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Short Communication

Production of biodiesel fuel from canola oil with dimethyl carbonate using an active sodium methoxide catalyst prepared by crystallization



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HIGHLIGHTS

- A novel method for the production of biodiesel using dimethyl carbonate is proposed.
- The catalytic activity was increased by the preparation of fine NaOCH₃ powders.
- The amount of dimethyl carbonate and catalyst required was dramatically decreased.
- A conversion greater than 95% was obtained at 65 °C under atmospheric pressure.

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ABSTRACT

In this study, a novel method for the production of biodiesel under mild conditions using fine particles of sodium methoxide formed in dimethyl carbonate (DMC) is proposed. Biodiesel is generally produced from vegetable oils by the transesterification of triglycerides with methanol. However, this reaction produces glycerol as a byproduct, and raw materials are not effectively utilized. Transesterification with DMC has recently been studied because glycerol is not formed in the process. Although solid-state sodium methoxide has been reported to be inactive for this reaction, the catalytic activity dramatically increased with the preparation of fine catalyst powders by crystallization. The transesterification of canola oil with DMC was studied using this catalyst for the preparation of biodiesel. A conversion greater than 96% was obtained at 65 °C for 2 h with a 3:1 M ratio of DMC and oil and 2.0 wt% catalyst.

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1. Introduction

The worldwide use of biodiesel fuel has increased over the last few decades because of environmental benefits of biodiesel. Many studies have been performed, and many review papers have been published on the subject. Raw materials of biodiesel are usually vegetable oils, which contain fatty acid triglycerides. Triglycerides are transformed to fatty acid methyl esters (FAMES) by transesterification with methanol. Although various reaction methods have been proposed, the main industrial production method is the alkali-catalyzed homogeneous process. In this method, catalysts such as NaOH, KOH, and NaOCH₃ are dissolved in methanol and used for the reaction. The methanolysis of triglycerides yields glycerol, which does not homogeneously mix with biodiesel fuels.

Approximately 10 wt% of the product mixture produced is glycerol. The amount of glycerol byproduct has increased with an increase in biodiesel production, which has led to a decrease in the price of purified glycerol (Ayoub and Abdullah, 2012). In the alkali-catalyzed homogeneous process, the glycerol produced contains alkali metals. In small-scale plants, the glycerol byproduct cannot be utilized, and is treated as industrial waste. In large-scale plants, the glycerol byproduct can potentially be utilized as a chemical raw material. However, this requires purification processes in addition to glycerol conversion. If glycerol is not formed as a byproduct in biodiesel plants, the biodiesel production process will be much more efficient.

It was reported that a methyl ester phase was obtained without glycerol production by using dimethyl carbonate (DMC) instead of methanol (Fabbri et al., 2007). The methyl ester phase of DMC–biodiesel contains fatty acid glycerol carbonate monoesters (FAGCs) in addition to FAMES. Glycerol carbonate and glycerol dicarbonate are

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also formed as byproducts but only in low concentrations (Fabbri et al., 2007). Since FAGCs are dissolved in the methyl ester-phase, the product can be used as fuel without separation (Notari and Rivetti, 2004).

Several studies have been published on transesterification using DMC by supercritical, enzymatic, and chemical methods. The supercritical method is advantageous because transesterification rapidly occurs in a non-catalytic manner. Although this method was originally developed for the reaction with methanol, DMC can be used instead of methanol (Ilham and Saka, 2009, 2010, 2011, 2012; Tan et al., 2010). However, high temperatures (above 300 °C) and pressures (above 15 MPa) are required for this method. As pointed out by Ang et al. (2014), higher energy consumption is the weakness of supercritical technology. In addition, the higher cost of reactor vessels is another disadvantage. The enzyme-catalyzed reaction can be performed under mild conditions. Immobilized lipase Novozym 435 has been used as a catalyst in the enzyme-catalyzed transesterification using DMC (Su et al., 2009; Zhang et al., 2010b; Seong et al., 2011; Min and Lee, 2011; Jung et al., 2012; Lee et al., 2013; Go et al., 2013; Gharat and Rathod, 2013; Jo et al., 2014). The optimum reaction temperature was in the range between 40 and 60 °C. The main limitation of this method is the long reaction time (Tan et al., 2010). Therefore, the reactor size must be increased for industrial production, and a catalyst amount greater than approximately 10 wt% is required.

