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ScienceDirect

Bioresource Technology 98 (2007) 2027–2033

BIORESOURCE TECHNOLOGY

Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive

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Received 11 July 2005; received in revised form 9 August 2006; accepted 10 August 2006
Available online 27 October 2006

Abstract

Transesterification of canola oil was carried out with methanol, ethanol, and various mixtures of methanol/ethanol, keeping the molar ratio of oil to alcohol 1:6 and using KOH as a catalyst. Mixtures of alcohol increased the rate of transesterification reaction and produced methyl as well as ethyl esters. The increased rate was result of better solubility of oil in reaction mixture due to better solvent properties of ethanol than methanol and equilibrium due to methanol. With 3:3 molar ratio of methanol to ethanol {MEE (3:3)} the amount of ethyl ester formed was 50% that of methyl ester. Properties (acid value, viscosity, density) of all esters including mixed esters were within the limits of ASTM standards. Lubricities of these esters are in the order: ethyl ester > methyl ethyl ester > methyl ester.

Keywords: Canola; Biodiesel; Lubricity; Transesterification

1. Introduction

Biodiesel derived from vegetable oils is gaining market share as a diesel fuel extender all over the world (Meher et al., 2006a). The reason being environmental benefits and renewable resource of biodiesel. The major hurdle in commercialization of biodiesel is high raw material cost (Kulkarni and Dalai, 2006). In European countries biodiesel is sold at prices competitive with petroleum diesel fuel because of the tax deductions given by the government for the use of biodiesel (Communication from the commission, 2006). Due to the lack of such tax relief in other countries, the cost of the biodiesel is very high compared to the petroleum diesel (Holbein et al., 2004). Hence various non-fuel uses of biodiesel have been investigated. One of the most promising alternatives for biodiesel application is its use as a diesel fuel lubricity additive.

In January 2001, the Environmental Protect Agency (EPA) made a rule that sulphur levels in diesel fuel be reduced from 500 to 15 ppm, a 97% reduction by 2006 (Lang and Dalai, 2001). Such low sulphur, unadditized diesel fuel has very poor fuel lubricity, resulting in shorter diesel injection pump and engine lives. The poor lubricity of ultra low sulphur diesel is mainly due to the removal of heterocyclic nitrogen and oxygen which are responsible for the lubricity during hydrotreatment along with sulphur (Barbour et al., 2000). To restore the lubricity of diesel fuel refiners regularly add various lubricity additives into the diesel fuels.

It is found that mono fatty acid low alkyl esters made from vegetable oil, are capable of enhancing the fuel lubricity to meet ASTM requirements (Van Gerpen et al., 1999). Various fatty acid esters such as methyl, ethyl, 2-propyl and butyl esters prepared from canola and linseed oil were tested as diesel fuel lubricity additives. At 1% treat rate, the canola methyl and 2-propyl esters increased the lubricity number of a reference fuel by 60% (Lang and Dalai, 2001). The effect of individual fatty acid methyl esters on lubricity of the fuel has been investigated (Geller and

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0960-8524/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2006.08.025

Goodrum, 2004). It was observed that lubricity of individual fatty acid methyl esters was less compared to that of mixture of various methyl esters derived from vegetable oils. The effects of type of alcohol and fatty acid profile of vegetable oil on lubricity of the ester were analysed by Drown et al. (2001). Ethyl esters showed noticeable improvement compared to methyl esters in the wear properties. No correlation was found between the lubricity improvement and fatty acid profile of the ester. Impact of various acetoacetic and dicarboxylic acid esters on lubrication properties of automotive diesel fuel was studied by Anastopoulos et al. (2001). Two of the three acetoacetic esters used, that were derived from the heavier hexyl and octyl alcohols, provided satisfactory HFRR mean wear scar diameter (WS 1.4) of less than 460 μm, at the concentration level of 750 ppm. Among the diesters derived from the same di-carboxylic acid, with increase in the chain length of the alcohol, lubricity of the ester also increased. Conversely, with the constant chain length of the alcohol, an increase in dicarboxylic acid chain length did not cause significant improvement in lubricity. Presently the research on use of fatty acid esters as lubricity additive is focussed on methyl and ethyl esters of fatty acids.

