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Synthesis and oxidative stability of trimethylolpropane fatty acid triester as a biolubricant base oil from waste cooking oil

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ABSTRACT

Trimethylolpropane fatty acid triester (TFATE), which was used as a biolubricant base oil, was synthesized by transesterification of fatty acid methyl esters from waste cooking oil with trimethylolpropane. The reaction parameters and the oxidative stability of TFATE have been studied. Under the selected conditions (potassium hydroxide as the catalyst, molar ratio of catalyst to trimethylolpropane of 1:4, molar ratio of fatty acid methyl esters to trimethylolpropane of 4:1, reaction temperature of 128 °C, and vacuum pressure at 200 Pa), TFATE with a yield of 85.7% was obtained. After being purified by molecular distillation at 120 °C, the content of TFATE in the product reached 99.6%. The addition of *alpha*-tocopherol, butylated hydroxyanisole, and *tert*-butylhydroquinone enhanced the oxidative stability of TFATE, while 2,5-di-tertbutyl-hydroquinone and rosemary extract R40 did not improve TFATE's oxidative stability. When being used with *alpha*-tocopherol, butylated hydroxyanisole had a positive synergistic effect on the oxidative stability of TFATE. In addition, the TFATE's chem–physical properties met the requirements of ISO VG32.

1. Introduction

The rising demand for mineral-based lubricants continuously adds to the petroleum energy supply tense and their concurrent harmful effects on the environment have led to increasing interests in the development of biolubricants from renewable resources. It is estimated that world lubricants demand will reach 4.13 hm^3 by 2017 according to Global Industry Analysts [1]. Since 50–60% of the lubricants directly come into contact with soil, water, and air [2], millions of tons of lubricants are released into the environment every year. Mineral-based oils are toxic to the environment and large amounts of money have been spent to clean up accidental oil

Abbreviations: BHA, butylated hydroxyanisole; DTBHQ, 2,5-di-tertbutyl-hydroquinone; FAME, fatty acid methyl esters; FFA, fatty acids; IP, induction period; MD, molecular distillation; TBHQ, *tert*-butylhydroquinone; TFATE, trimethylolpropane fatty acid triester; TG, triacylglycerol; TMP, trimethylolpropane; SZA, sulfated zirconia supported by alumina; WCO, waste cooking oil; α-T, *alpha*-tocopherol.

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spills [3]. Therefore, to meet this future demand and to curb pollution, biodegradable lubricants have been extensively explored.

Trimethylolpropane fatty acid triester (TFATE) is a type of potential biodegradable base stock for lubricants production because of its excellent lubricity, biodegradability, viscosity–temperature characteristics, and low volatility [4]. Several synthetic approaches are available for the production of TFATE by the transesterification of fatty acid methyl ester (FAME) [5,6] or the esterification of free fatty acids (FFA) with trimethylolpropane [7–9]. Transesterification is reportedly superior to esterification in terms of TFATE production because transesterification requires lower capital and energy consumption. In contrast, esterification requires a longer reaction time and may produce a lower yield of TFATE than transesterification [10].

One of the critical barriers to the wide application of biolubricant is the relatively high cost of production, which is four to fifteen times higher than that of conventional mineral-based oil [11]. Although the synthesis of biolubricant has been studied before, the raw material of the biolubricant was primarily expensive virgin vegetable oils, such as palm oil [12], rapeseed oil [13], etc. which account for 70–80% of the total production cost [14]. Therefore, finding cheaper feedstocks to produce biolubricant is of great interests. Waste cooking oil (WCO) is typically around 30–60% cheaper than the edible vegetable oil and its sources are continually expanding as a result of the increasing food consumption around the world [15]. Particularly, it is estimated that the production of WCO in Guangzhou, the third largest city in China with a population of above 25 million, is about 20 Gg per year [16]. The conversion of WCO into biolubricant or other bioproducts would not only eliminate the negative effect of WCO on the environment, but also prevents the illegitimate recycling of WCO as fake edible vegetable oil [16]. Chowdhury et al. have proposed a method of producing biolubricant from WCO through the *Candida rugosa* lipase-mediated hydrolysis of WCO to FFA followed by Amberlyst 15H esterification of FFA with octanol [17]. Generally, enzyme-catalyzed reaction is of comparatively high costs than chemical approach and it is not commonly used in industrial production. However, the chemical synthesis of TFATE as a biolubricant base oil from WCO with a high yield of TFATE was rarely reported.

