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Comparative study of tribological properties of trimethylolpropane-based biolubricants derived from methyl oleate and canola biodiesel

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ABSTRACT

A class of industrial-grade biolubricants was synthesized from methyl oleate and canola (*Brassica napus*) biodiesel by transesterification with trimethylolpropane (TMP) using sodium methoxide as catalyst. Model transesterification reactions were performed with methyl oleate to optimize the reaction conditions to obtain maximum yield of TMP trioleate. Methyl oleate-derived biolubricant with TMP triester composition of 91.2% was obtained after 5 h. Under similar reaction conditions, canola biodiesel-derived biolubricant comprising of 90.9% of TMP triesters was obtained. Both biolubricants were evaluated for their tribological properties using ASTM and AOCS standards. They exhibited very high viscosity indices, excellent low temperature properties and moderate oxidative stabilities. The lubricity of the biolubricants was tested on a High Frequency Reciprocating Rig (HFRR) apparatus by measuring wear scar diameter on a test sample. Canola biodiesel-derived biolubricant was found to perform better than methyl oleate-derived biolubricant based on HFRR test. Both biolubricants met ISO VG 46 specifications.

1. Introduction

Lubricants serve great applications in industries, automobiles, aviation machinery, helicopter transmissions, etc. by performing critical functions such as reducing friction, removal of wear particles, increasing efficiency, minimizing energy losses, uniformly distributing heat, etc. The most common types of lubricants in current use are automotive transmission fluids, hydraulic fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils, neat cutting oils and automotive gear lubricants (Nagendramma and Kaul, 2012). Since 1991, the world demand for lubricants has been around 35 million tons/year (Nagendramma and Kaul, 2012). The consumption sector of lubricants comprises of 53% automotive lubricants, 32% industrial lubricants, 5% marine oils and 10% process oils (Mang and Dresel, 2007). The world lubricant demand is anticipated to increase 1.6% per year (Mang and Dresel, 2007). A vast majority of these lubricants are mineral oil-based and are obtained primarily from petroleum derivatives.

It has been estimated that about 5–10 million tons of petroleum products enter the environment each year, with more than half ending up polluting the environment through total-loss applications, accidental spillage, nonrecoverable usage, volatility, industrial and municipal waste, urban runoff and refinery process (Carnes, 2004; Erhan et al., 2008). These lubricants are highly toxic to the environment and have poor biodegradability (Horner, 2002). Strong environmental concerns and growing regulations over contamination and pollution in the environment have increased the need for renewable and biodegradable lubricants (Fox and Stachowiak, 2007; Sallimon et al., 2010; Sharma and Dalai, 2013). Considering the spillage of lubricants, their polluting nature and environmental concerns, there is a need for cheap and renewable feedstocks for the production of biodegradable feedstocks. Vegetable oils are renewable and have biodegradability of over 95% (Kodali and Nivens, 2001). A chromatographic analysis of vegetable oils (Aluyor et al., 2009) elucidates their applicability as lubricants with a wide range of advantages such as high biodegradability (Emmanuel et al., 2009), low pollution of the environment, and compatibility with additives, low production cost, wide production possibilities, low toxicity, high flash points, low volatility and high viscosity indices.

Transesterification is defined as the reaction (Leung et al., 2010) in which a triglyceride molecule reacts with three moles of methanol to result in glycerol and mixtures of fatty acid methyl esters. The transesterification of vegetable oil-derived methyl esters with polyols is essentially the reverse of the transesterification reaction, in which glycerol is replaced by a commercial polyol. The most significant advantage of using a polyol instead of glycerol is that the absence of β-hydrogens enhances the thermal

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stability of the lubricant at high temperatures by preventing self-polymerization to form free fatty acids (Leung et al., 2010). There have been a lot of studies on transesterification of fatty acid methyl esters derived from a variety of vegetable oils including rapeseed (*Brassica napus* L.) oil (Linko et al., 1997; Gryglewicz et al., 2003; Uosukainen et al., 1998), olive (*Olea europaea*) oil (Gryglewicz et al., 2003), palm oil and palm kernel (*Elaeis gueneensis*) oil (Yunus et al., 2002, 2003a,b, 2004, 2005) and jatropha curcas (*Jatropha curcas* L.) oil (Ghazi et al., 2009). Several polyols such as neopentyl glycol (NPG), pentaerythritol, trimethylolbutane, trimethylolethane and trimethylolpropane have been used for this purpose.

