

SYNTHESIS OF BIODEGRADABLE LUBRICANT FROM JATROPHA OIL WITH HIGH CONTENT OF FREE FATTY ACIDS

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ABSTRACT

Plant oil extracted from a non edible plant has the potential application as biodegradable lubricant. Such plant as toxic contained *Jatropha curcas* inhibits human consumption and thus making it suitable for such application since it does not compete with the food production. However, high content of free fatty acids (FFA) in the jatropha oil (triglycerides) is found to have significant effect in the production of bio-lubricant. The formation of fatty acids occurs when the triglycerides are hydrolysed with moisture due to poor storage and handling. This paper discusses the techniques performed to produce high yield of bio-lubricant from jatropha oil containing high content of FFA up to 30%. It is reported that more than 80% yield of jatropha bio-lubricant was successfully achieved. Lubricity characteristics such as the pour point, viscosity and thermal oxidative stability for the produced jatropha bio-lubricant are found to be comparable with the other vegetable oil based lubricants.

Keywords: jatropha curcas, free fatty acids, trimethylolpropane, biodegradable lubricant.

Introduction

In recent years, increasing attention has again been paid to natural triglycerides, fatty acids derived from them, and their potential applications (Vizintin et al., 2000; Arnsek and Vizintin, 2000). This raw material is cheap and renewable. Moreover, natural fats and products derived from them are generally environmentally friendly. They have the attractions of being natural, renewable, non-toxic, non polluting and cheaper than synthetics. In general, synthetic lubricants cost four to eight times higher than the mineral oil-based lubricants

(Bartz 1993). Vegetable oil-based lubricants are 50% cheaper than synthetic oils but are easily degradable and have poor lubricity. Nevertheless, they are plentiful in supply and can be used as biodegradable lubricant base stock. Lubricants based on vegetable oils still comprise a narrow segment; however, they are finding their way into such applications as chainsaw bar lubricants, drilling muds and oils, straight metalworking fluids, food industry lubricants, open gear oils, biodegradable grease, hydraulic fluids, marine oils and outboard engine lubricants, oils for water and underground pumps, rail flange lubricants, shock absorber lubricants, tractor oils, agricultural equipment lubricants, elevator oils, mould release oils, two stroke engine lubricants and other. Hydraulic fluids, which are consumed at 5 million metric tons per year rate in the US (Padavich and Honary, 1995), have the highest need for biodegradable lubricants. Although vegetable oils have reputation of a low-cost candidate for the biodegradable replacement of mineral oils due to their high inherent biodegradability (Battersby et al., 1992; Randles and Wright, 1992), unsatisfactory performance curbs their more widespread utilization as lubricants.

However, glycerol, a component of the triglyceride molecule is readily destructible at high temperatures. This disadvantageous property stems from the presence of hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule. This structural feature is conducive to the partial defragmentation of the molecule and the formation of unsaturated compounds (Bueunemann et al., 2000). The compounds formed undergo polymerisation, increasing the liquids viscosity and resulting in the formation of precipitate particles. The problem can be solved by replacing glycerol with another polyhydric alcohol which does not contain β -hydrogen atoms, i.e., neopentyl glycol (NPG), trimethylol propane (TMP) or pentaerythritol. Although such alcohols also decompose at high temperatures, their thermal decomposition has a radical character and proceeds slowly. Synthetic esters produced from natural acids cannot be used at extremely high temperatures, but they are very suitable in less extreme applications such as two-stroke engine oils, chain bar oils, cutting oils, concrete mould release agents and cosmetics ingredients.

The properties of esters also depend on the structure of the constituent fatty acids and alcohols, i.e., on the length of their aliphatic chain and the number and relative position of unsaturated bonds. Saturated acids are highly resistant to oxidation and high temperature, but their esters pour point is high due to the linear structure of the acids. The high pour point of saturated fatty acids makes it possible to separate the latter from unsaturated acids by

physical methods, e.g., through freezing out. Polyunsaturated fatty acids, especially those which contain conjugated bonds, are the most susceptible to oxidation and thermal degradation. As a rule, these acids, particularly their cis-isomers, are characterized by very low pour points down to -30°C .