The main objective of this research was to provide a practical process to convert WCO into TFATE as a biolubricant base oil through a two-step chemical approach. In the first step, FAME was produced by the transesterification of triacylglycerol (TG) with methanol. In the second step, by the transesterification of FAME with TMP, the final product of TFATE was obtained. Reaction conditions, including the type of catalyst, molar ratio of catalyst to TMP, molar ratio of FAME to TMP, reaction temperature, reaction time, and vacuum pressure were investigated. Molecular distillation (MD) was employed to purify TFATE. Furthermore, the oxidative stability of TFATE was determined according to the Rancimat method by the addition of a series of different kinds of antioxidants and the chem–physical properties of TFATE were determined.

2. Materials and methods

2.1. Materials

Waste cooking oil (WCO) from restaurants with an acid value measured as KOH of 59.8 mg kg^{-1} was provided by Guangzhou Balis Waste Treatment Co., Ltd. (Guangzhou, China) authorized by the local government. Food and water remaining in the WCO were removed through filtration and evaporation after settling. Trimethylolpropane (2-ethyl-2-(hydroxymethyl)-1,3-propanediol) was obtained from Tianjin Keoumi Chemical Reagent Co., Ltd. (Tianjin, China). Solid superacid, sulfated zirconia supported by alumina (SZA) ($SO_4^{2-}/ZrO^2-Al_2O_3$)was bought from Taide Chemical Scientific Co., Ltd. (Zibo, Shandong, China). *Alpha*-tocopherol (α-T), butylated hydroxyanisole (BHA), *tert*-butylhydroquinone (TBHQ), and rosemary extract R40 (R40) were purchased from Kemin Industries Inc. (Iowa, USA). 2,5-Di-tertbutyl-hydroquinone (DTBHQ) was obtained from Guangzhou Taijun Chemical Co., Ltd. (Guangzhou, China). All other reagents were of analytical grade, unless otherwise indicated.

2.2. Preparation of FAME from WCO

FAME was produced from WCO by a two-step process which had been developed in our previous study [18]. In the first step, WCO was esterified with glycerol to lower the fatty acid content catalyzed by SZA. In the second step, after removal of SZA by filtration, the esterified WCO was sent directly to produce crude FAME by using potassium hydroxide as a catalyst. The residual methanol in the crude FAME was removed by a rotary evaporator and then twice subjected to hot water (80 °C) washing to remove residual glycerol and soap. The washed FAME was then dried and purified FAME was obtained.

2.3. Transesterification of TMP with FAME

The transesterification was performed under different operating conditions, including four molar ratios of fatty acid methyl esters (FAME) to trimethylolpropane (TMP) = 3:1, 3.5:1, 4:1, and 4.5:1, five molar ratios of catalyst to TMP = 0.1:1, 0.15:1, 0.2:1, 0.25:1, and 0.3:1, at six reaction temperatures = 108, 118, 128, 138, 148, and 158 °C, and five reaction times = 1, 1.5, 2, 3, and 4 h.

The synthesis of trimethylolpropane fatty acid triester (TFATE) was carried out in a three-necked flask. Firstly, TMP was introduced and then the catalyst was loaded. FAME was loaded during the reaction for 30–40 min by continuous drip into the TMP from a constant-pressure dropping funnel. The reaction was conducted under vacuum conditions (2000 Pa) using a water ring pump inserted through a glass condenser with circulating cooling water, which was connected with the second neck of the flask. The flask was heated by an oil bath. A magnetic stirrer of 2.0 cm radius was used to stir the reaction mixture at 5 Hz. After the reaction was completed, the mixture was chilled to 80 °C and 50 cm^3 of phosphoric acid solution with concentration of 0.27% was added to the mixture to neutralize the catalyst. The mixture was stirred for a period of 20 min at 80 °C in a water bath. Then, the mixture was placed

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