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Chemical Modification of Palm Oil for Low Temperature Applications and its Study on Tribological Properties

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ABSTRACT

Despite having a better performance, mineral oil based lubricants causes serious issues on environment and tamper the harmony of our ecosystem. Moving in a path that can add more to life than burning harmful oils brought the finest environmentalists and tribologists to go in search of promising alternative oils. Vegetable oils are found to be biodegradable and possess good tribological properties but have low thermal-oxidative stability and very poor low temperature fluidity. Therefore selection of vegetable oil as base oil for lubricant is crucial. This paper focus on the tribological study of palm oil methyl ester (POME) extracted from palm oil by the process of alkali esterification. By optimizing the percentage of catalyst (1% KOH) and alcohol (25% methanol), maximum yield of methyl ester was achieved during esterification process. The friction and wear test conducted over crude palm oil and POME shows the domination of crude oil by 52.3% and 12.3% respectively. Removal of glycerol molecules have resulted in drastic fall in viscosity but have improved the flow properties from 23.6ºC to 9ºC thereby extending its application to lower temperatures.

Keywords – Palm oil, POME, Pour point, Transesterification, Friction-wear

1. INTRODUCTION

Vegetable oils and animal fat used to be the primary source for lubrication until mineral oil based lubricants came into existence [1, 2]. Petroleum based lubricants are non-degradable and cause soil-water-air pollution. The toxicity of the commercial lubricant increases drastically after its service life, becoming highly hazarded when exposed to the environment [1]. Vegetable oils are biodegradable and non-toxic in nature. They have better lubricity, higher viscosity index and higher flash point. However, the major problems in commercializing vegetable oils as lubricants are their low oxidative stability and poor low temperature fluidity.

Over recent years, researchers have proposed several methods to transform vegetable oils into a good lubricant for commercial applications. The commonly used methods are chemical modification, genetic modification and use of additives like anti-wear additives, depressant and viscosity modifiers. Chemical modification is one of the most promising methods which is basically the modification of the acyl (C=O) and the alkoxy (O-R) functional groups [1].

Palm oil is vegetable oil having equal amount of saturated and mono-unsaturated fatty acids as shown in Table 1. Crude Palm oil is orange in color and semisolid at room temperature. Palm oil is more stable when compared to other vegetable oils due to the high percentage of saturated palmitic acid (42.6%) and mono-unsaturated oleic acid (41.9%) [3]. Flash point of the oil is close to 252ºC and has a density of 919 kg/m^3. The acid value of the oil is 1.4 due to 0.7 percentage of free fatty acid. Palm oil has the highest yield in terms of oil production per hectare of plantation when compared to other vegetable oils [4].

The major drawback of palm oil is its low temperature fluidity. The poor pour point property of palm oil (23.6ºC) restricts its applications at lower temperatures. The pour point of palm oil can be improved through transesterification process. The triglyceride molecules are broken down into free fatty esters resulting in free movement of fatty acids thereby improving its flow properties.

Transesterification is a very popular process of producing biodiesel where vegetable oils (triglycerides) are reacted with alcohol in presence of a catalyst as shown in Fig. 1. The catalyst can be an acid like H_2SO_4

[6] or an alkali such as NaOH or KOH [7-9] based on the free fatty acid content (FFA) of the oil.

Table 1 Palm oil properties and fatty acid composition [3, 5]

Fatty acid	% Composition
Lauric acid	0.64
Myristic acid	1.02
Palmitic acid	40.2
Stearic acid	4.6
Arachidic acid	0.08
Palmitoleic acid	0.36
Oleic acid	42.4
Linoleic acid	9.9
Linolenic acid	0.47
Gadolic acid	0.33
Physical Properties	
Flash point (°C)	252
Density (kg/m^3) at 40 °C	919
Pour Point (°C)	23.6
% FFA	0.7
Acid value	1.4

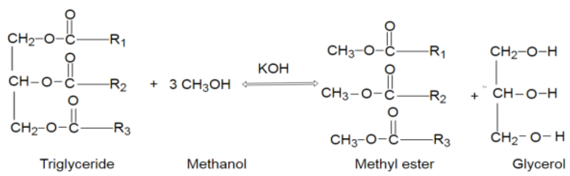

Fig. 1 Transesterification reaction of vegetable oil and Methanol with KOH. R_1, R_2 and R_3 are different hydrocarbon chains

In the present study, methanol (alcohol) and KOH (catalyst) was used in transesterification process for the production of the palm oil methyl ester (POME). The consumption of methanol and KOH was optimized for maximum yield in the production of POME. The tribological properties of the newly developed POME was analysed and compared to the crude palm oil. The pour point of POME had improved by 61% but has inverse effect on friction wear and viscosity when compared to crude palm oil.

2. MATERIALS AND METHODS

2.1. Materials

Crude palm oil was obtained from Parisons food private limited, Calicut, India. Methanol and potassium hydroxide used from the reaction was procured from Chemind Pvt. Ltd., Calicut, India.

