be used as: synthetic lubricating oil, mixed with mineral oil or synthetic lubricating oil, improved as properties with present or new additives, or used as lubricating oil additive.

Conclusion

Nowadays, ester-based lubricants have importance in synthetic lubricating oil technology. In this study, the esterification product of oleic acid with a fraction of molasses fusel oil has been investigated lubricating oil candidate. The results of this study are summarized:

1. The lubricating oil properties of the ester product were determined with the help of the standard tests and no negative properties were found. The positive lubricating properties of the ester product are listed below:
   a. The ester product is bright, clear, and yellow.
   b. The flash point of the ester product is high energy to ensure stability during storage, transportation, and usage.
   c. The very low pour-point of ester product shows an advantage if it is used in cold climates or in low-temperature processes.
   d. The viscosity of the ester product is very close to the viscosity of diester or polyol-based synthetic lubricating oils.
   e. The viscosity index of ester product is very high; the viscosity of ester product changes only slightly with temperature.
   f. The low carbon residue value of ester product shows that the ester product tends to coke in a very limited way.
   g. The ester product shows a positive result in the copper strip tarnish test.
2. Two renewable resources were used as raw materials in esterification reaction. Oleic acid esterified with the fraction of fusel oil and

Table 2
Comparison of the Properties of Other Ester Type Synthetic Lubricating Oils With the Properties of the Ester Product[a]

Properties	Diesters	Phthalates	Trimellitates	C_{36} Dimer esters	Polyols	Polyoleates	Ester product
Flash point, °C	200–260	200–270	270–300	240–310	250–310	220–280	190
Pour point, °C	−70–−40	−50–−30	−55–−25	−50–−15	−60–−9	−40–−5	−21
Kinematic viscosity, 100°C, cSt	2–8	4–9	7–22	90–185	3–6	10–15	2.4
Viscosity index	90–170	40–90	60–120	120–150	120–130	130–180	204.9
Conradson carbon residue, w/w %	0.01–0.06	0.01–0.03	0.01–0.40	0.20–0.70	0.01–0.10	–	0.06

[a]Adapted from ref. *1*.

the ester of fusel oil fraction was for the first time presented as a lubricating oil candidate. In this reaction, i-amyl alcohols can be used instead of fusel oil fraction.

3. In this study, the biodegradability of ester product was not tested. However, it is known that fatty-acid esters and vegetable oils are the most biodegradable oils. It is therefore believed that this ester product is an environmentally friendly product.
4. The ester product can be used as a synthetic lubricating oil, and can be blended with present mineral oils or synthetic lubricating oils. Its properties can be improved with present or new additives, and can also be evaluated as lubricating oil additive.

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