

Tribological Evaluation of Biobased Lubricant Basestocks from Cottonseed and Soybean Oils

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ABSTRACT

The aim of this study was to synthesize environmentally adapted Trimethylolpropane (TMP) esters from cottonseed and soybean oils and to examine their quality parameters and tribological properties as potential lubricant basestocks. A two stage production process was followed. At first the above mentioned vegetable oils were transformed to the corresponding methyl esters via methanolysis in the presence of sodium methoxide. The desired TMP esters were finally synthesized by alkaline transesterification of the previously produced methylesters with TMP using sodium methoxide as catalyst. Following the purification phase the physicochemical characteristics of the synthesized TMP esters were examined. The tribological properties were evaluated by employing a Four-Ball apparatus. An additive-free mineral oil base oil was used as a reference lubricating fluid. Furthermore, the synthesized esters were treated with a commercially available EP/AW additive and a comparative assessment of the load-carrying properties was conducted by repeating the four ball measurements.

INTRODUCTION

During the last decades the environmental awareness has led to the development of biobased lubricants since almost half of all lubricants sold - mainly mineral oil based- end up in the environment via loss and high risk applications [1]. Intense research activity is ongoing worldwide concerning production of biolubricants from renewable raw material like vegetable oils, fats and their derivatives. Besides, the European Committee for Standardization (CEN) recognizing the crucial role the biobased products play on the economy and the environment, is moving towards the development of terminology along with technical specifications and standards for biolubricants (CEN/TC 19 Working Group 33).

Nevertheless, the poor thermal stability and low temperature characteristics of the neat natural oils and fats make necessary their modification or stabilization in order them to fulfill the basic requirements as lubricant basestocks [2,3]. An improvement of the instability of vegetable oils and fats can be achieved by chemical modification techniques, genetic enhancement of oilseeds and development of additive technologies. One of the most important chemical modifications is the transesterification to their corresponding polyolesters. These are formed from polyols with a quaternary carbon atom (neopentylalcohols) like neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). This class of products offer extraordinary stability due to the absence of a secondary hydrogen in the β -position and the presence of a quaternary C-atom in the centre [1,3]. These biobased esters cannot be used at extremely high temperatures however can be suitable in less extreme applications. Several studies exist demonstrating the preparation and the lubricating properties of polyol esters from naturally deriving fats and oils with the most common of them being rapeseed oil, sunflower oil, castor oil, soybean oil, olive oil and palm oil [4,5,6,7,8]. Cottonseed oil is one of the vegetable oils whose usage as a starting material for biobased lubricant basestocks is found in limited studies in the literature. Cotton is one of the second best potential sources for plant proteins after soybean and the ninth best oil-producing crop [9].

Based on this background, the tribological characteristics of biobased esters from cottonseed and soybean oil as potential lubricants basestocks were investigated. These fatty oils were chemically modified to their corresponding trimethylolpropane (TMP) esters using sodium methoxide as catalyst. The synthesized esters were evaluated regarding their quality parameters and their load-carrying properties were determined by employing a Four-Ball Test Machine.

EXPERIMENTAL

MATERIALS

- Refined Cottonseed Oil (CO) and Soybean Oil (SBO) were obtained from domestic oil manufacturers and were used without further processing. Their typical properties are presented in [Table 1](#).

- Trimethylolpropane (TMP), > 99% purity, was obtained from Merck

- Methanol, 99,99% purity was obtained from Fisher Scientific

- Sodium Methoxide, pure, anhydrous powder was obtained from Acros Organics

See [Table 1](#) after last section of paper

METHODOLOGY

Synthesis of the biobased TMP esters

In order to synthesize the cottonseed and soybean esters of trimethylolpropane (COTMPE & SBOTMPE) a two stage transesterification methodology was applied. Initially the triglycerides were converted to cottonseed oil methylesters (COME) and soybean oil methylesters (SBOME) respectively. Subsequently, the COME and SBOME were transesterified with trimethylolpropane (TMP) producing the desired polyol esters.