2.2. Alkali esterification

Initially, required amount of palm oil was heated up to 110ºC to remove the moisture content from the oil. The pre-mixed solution of KOH (catalyst) and methanol (alcohol) was added to palm oil under constant temperature (60ºC) and stirring action using a hot plate magnetic stirrer.

The reaction temperature was taken as 58 - 61ºC and reaction time was taken as 1 hour. The stirring speed was kept constant at 500 rpm. As the reaction continues, the mixture becomes darker in nature that signifies the formation of glycerol [10].

After completion of reaction, mixture was poured into a separating funnel for the glycerol separation. After 8 hours, two separate products were clearly visible in the separation flask due to the fact that the low density POME moves to the top and denser glycerol moves to the bottom of the separating funnel. Glycerol was carefully removed from the separating flask and was measured. The remaining product, POME, is washed five times with warm water to remove the catalyst. POME is then heated again up to 105ºC to remove the moisture. It is later cooled and preserved for further use.

2.3. Testing Methods

Friction and wear test was conducted on four ball test as per ASTM D5183 and ASTM D4172 standard respectively. Low temperature flow properties of the oil was found using ASTM D97 standard. The viscosity of the oil was measured using a rheometer.

3. RESULTS AND DISCUSSIONS

Catalyst and alcohol concentration were optimized to maximize the yield for production of palm oil methyl ester. The variation in tribological properties due to the chemical modification of palm oil was studied using four ball tester, rheometer and pour point apparatus.

3.1 Catalyst concentration

The potassium hydroxide concentration (w/w % of oil) was varied from 0.5 to 1.5 by keeping concentration of methanol as constant (35% v/v) as shown in figure 2. Higher percentage of methanol was initially selected to ensure the availability of alcohol for the reaction.

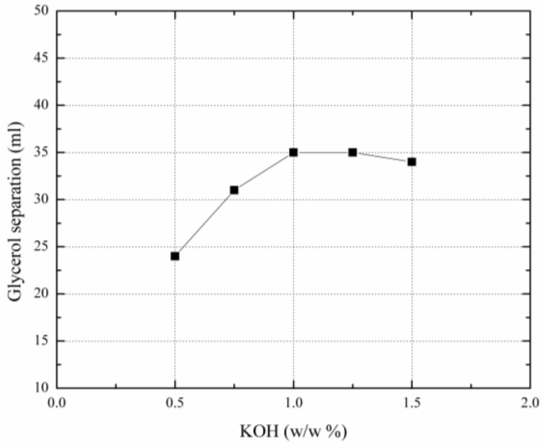

Fig. 2 Influence of catalyst concentration in the production of POME.

A proportional increase in the formation of glycerol molecules was observed up to the addition of 1% of KOH and was found to be reducing on further increase in concentration. The reduction in glycerol formation above 1.25 % can be attributed to the formation of soap molecules in the sample.

3.2. Alcohol concentration

The optimum methanol consumption was found by varying methanol concentration from 15 % to 35% (v/v) by keeping the optimum catalyst concentration (1%) as constant as shown in figure 3.

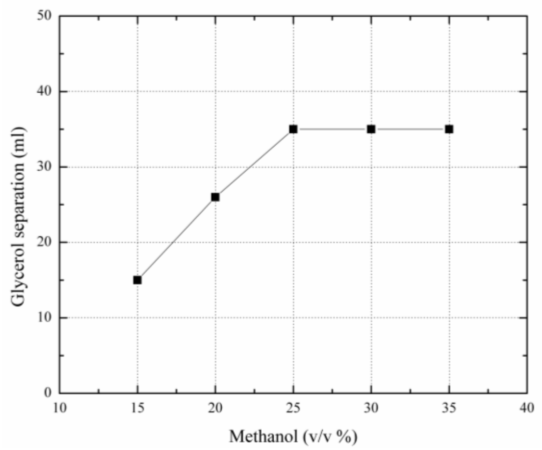

Fig. 3 Influence of alcohol concentration in the production of POME.

The increase in methanol concentration up to 25% has resulted in maximum production of glycerol molecules. Glycerol separation remained constant on further increase in alcohol concentration. Hence 25 % (v/v) was selected as the optimum alcohol concentration for the production of methyl ester.

3.3. Pour point test

The flow property of a lubricant at low temperature is studied using pour point apparatus. The phase transition temperature of liquid lubricant to solid when exposed to low temperature is identified as the pour point of the sample. By the process of alkali esterification, the free movement of fatty acid esters is enabled, resulting in the improvement of pour point by 61% (23.6ºC to 9ºC).

3.4. Frictional test

Coefficient of friction of crude palm oil (CPO) and palm oil methyl ester (POME) was studied using a four ball tester as shown in figure 4. SAE 52100 steel balls of 12.7 mm diameter were used for the test. The test was conducted at 600 rpm under constant temperature (75ºC) and 40 kg load for a duration of 60 minutes (ASTM D5183).