A detailed study was reported on transesterification of TMP and a mixture of rapeseed (*B. napus* L.) oil fatty acid methyl esters by immobilized lipase without using additional organic solvent (Linko et al., 1997). Another work reported the synthesis of TMP esters of rapeseed (*B. napus* L.) oil fatty acids by enzymatic and chemical means and obtained near complete conversions in both cases (Uosukainen et al., 1998). The use of natural fats such as rapeseed (*B. napus* L.) oil, olive (*O. europaea*) oil and lard was reported for the preparation of NPG and TMP esters using calcium methoxide as catalyst (Gryglewicz et al., 2003). NPG esters were characterized by higher stability in thermo-oxidative conditions, while the olive (*O. europaea*) oil based esters showed the highest thermo-oxidative resistance due to the low content of polyunsaturated acids. The optimum reaction conditions for synthesizing TMP esters of palm (*E. gueneensis*) oil were determined in another work (Yunus et al., 2003a), and the effects of temperature, pressure, molar-ratio of palm (*E. gueneensis*) methyl esters-to-TMP and catalyst amount of sodium methoxide were studied. In another work, palm kernel (*E. gueneensis*) oil was used to synthesize TMP esters using sodium methoxide as catalyst and they were able to obtain approximately 98% conversion to palm kernel (*E. gueneensis*) TMP triesters (Yunus et al., 2003b). As an extension to their earlier work, they synthesized TMP esters of palm (*E. gueneensis*) oil with high oleic acid content which had pour points between 10 °C and −32 °C (Yunus et al., 2005). They fractionated the palm (*E. gueneensis*) oil methyl esters at 150–180 °C and 0.1 mbar prior to the synthesis and concluded that the concentration of $C_{16:0}$ methyl ester in the starting material should be below 10% for the pour points of the TMP esters of palm (*E. gueneensis*) oil to be below −30 °C. The production of jatropha (*J. curcas* L.) oil-based lubricant was studied via a two-step process (Ghazi et al., 2009) in which first, the jatropha curcas-derived (*J. curcas* L.) oil was transesterified to obtain jatropha (*J. curcas* L.) methyl esters and second, the jatropha (*J. curcas* L.) methyl esters were transesterified with TMP in the presence of sodium methoxide as catalyst. They found the conversion of jatropha (*J. curcas* L.) methyl esters to jatropha (*J. curcas* L.) biolubricant to be more than 80%.

In this study, model transesterification reactions are performed with methyl oleate and trimethylolpropane using sodium methoxide as catalyst to optimize the reaction condition to obtain maximum yield of TMP triester. The lubricating properties of trimethylolpropane-based biolubricants are obtained from direct synthesis of trimethylolpropane with methyl oleate and canola (*B. napus*) biodiesel are evaluated and a comparative study has been presented.

2. Materials and methods

2.1. Materials

Oleic acid, technical grade, 90% purity was procured from Alfa Aesar, Edmonton, Canada (Johnson Matthey Company). TMP, ACS Grade, 99.8% purity, was procured from Alfa Aesar, Edmonton, Canada (Johnson Matthey Company). Methanol, anhydrous, ACS Grade, 99.8%; Ethyl acetate, anhydrous, 99.8% and hexane, mixture of isomers, anhydrous, ≥99%, were all purchased from Sigma–Aldrich, Ontario, Canada. Sulfuric acid, Certified ACS Plus, 99.8%, 35.2 N/17.6 M and alumina, basic, 60–325 mesh was purchased from Fisher Chemical (Fisher Scientific, Edmonton, Canada). Canola (*B. napus*) biodiesel is procured from Milligan Biofuels, Saskatchewan, Canada. N,O-bis trimethylsilyl trifluoroacetamide (BSTFA), derivatization grade was purchased from Supelco (Sigma–Aldrich, Ontario, Canada). Anhydrous sodium sulfate, Certified ACS Grade, >99% was purchased from Fluka, Edmonton, Canada.

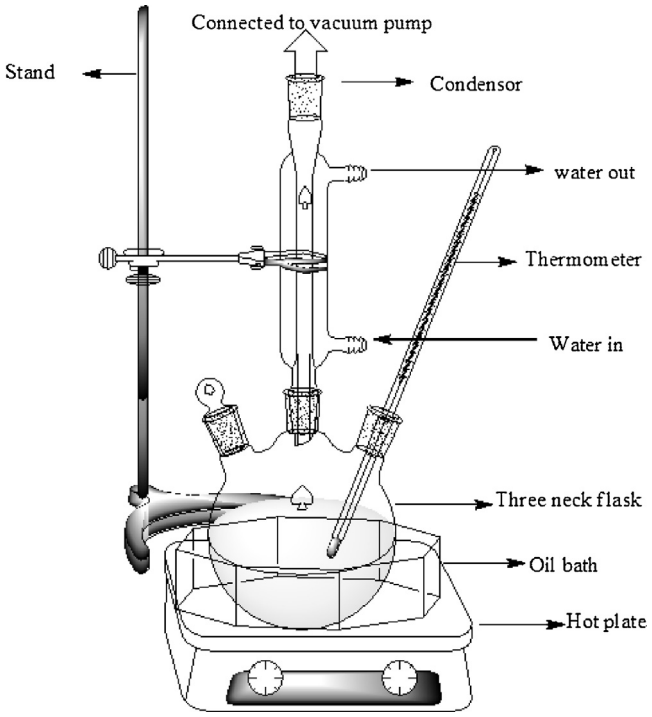

Fig. 1. Schematic of reaction setup for transesterification reactions of methyl oleate and canola biodiesel with trimethylolpropane.

2.2. Synthesis of biolubricants

2.2.1. Synthesis of methyl oleate

Methyl oleate was synthesized from oleic acid via concentrated sulfuric acid-catalyzed esterification with methanol. Batch runs of esterification were performed in a reaction set-up proposed earlier (Sepúlveda et al., 2011). Fig. 1 shows the schematic diagram of the experimental setup used in this study to perform the transesterification reactions of methyl oleate and canola (*B. napus*) biodiesel with trimethylolpropane. The batch weight of oleic acid in each experiment was 150 g. The produced methyl oleate was used as starting material for synthesis of methyl oleate-derived biolubricant.

2.2.2. Synthesis of biolubricants from methyl oleate and canola (*B. napus*) biodiesel

The transesterification reaction of TMP with methyl oleate was investigated to obtain methyl oleate-derived biolubricant. The following range of reaction parameters, viz., temperature: 80–140 °C, molar-ratio of methyl oleate-to-TMP: 3–5 and sodium methoxide amount: 0.5–1.5% was used to find the optimum reaction conditions. The pressure was maintained constant at 1 mbar. The transesterification reactions of TMP with methyl oleate were designed using central composite design approach implemented