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The synergistic effect of alcohol mixtures on transesterification of soybean oil using homogeneous and heterogeneous catalysts

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A B S T R A C T

In an effort to enhance the transesterification reaction of soybean oil and thereby the lubricity properties of the resulting biodiesel as well, the alcohol component of the reaction blend was altered to include several different combinations of methanol, ethanol, and propanol, rather than a single alcohol. For this work, various concentrations of a homogeneous catalyst, such as CH_3ONa or C_2H_5ONa, or a heterogeneous catalyst, $CaO–La_2O_3$ or an anion exchanged resin, were used in the reaction. Ethanolysis was found to be faster than methanolysis with highly basic homogeneous catalysts due to the higher nucleophilicity of ethoxide relative to methoxide. The ethyl-ester yield approached a maximum earlier than the methyl-ester yield, even though the methyl-ester yield continuously increased with reaction. Also, methanolysis became linked with ethanolysis when a methanol–ethanol equimolar mixture was used as an alcohol source. In addition, significant improvement in the transesterification activity was observed at very earlier reaction times when a methanol–ethanol mixture was used and a high basicity condition existed where ethoxide can be formed. To explain this effect, a combined structure of methoxide–ethanol or ethoxide–methanol has been proposed and tentatively supported by reaction measurements and FTIR. In this model, the formed alkoxide generates two reactive sites resulting in an accelerated transesterification rate.

1. Introduction

Biodiesel is a processed fuel derived from the esterification of free fatty acids (FFAs) and transesterification of triglycerides that are naturally present in renewable biological sources such as plant oils and animal fats [1]. Unfortunately, the major hurdle in the successful commercialization of biodiesel is the high raw material cost [2]. One way to reduce the cost of biodiesel production is to improve the transesterification process. Many research groups have attempted to develop heterogeneous catalyst systems [3–7], but only a few have investigated comparing methanolysis and ethanolysis in the presence of several classic catalytic systems [8,9]. Prior work showed that the rate of alkyl-ester formation depended upon the carbon number of the alcohol. As the carbon number increased, the rate of base-catalyzed ester formation tended to decrease [9–14]. Bokade and Tadav reported that clay (K-10) supported heteropolyacids showed the following yield with alcohol: methanol (84%) > ethanol (80%) > n-propanol (76%) > n-octanol (72%) [9]. However, this behavior is not observed in all cases. For instance, it was reported that rapeseed oil transesterification occurred faster with ethanol than with methanol using a homogeneous heteropolyacid catalyst [8]. This result was attributed to enhanced contact between the ethanol, oil, and their products [8,12,15]. It should be noted, though, the relative rates of methanolysis to ethanolysis are dependent upon the catalysts and reaction conditions used. Kulkarni et al. have shown that, in order to increase the transesterification rate of triglycerides and to provide a mixture of methyl and ethyl-esters for lubricity improvement, methanol–ethanol mixtures were needed as alcohol feeds [16,17]. This suggests that a higher rate of transesterification of triglycerides using a mixture of alcohols has several advantages. First, higher reaction rates can save reaction time in biodiesel production facilities. Secondly, the creation of ethyl and methyl-ester can provide better fuel lubricity properties than methyl-ester alone [16,18]. Thirdly, ethanol, derived from agriculture products, is less hazardous to the environment than methanol [15].

Additionally, one of the drawbacks of using biodiesel as a fuel has been its cost disadvantage relative to diesel fuel. This cost disadvantage can be addressed not only by improving the transesterification process, but also by recognizing that biodiesel

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is a promising, non-sulfur, and highly effective diesel fuel lubricity additive and cetane improver [17,19]. This is especially relevant for two reasons. First, sulfur levels in diesel fuel have been government mandated to decrease 500–15 ppm, beginning in 2006. Secondly, the relatively poor lubricity of ultra low sulfur diesel is mainly due to the removal of heterocyclic nitrogen and oxygen, along with sulfur, during hydro-treatment. Biodiesel, however, is made from vegetable oil and contains alkyl-esters capable of enhancing the fuel lubricity of diesel. As an example, by adding just 1% FAME biodiesel to ultra low sulfur diesel, the lubricity of the fuel was increased by 60% [17]. The advantage of a mixed alcohol derived biodiesel is apparent when one compares the reported order of lubricity improvement for methyl-ester, ethyl-ester, and mixed esters of methyl and ethyl-ester: ethyl-ester > methyl-ethyl-ester > methyl-ester [17,20].

Kulkarni et al. reported that a mixture of alcohols increased the rate of the transesterification reaction and produced methyl-esters as well as ethyl-esters. They also reported the increased rate was the result of improved solubility of the oil in the ethanol reaction mixture relative to a methanol mixture [17]. Although an alcohol mixture has advantages for transesterification, with respect to both reaction rate and lubricity, literature information for the reason why is still somewhat limited and sometimes contradictory. In particular, the transesterification of an oil with a methanol–ethanol blend over a heterogeneous catalyst does not appear to have been attempted yet.

In this study, methanol, ethanol, propanol, and mixtures of those alcohols were reacted with soybean oil over homogeneous (CH_3CH_2ONa and CH_3ONa) and heterogeneous ($CaO–La_2O_3$ and anion exchanged resin) catalysts to investigate a possible increased reaction rate of alcoholysis reactions. Better understanding of the transesterification reaction with different alcohol mixtures, the interaction between catalyst surface properties, and alcohols having different carbon number can help provide an improved biodiesel production process and a more valuable biodiesel fuel because of its enhanced lubricity and cetane value.