In the conventional process for producing MeOH-biodiesel, alkali catalysts are typically used. If these catalysts can be used for the production of DMC-biodiesel, the existing facilities are available, and production cost can be reduced. Zhang et al. (2010a) used KOH to lower the production cost for future industrial applications. A maximum FAME yield of 96.2% was obtained when the reaction time was 8 h, catalyst amount was 8.5 wt% (based on the oil weight), molar ratio of DMC to palm oil was 9:1 (0.96 w/w), and temperature was 75 °C. The method required more KOH than the conventional method to produce MeOH-biodiesel, and the reaction time was longer. Panchal et al. (2013) also reported the activity of the KOH catalyst, and they achieved a maximum conversion of 96% when the temperature was 90 °C, reaction time was 6 h, catalyst amount was 4 wt%, and weight ratio of DMC to oil was 3:1, meaning that the molar ratio of DMC to oil was approximately 30:1. Thus, the molar ratio was about 10 times larger than that used by Zhang et al. (2010a). Fabbri et al. (2007) used NaOCH₃ (30% in methanol) for the transesterification of soybean oil with DMC, and the conversion was greater than 99%. The reaction temperature was 90 °C, reaction time was 6 h, catalyst amount was 0.83 wt%, and the molar ratio of DMC to oil was approximately 8 (DMC/oil, 0.81 w/w).

In previous studies using alkali catalysts, a high yield of FAMES has not been achieved under mild conditions such as those used in the production of MeOH-biodiesel. Those conditions typically involve 1–2 wt% alkali catalysts, reaction times of approximately 2 h, reaction temperatures below 60 °C, and a low ratio of DMC to oils. However, these mild reaction conditions will be important for utilizing existing production facilities and suppressing the consumption of DMC and catalysts. In this study, a new catalyst preparation method was proposed for NaOCH₃. The effects of reaction conditions on the conversion of oil were studied to obtain the optimum conditions.

2. Experimental

Fresh commercial canola oil was used as a reactant. The main components of this oil are triacylglycerol esters of oleic acid and linoleic acid with glycerol. Anhydrous methanol, DMC, NaOCH₃, and other chemical reagents were purchased from Kanto Kagaku Co. (Tokyo, Japan).

The reaction was performed in a 100 mL glass batch reactor equipped with a heat exchanger to condense and return the DMC vapor to the reactor. The reaction temperature was maintained at a prescribed temperature using a constant temperature bath, and the reactants were stirred by a magnetic stirrer (600 rpm). The molar ratio of DMC to vegetable oil was varied from 2:1 to 10:1. Since the average molecular weight of vegetable oil was not obtained, the molecular weight of the oil was approximated by 885.4 g, weight of triolein. When the ratio was 2:1, the amount of DMC was two times the stoichiometric value of the reaction of FAGC formation. The catalyst amount was varied from 1.0 to 15 wt% based on oil weight. The reaction time was 2 h for each batch operation under standard conditions.

When chemical reagents were used as catalysts, powdered reagents were added to the reactant mixtures since the reagents were not dissolved in DMC. In this study, a new catalyst preparation method using crystallization was proposed. In this case, the catalyst was prepared as follows. NaOCH₃ was dissolved in methanol by stirring at room temperature. Subsequently, DMC was added to the solution. Since NaOCH₃ is not soluble in DMC, NaOCH₃ crystallized as more DMC was added to the solution. The fine particles of NaOCH₃ were suspended in the single-phase solution of methanol and DMC. After DMC was added, methanol was removed by vacuum distillation at room temperature. The pressure was carefully controlled to avoid bumping and was slowly reduced when the pressure was below 100 mbar. After methanol was removed, the slurry of DMC and NaOCH₃ was mixed with vegetable oil and transesterification was performed.

After the reaction, the solid catalyst separated from the liquid phase was analyzed by a high-performance liquid chromatography system (Shimadzu Corporation, Kyoto, Japan) equipped with a gel permeation chromatography column (GPC-801, Shimadzu Corporation). The acid value was determined by titration with KOH and the water content was measured using the Karl Fisher titration method.

3. Results and discussion

3.1. Powdered alkali catalyst

Because KOH and NaOCH₃ are generally used for the transesterification reaction with methanol, they were tested as catalysts in this study. When 8.5 wt% of KOH catalyst was used, the conversion was only 2% after 4 h at 85 °C with a 10:1 M ratio of DMC to oil. This result shows that the amount of KOH and/or methanol must be substantially increased to achieve high conversion. However, it is unrealistic to significantly increase the amount of catalysts and methanol in industrial processes.

When NaOCH₃ (28% in methanol) was used, methanolysis proceeded since methanol was present in the reactant mixture, and glycerol was produced. To prevent glycerol formation, a heterogeneous reaction was performed using powdered NaOCH₃ purchased as a reagent. For the reaction, NaOCH₃ was added to the mixture of canola oil and DMC. The conversion of the oil was approximately 99% after 4 h. The molar ratio of DMC to oil was 10:1, the reaction temperature was 85 °C, and the catalyst amount was 8.5 wt%.

Fig. 1 shows the effect of catalyst amount on oil conversion when the ratio of DMC to oil was reduced to 3:1. To increase the conversion to approximately 100%, 15 wt% of the catalyst was required when the ratio of DMC to oil was 3:1. In the conventional production of biodiesel with methanol, the amount of alkali catalyst is usually below 2.0 wt%. This indicates that powdered NaOCH₃ is unsuitable for industrial use for the production of DMC-biodiesel because of its low activity.

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