The objective of this research was to explore the possibilities of producing esters of TMP. *Jatropha curcas* were used as the sources of fatty acids. The esters evaluated in this study were synthesized through transesterification.

JME preparation

Four hundred and fifty grams (450g) of the *Jatropha* triglyceride and 0.5 g of NaOH dissolved in 35 g of methanol were placed in a 1000 ml glass bath reactor equipment with a magnetic stirrer and capped with a reflux condenser. The reactor temperature was maintained between 65 and 70 C, slightly below the boiling point of methanol. The reaction was carried out for 60 minute. The reaction mixture was cooled down to ambient temperature and the resulting two layers were separated. The upper layer contained a solution of methyl esters.

Chromatographic analysis

Analysis of JME was performed on a HP 5890II gas chromatograph fitted with a capillary inlet system and flame ionization detector. The capillary column, HP INNOWAX, was 30 m long, with 0.32 mm i.d. and 0.25 μm film thickness. A split injection system 10:1 was used with nitrogen carrier gas. The column temperature was held at 80 C throughout the entire 6 min run. Temperature programming was initiated at 80 C at the rate of 10 C min^{-1} to reach a temperature of 250 C. The inlet temperature was 250 C and the detector temperature was 280 C. The oil reference standard, AOCS for Low Erucic Rapeseed Oil from Sigma—Aldrich, Steinheim, Germany was used as an external standard for quantitative analysis. For one sample, the GC analysis was performed in duplicate. Relative standard deviations of duplicate measurements of fatty acids composition was below 5%.

Physicochemical properties determination

The physical properties of the prepared esters were determined according to the following standard test methods, i.e., acid number to ASTM D 974, viscosity to ASTM D 445, viscosity index to ASTM D 2270 and pour point to ASTM D 97.

Kinematic viscosities of the fluids were measured according D 445 (ASTM, 1991b). Cannon-Fenske capillary viscometers and the constant temperature bath were from Cannon Instruments, State College, PA. Temperature of 40±0.2°C was maintained throughout the experiments. The viscometers were calibrated for 10–50 cSt viscosity range using calibration fluids provided by the manufacturer.

Pour points were measured strictly according D 97 (ASTM, 1991a), which determines pour points by placing a test jar containing 50 ml of the sample into a metal cylinder submerged into cooling media. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring, whereas the temperature of cooling media was kept constant below the sample temperature. When the sample temperature reached the specified range (e.g. three of the ranges are +9 to –6, –6 to –24 and –24 to –42°C), the temperature of cooling media was also reduced to the specified value (–18, –33 and –51°C, respectively). The pour point is defined as temperature where sample still pours. Statistically, the test has shown satisfactory accuracy; as described in a precision statement (ASTM, 1991a,b), the difference between two test results from independent laboratories exceeding 6°C in only one case of 20 with repeatability of 2.87°C at 95% confidence.

Results and discussion

TMP is a well-known neopentylpolyol-like compound used in lubrication fields [10]. The transesterification with TMP took place in accordance with the following reaction (Fig. 1). Sodium Methoxide at a concentration of 1.0%(wt) was used as catalyst in the reaction mixture. The conditions of the reaction are the following:

- branched methyl esters/TMP ratio: 3.9:1
- temperature: 110–120 °C
- reaction time: 3 h.

The reaction was performed under vacuum (10 mbar) up to 120 °C. The methanol was continuously recovered in a condenser. The catalysts were removed by filtration treatment. Conversion yields in triesters of TMP is higher than 80%(wt) and the remaining branched methyl esters are less than 15%. This new product was compared with some other TMP esters (Table 1). This lubricant base coming from TMP has very interesting physical and characteristics with a Viscosity Index higher than 180, and noteworthy properties of thermal stability and cold behaviours often better than the commercial products.