2. Experimental

2.1. Materials

Calcium nitrate, lanthanum nitrate, sodium ethoxide, sodium methoxide, and a strong basic anion exchange resin (Marathon A) were purchased from Sigma–Aldrich (St. Louis, MO). Anhydrous HPLC grade methanol, ethanol, n-propanol, and iso-propanol were obtained from Fisher Chemical (Fair Lawn, NJ). Ethyl alcohol (200 Proof) was purchased from Decon Labs Inc. (King of Prussia, PA). Commercial, edible grade soybean oil (total acid number (TAN) = 0.046 mg KOH/g) was obtained from a retail source (COSTCO) and evacuated in a vacuum (5×10^{-2} Torr) at 23 °C to remove water and gases dissolved in the oil phase. The titrant for TAN measurements (0.1 N KOH in iso-propanol) was purchased from LabChem Inc. (Pittsburgh, PA). Various methyl-esters and ethyl-esters were purchased from Nu-Chek Prep Inc. (Elysian, MN) for internal standards and calibration of the gas chromatography–mass spectrometer.

2.2. Catalyst preparation (homogeneous and heterogeneous)

The homogeneous catalysts, sodium methoxide and sodium ethoxide, were dissolved in methanol and ethanol, respectively. These catalysts (0.2 M in alcohol) were then added to a reaction mixture composed of 10 g soybean oil and alcohol at a molar ratio of 10.

The heterogeneous catalyst, Dowex Marathon A, which is made of styrene–divinylbenzene copolymer backbone, quaternary amine functional groups, and strong base anions (OH^-) was purchased from Sigma–Aldrich (St. Louis, MO). The mean particle size was 610 ± 50 μm and total exchange capacity was 1.0 equiv./L. This strong basic anion exchange resin was activated in a 1.0 M NaOH solution with alcohol (methanol or ethanol) for 12 h. The activated resin was then rinsed in pure alcohol for 12 h and then filtered and washed with alcohol in order to remove any physically adsorbed NaOH. Moreover, all the resins were repeatedly rinsed with alcohol until the pH of the alcohol rinsate stabilized at 7.0. Finally, 10 g of the resin was added to the reaction mixture. The amount of alcohol wetted on resin catalyst was not included because the resin catalyst was maintained in a swelled state with alcohol through the reaction.

For this work, the $CaO–La_2O_3$ heterogeneous catalysts were prepared using the sol–gel method. A solution mixture containing an appropriate amount of $Ca(NO_3)_2{\cdot}4H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ was heated while stirring until the solution transformed to the gel phase. The gel was then calcined at 750 °C for 30 min and then 0.8 g of the catalyst was heated to 750 °C and maintained at 750 °C for 30 min for the catalytic test. The catalyst was immediately added to a mixture of methanol and soybean oil to minimize absorption of moisture and carbon dioxide from the ambient air.

2.3. Transesterification procedure and analysis methods

Erlenmeyer flasks (25 mL) containing catalyst, soybean oil, methanol or ethanol, or a combination of the two alcohols, were prepared as batch reactors. For each batch, 10.0 g of soybean oil and a 10:1 molar ratio of alcohol:oil was used. Homogeneous catalysts (sodium methoxide or sodium ethoxide) dissolved in alcohol were used. Sodium methoxide weight percents to oil of 0.05% (equivalent 0.063% sodium ethoxide), 0.1% (equivalent 0.126% sodium ethoxide), and 0.3% (equivalent 0.38% sodium ethoxide) were used, respectively. The alcohol contained in the homogeneous catalyst solution was included in the calculation of reaction mixture composition (methanol to oil ratio).

The amount of heterogeneous catalyst used was 0.8 g (8.0%) for the $CaO–La_2O_3$ catalyst and 3.3 g for the resin catalyst, respectively. The reaction temperature was 64 °C for both homogeneous and heterogeneous ($CaO–La_2O_3$) catalyzed reactions. The reaction temperature of 54 °C was used for the reaction catalyzed with the resin catalyst due to the temperature limitation of the resin catalyst. All batches were agitated at a shaking speed of 450 rpm.

Before the reactions were initiated, the flasks containing reaction mixtures were first heated at the reaction temperature for 20 min at 0 rpm in a shaking bath (Series 25 incubator, New Brunswick Scientific Co.). Generally, the reaction mixture was composed of two immiscible phases (alcohol and oil). The reaction was considered to have started when shaking began at 450 rpm. In order to measure the alkyl-ester yield, 0.7 mL of the reacted mixture was taken from the reactor and then pipetted into vials containing 0.2 mL of aqueous HCl solution (1.0 M) to quench the reaction. The vials were then placed in a hood. The product was dried to remove alcohol and to separate glycerol phase from the FAME phase by letting an air stream flow over the opened vials for more than 2 h. At this point, the top ester phase was clearly separated from the glycerol phase at the bottom of the vials. The glycerol phase was carefully removed from the vials with a pipette (200 μL) and dried an additional 24 h in a hood to remove alcohol and glycerol from the FAME phase. The top phase in the vials, containing the esters and unreacted triglycerides and partially reacted mono- and di-glycerides, was sampled for GC–MS analysis. The biodiesel yield (%) was defined as the weight percent of esters recovered divided by the theoretical weight of esters that should have resulted from all of the mono, di, and triglycerides in the original oil feed being converted to esters. The amount of fatty acid esters in the samples were quantified using a GC–MS (Clarus 500