Although methyl and ethyl esters are good lubricity additives, their preparation methods have their own advantages and disadvantages. The formation of ethyl esters is environmentally attractive because unlike methanol, ethanol is produced from renewable resources. Also, ethanol has better solvent properties than methanol for solubility of oil. However, formation of emulsion after the transesterification reaction makes ethanolysis more complicated and impractical (Meher et al., 2006b). In case of methanolysis the reaction mixture remains in two phases due to the low solubility of oil in methanol (Boocock et al., 1996). Hence, the mass transfer limitations make the rate of the reaction slower. It was reported that the rate of formation of methyl esters from soybean oil is 15 times slower than the butyl esters (Boocock et al., 1996).

The aim of the present work is to synthesize canola oil esters using methanol, ethanol and mixture of methanol/ethanol, and use of these esters as lubricity additive. The purpose of using mixture of methanol and ethanol is to take the advantage of better solubility of oil in ethanol than methanol and better reactivity of methoxide ion than ethanoxide to attain the desired equilibrium. Also, mixed esters may act as a better lubricity additive than pure methyl esters. Another advantage of using mixture of methanol and ethanol is, if part of the methanol is replaced by ethanol, then there would be less dependency on the synthetic sources for methanol.

2. Methods

2.1. Materials

Degummed, refined canola oil was purchased locally. Methanol, anhydrous (99.8%) was purchased from Sigma–Aldrich, Canada. Ethanol (100%) was purchased from Commercial Alcohols Inc., Ontario. All other reagents were analytical grade or higher.

2.2. Ester Preparation

2.2.1. Methyl ester

Methyl ester was synthesized in a batch type reactor using potassium hydroxide as catalyst as per the method given by Lang et al. (2001). The reaction was carried out using 100% excess methanol, i.e. molar ratio of methanol to oil is 6:1 and catalyst concentration of 1%. After completion of reaction, crude glycerol was separated by gravity. The catalyst was removed by hot water washings. The complete removal of the catalyst was checked by phenolphthalein indicator. Traces of moisture and unreacted methanol were removed by vacuum distillation. The distillation was continued until the loss in weight of ester was constant thus confirming the complete removal of moisture and unreacted methanol. Finally esters were dried over anhydrous sodium sulphate.

2.2.2. Ethyl ester

Ethyl ester of canola oil was prepared in a similar way as methyl esters. The transesterification was carried out at 70 °C for 2 h with vigorous agitation in order to achieve full conversion. In order to avoid the emulsion after the transesterification reaction, 0.1% aqueous tannic acid was used as a washing solution to remove catalyst. With mild agitation in a flask, the alcohol and most of the soap could be removed by three washes. Purification of ester was done as per the method given in Section 2.2.1.

2.2.3. Mixture of esters

Different molar ratios of methanol and ethanol (such as 3:3, 3.5:2.5, 4:2, 4.5:1.5, and 5:1) were used for the transesterification reaction, keeping the molar ratio of oil to alcohol 1:6. The reaction was carried out in a batch type of reactor. One hundred gram of oil were placed in a dry Erlenmeyer flask equipped with a magnetic stirrer and thermometer. In another dry Erlenmeyer flask 1.0 g of potassium hydroxide was mixed with mixture of methanol and ethanol. This mixture was then added to the oil and stirred vigorously for 40 min at 25 °C. After separation of glycerol in separating funnel, the ester layer was washed 3–4 times with warm water to remove the unreacted alcohol and catalyst. Esters synthesized using of 3:3, 3.5:2.5, and 4:2 molar ratios of methanol and ethanol were washed using 0.1% tannic acid solution to reduce emulsification. Purification of the ester was done as per the method given in Section 2.2.1.

2.3. Ester characterization

Preliminary analysis of the ester phase was carried out by thin layer chromatography using the solvent system hexane: diethyl ether (90:10 v/v). Fatty acid components of the