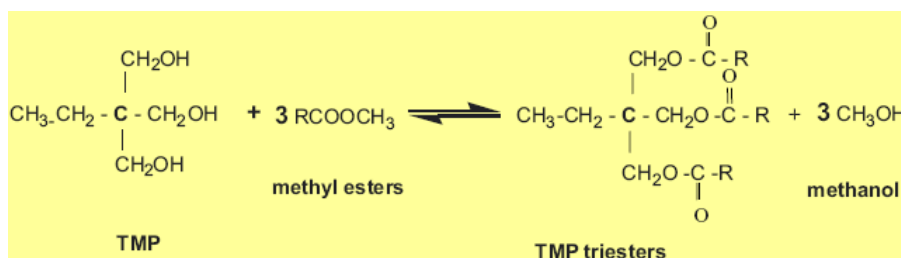


Fig. 1: Reaction of transesterification of TMP with methyl esters.

Table 1: Physical characteristics of the different lubricant bases

Fluid		Standard Requirement by ISO VG46	Mineral Oil	Synthetic*		Bio-based Synthetic	
				Olefin Oligomers	Propane Alkylated Aromatics	Oil Palm	Jatropha
Kinematic Viscosity (cSt)	40°C	>41.4	568	399	109	52.4	43.9
	100°C	>4.1	27.8	40	12.4	10.2	8.71
Viscosity Index (VI)		>90	62	147	105	186	180
Pour point (°C)		-10	-4	-36	-36	-5	-6

The GC analysis of the JME is given in Table 2. Jatropha oil, whose major constituent is oleic acid, contains a relatively small amount of linoleic acid (7.2%), and about 14% saturated fatty acids. In comparison to Jatropha oil, rapeseed oil has a lower saturated acid content (8.3%), which is advantageous, and a higher polyunsaturated fatty acids content (28%). The presence of large amounts of polyunsaturated acids results in lowering the resistance to oxidative-thermal treatment. Lard-based FAMES have the lowest polyunsaturated acids content, but the saturate content is as high as 50%. The transesterification of JME with TMP, being actually an opposite reaction, proceeds at a much lower rate. Sodium methoxide, which is sparingly soluble and can be easily separated from

the reaction products by filtration, was used as the catalyst. Generally, TMP esters of fatty acids have higher viscosity probably due to the fact that there are three acid groups in the structure of TMP esters and only two such groups in the molecules of NPG esters. Both the synthesized esters and native triglycerides studied have a high viscosity index, around 150 and higher. Moreover, the viscosity index is slightly higher for the synthesized esters than that of native triglycerides. This is a highly desirable property in view of their use as lubricants. The viscosity of liquid with high viscosity indices changes very little with temperature. High viscosity index is characteristic of compounds which have long, unbranched hydrocarbon chains, e.g. fatty acids of most natural triglycerides.

Generally, the synthesized esters show moderate thermal-oxidative stability. This is a characteristic feature of most synthetic oils produced from natural triglycerides. In similar thermal-oxidative conditions, the viscosity and acid number of hydrocarbon oils increased only slightly. However, in many technological applications high stability is not required. Oils synthesized from natural products are generally approved of as environmentally friendly functional fluids and therefore they can be used widely.

Initially, kinematic viscosities at 40°C and pour points of the fluids were determined, results shown in Table 1. It appears that low temperature properties of vegetable oils are much more inferior to those of synthetic basestocks or even mineral oil.

Chemical modification is necessary to improve these performance limitations with the focus on optimal extent of structural alteration for improved low temperature performance. Sufficient experimental evidence is not yet available, however, it can be suggested that such modification pathways as alkylation, alkoxylation, interesterification and oligomerization might appreciably improve overall lubricant properties of vegetable oils.

Conclusion

This new synthesis of branched fatty acids methyl esters from *Jatropha* oils has been largely optimised and good conversion yields have been achieved. After transesterification with TMP this product behaves as an excellent lubricant. This could be a new way of development of *Jatropha* oil, which are renewable feedstock. Other fields of applications than lubrication can

be considered, in particular detergency where the soaps of branched fatty acids have noteworthy foaming, antistatic and emulsifying properties. The cosmetic industry can be also considered. The oxidative stability and low temperature performance of raw *Jatropha* oils is poor. Thus,

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