The COME and SBOME were prepared by methanolysis of cottonseed and soybean oil respectively, using sodium methoxide (CH_3ONa) as catalyst at a concentration of 0.75wt %. In all cases the reaction was carried out in 2L flask at 65° C for 2h using 500g of oil and a 6:1 methanol/oil molar ratio. After the completion of the transesterification, the upper methyl esters phase was separated from the glycerol phase and was purified by washing with 5% w/w sulfuric acid (H_2SO_4) followed by warm water. The excess of methanol was removed by rotary evaporator. The purified methyl esters were dried over anhydrous sodium sulphate (Na_2SO_4) and after vacuum filtration the final COME and SBOME were obtained. Both FAMES were analyzed with regards to their quality parameters and their fatty acid composition.

The transesterification reaction of COME and SBOME to their corresponding TMP esters was carried out in a 500ml three-neck round bottom flask equipped with a Dean-Stark cap and a reflux condenser. Each time the flask was filled with 80g of FAME (COME or SBOME) and 12.2-12.3 g of TMP. The mixture was heated to the melting point of TMP and 50ml of isooctane (C_8H_{18}) - used as azeotropic agent - were then added, followed by the addition of 1wt% sodium methoxide as catalyst. The temperature was raised and the reaction was carried out at the boiling point temperature of the mixture. During the reaction the formed methanol was

continuously removed by azeotropic distillation with isooctane. The removal of the methanol favours the forwards reaction thus facilitating the obtainment of high yields. Moreover the quantity of methanol trapped in the Dean-Stark was used as a means for estimating the conversion of the reaction. When the reaction was complete the catalyst was separated from the synthesized ester either by vacuum filtration or by centrifuge. The isooctane was removed by vacuum distillation.

Physicochemical properties of the synthesized esters

The synthesized esters were evaluated regarding their physicochemical properties as potential lubricant basestocks. The kinematic viscosities (KV) at 40°C and 100°C and the viscosity index (VI) were determined according to methods ASTM D445 and ASTM D2270 respectively. The pour point (PP) measurements were carried out in accordance to ASTM D 97 standard method. For the determination of acid value (AV) the European Standard EN14104 for Oil and Fat derivatives was followed. A Karl-Fischer Coulometer was used for the determination of the water content.

Tribological Evaluation of Synthesized Esters

The tribological properties of the synthesized TMP esters were examined by employing a Four-Ball Test Machine in accordance to the methodology described in the ASTM D 2783 Standard Test Method. By performing determinations regarding their Load-Wear Index (LWI) and the Weld Point (WP) their load-carrying properties were evaluated. The load-wear index is indicative of the ability of a lubricant to minimize wear at applied loads. On the other hand the weld point is the lowest applied load that leads to the welding of the rotating ball to the three stationary balls, indicating that the Extreme Pressure (EP) levels of the lubricants-force has been exceeded [10]. For each given sample a series of tests of 10-s duration were made at increasing loads until welding occurred. Ten tests were performed below the welding point. After each test the scar diameter was measured in all three stationary balls, using a microscope and the mean value was reported. A conventional additive-free mineral base oil SN-150 was used as a reference lubricating fluid. The properties of the mineral oil are listed in [Table 4](#). Furthermore the COTMPE and SBOTMPE were treated with a commercial ashless Extreme Pressure/Antiwear (EP/AW) additive at a rate of 1.5% w/w, and their EP properties were determined and compared to that of the untreated ones. The additive comprised of phosphorous-sulphur compounds. The repeatability of the LWI and WP values is calculated to be 17% of the mean value and one increment loading respectively [10].

RESULTS AND DISCUSSION

PHYSICOCHEMICAL PROPERTIES OF COME AND SBME

The quality parameters and the fatty acid profile of the prepared FAMES (COME and SBOME) are listed in [Table 2](#) and [Table 3](#) respectively. Both FAMES satisfy the generally applicable requirements outlined in the European Standard EN14214 with the exception of the kinematic viscosity of COME - which is above the maximum limiting value of 5 cSt - and their oxidation stability which is below 6h. Concerning their fatty acid profile linoleic acid (C18:2) is the major constituent in both FAMES. However SBOME have higher levels of oleic (C18:1) and linolenic acid (C18:3) and the total unsaturated fatty acids content accounts for 81.25%. On the other hand the COME contains higher amounts of palmitic acid (C16:0) which results in a lower unsaturated fatty acid content and consequently in a higher oxidation stability. It is known that increased levels of poly - unsaturated fatty acid, lead to a decrease in the oxidation stability, with the trend of increasing stability to be linolenic < linoleic < oleic [11].