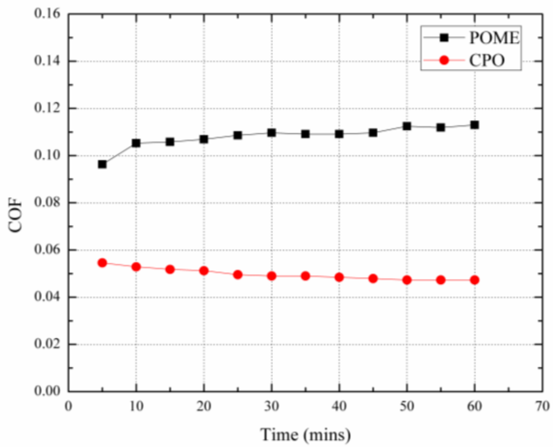

Fig. 4 Variation of coefficient of friction with time

After initial 10 minutes, the frictional values seem to be constant through the test with a slight deviation (± 0.005). The average COF of CPO and POME was 0.051 and 0.107 respectively. The impurities, wax and the free fatty acids present in the crude palm oil have resulted in low frictional values when compared to pure POME.

3.5. Wear test

The anti-wear property of a lubricant is identified by measuring the wear scar diameter on the steel balls as shown in figure 5. Test is conducted at 1200 rpm under constant temperature (75ºC) and 40 kg load for duration of 60 minutes (ASTM D4172). The scar diameter varies proportionally to the anti-wear property of the lubricant.

The mean wear scar diameter of CPO and POME was 0.556 mm and 0.634 mm respectively. The reduction in film thickness due to the breakdown of glycerol molecules into fatty esters have resulted in poor wear characteristics in the case of methyl ester.

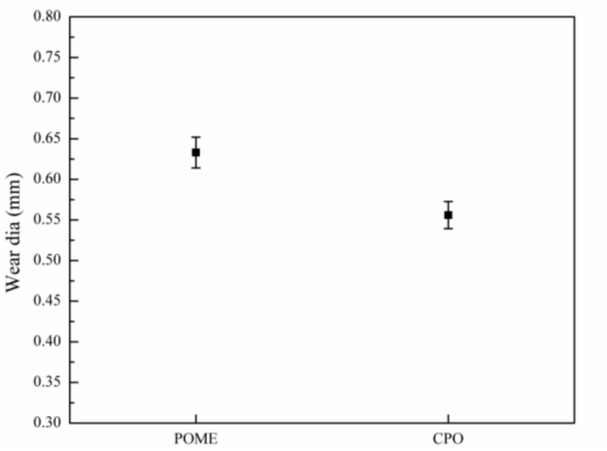

Fig. 5 Comparison of anti-wear property of palm oil methyl ester (POME) and crude palm oil (CPO)

3.6. Viscosity

The variation in dynamic viscosity of crude palm oil and palm oil methyl ester was studied using a rheometer as shown in figure 6.

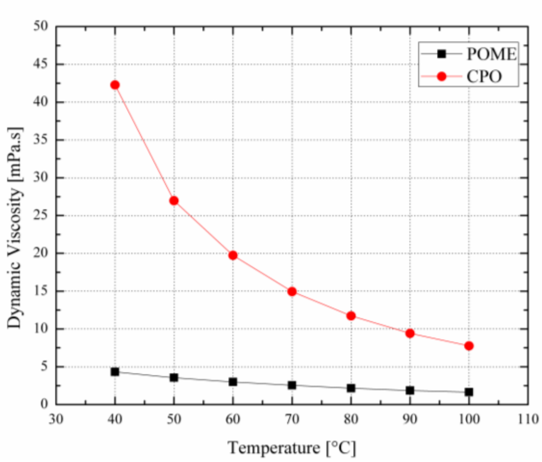

Fig. 6 Variation in viscosity with temperature

The removal of glycerol molecules from triglycerides through the process of alkali esterification has resulted in the drop in viscosity. The viscosity of CPO at 40ºC (42.2 mPa.s) has dropped by 89.8% (4.3 mPa.s) and a drop of 79.48% (7.8 mPa.s to 1.6 mPa.s) was observed at 100ºC when converted into methyl esters.

4. CONCLUSIONS

Palm oil is an excellent alternative for base oil in lubricant applications due to its high yield, low cost and good stability. The application of palm oil as lubricant is restricted by its low pour point characteristics. By converting crude palm oil into palm oil methyl ester by the process of alkali esterification (1% w/w KOH and 25% v/v methanol) has improved its pour point by 61% (from 23.6ºC to 9ºC). Due the chemical modification of palm oil, tribological properties like friction, wear have increased by 52.3%, 12.3% respectively and viscosity has reduced by 89.8%. Therefore, additives have to be identified to match the tribological properties of the commercial lubricating oil.

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