See [Table 2](#) after last section of paper

Table 3. Fatty acid profile of the prepared FAMES

Fatty Acids	COME	SBOME
C14:0	0.72%	-
C16:0	21.80%	10.19%
C16:1	0.13%	-
C18:0	2.50%	4.04%
C18:1	15.54%	22.56%
C18:2	53.15%	52.63%
C18:3	0.38%	6.06%
Saturated F.A. content	25.02%	14.23%
Unsaturated F.A. content	69.21%	81.25%

SYNTHESIS OF BIOBASED TMP ESTERS

In [Fig.1](#) the progress of the transesterification reactions of COME with TMP and SBOME with TMP are illustrated. It is obvious that the catalytic activity of sodium methoxide in quantity of 1% wt was very good. Almost complete conversion was obtained after 12h reaction time although no excess of the FAME was used. Particularly in the transesterification reaction of COME with TMP, a yield of 96.5% of COTMPE was achieved and likewise in the transesterification reaction of SBOME with TMP the yield of SBOTMPE was 97.3%. The reactions were very fast at the beginning, as shown in [Fig 1](#), and even after 4h of reaction

time the TMP esters' yield was more than 80% in both cases. In similar studies a conversion of almost 99% was achieved in the transesterification of rapeseed oil methyl esters with TMP using sodium methoxide as catalyst [5]. Moreover a maximum yield of 86% had been reported in the sodium methoxide catalyzed transesterification of TMP with palm oil methyl esters. [8]. In those studies an excess of FAME was used with the molar ratio of FAME/TMP being 3.2:1 and 3.8:1 respectively. In the present study the stoichiometric molar ratio (3:1) was maintained in all cases and so the high vacuum distillation process for the removal of the unreacted methyl esters could be omitted.

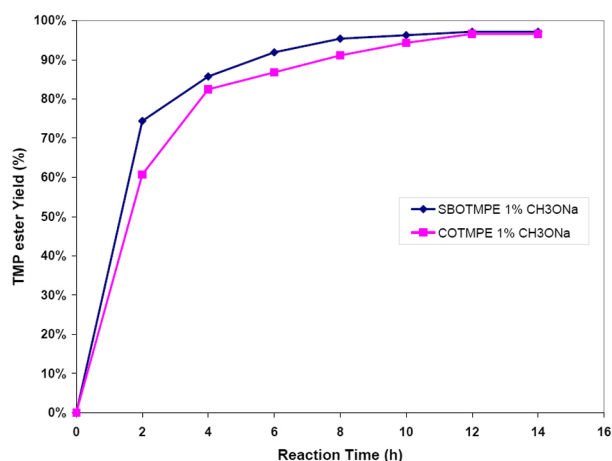


Figure 1. Progress of the cottonseed oil and soybean oil TMP ester syntheses (FAME/TMP molar ratio 3:1, reaction temperature 110-120°C, catalyst sodium methoxide 1%wt)

PHYSICOCHEMICAL PROPERTIES OF THE SYNTHESIZED ESTERS

[Table 4](#) summarizes the physicochemical properties which have been determined for the synthesized TMP esters of cottonseed and soybean oil. The kinematic viscosity of the synthesized COTMPE is higher than the kinematic viscosity of SBOTMPE. This can be explained by the difference observed in the viscosities of the starting materials COME and SBOME. Both esters exhibit high viscosity index values, with the soybean based one having the higher VI. Furthermore, the synthesized esters possess satisfactory low temperature characteristics as indicated by the pour point measurements. The lower pour point of SBOTMPE comes as a result of its higher unsaturated fatty acid content.

See [Table 4](#) after last section of paper