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

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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 molar ratio of DMC and oil and 2.0 wt% catalyst.

Keywords: Transesterification; Biodiesel; Dimethyl carbonate; Sodium methoxide

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.

1 It was reported that a methyl ester phase was obtained without glycerol production by
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3 using dimethyl carbonate (DMC) instead of methanol (Fabbri et al., 2007). The methyl
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5 ester phase of DMC–biodiesel contains fatty acid glycerol carbonate monoesters
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7 (FAGCs) in addition to FAMEs. Glycerol carbonate and glycerol dicarbonate are also
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9 formed as byproducts but only in low concentrations (Fabbri et al., 2007). Since FAGCs
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11 are dissolved in the methyl ester-phase, the product can be used as fuel without
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13 separation (Notari and Ribetti, 2004).
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17 Several studies have been published on transesterification using DMC by supercritical,
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19 enzymatic, and chemical methods. The supercritical method is advantageous because
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21 transesterification rapidly occurs in a non-catalytic manner. Although this method was
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23 originally developed for the reaction with methanol, DMC can be used instead of
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25 methanol (Ilham and Saka, 2009, 2010, 2011, 2012; Tan et al., 2010). However, high
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27 temperatures (above 300 °C) and pressures (above 15 MPa) are required for this method.
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29 As pointed out by Ang et al. (2014), higher energy consumption is the weakness of
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31 supercritical technology. In addition, the higher cost of reactor vessels is another
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33 disadvantage. The enzyme-catalyzed reaction can be performed under mild conditions.
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35 Immobilized lipase Novozym 435 has been used as a catalyst in the enzyme-catalyzed
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37 transesterification using DMC (Su et al., 2009; Zhang et al., 2010a; Seong, 2011; Min
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39 and Lee, 2011; Jung, 2012; Lee et al., 2013; Go et al., 2013; Gharat and Rathod, 2013; Jo
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41 et al., 2014). The optimum reaction temperature was in the range between 40 °C and
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43 60 °C. The main limitation of this method is the long reaction time (Tan et al., 2010).
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45 Therefore, the reactor size must be increased for industrial production, and a catalyst
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47 amount greater than approximately 10 wt% is required.
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57 In the conventional process for producing MeOH–biodiesel, alkali catalysts are
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59 typically used. If these catalysts can be used for the production of DMC–biodiesel, the
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existing facilities are available, and production cost can be reduced. Zhang et al. (2010b) 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. (2010b). 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

1 Fresh commercial canola oil was used as a reactant. The main components of this oil
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3 are triacylglycerol esters of oleic acid and linoleic acid with glycerol. Anhydrous
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5 methanol, DMC, NaOCH_3 , and other chemical reagents were purchased from Kanto
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7 Kagaku Co. (Tokyo, Japan).
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10 The reaction was performed in a 100 mL glass batch reactor equipped with a heat
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12 exchanger to condense and return the DMC vapor to the reactor. The reaction
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14 temperature was maintained at a prescribed temperature using a constant temperature
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16 bath, and the reactants were stirred by a magnetic stirrer (600 rpm). The molar ratio of
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18 DMC to vegetable oil was varied from 2:1 to 10:1. Since the average molecular weight of
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20 vegetable oil was not obtained, the molecular weight of the oil was approximated by
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22 885.4 g, weight of triolein. When the ratio was 2:1, the amount of DMC was two times
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24 the stoichiometric value of the reaction of FAGC formation. The catalyst amount was
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26 varied from 1.0 to 15 wt% based on oil weight. The reaction time was 2 h for each batch
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28 operation under standard conditions.
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35 When chemical reagents were used as catalysts, powdered reagents were added to the
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37 reactant mixtures since the reagents were not dissolved in DMC. In this study, a new
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39 catalyst preparation method using crystallization was proposed. In this case, the catalyst
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41 was prepared as follows. NaOCH_3 was dissolved in methanol by stirring at room
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43 temperature. Subsequently, DMC was added to the solution. Since NaOCH_3 is not
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45 soluble in DMC, NaOCH_3 crystallized as more DMC was added to the solution. The fine
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47 particles of NaOCH_3 were suspended in the single-phase solution of methanol and DMC.
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49 After DMC was added, methanol was removed by vacuum distillation at room
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51 temperature. The pressure was carefully controlled to avoid bumping and was slowly
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53 reduced when the pressure was below 100 mbar. After methanol was removed, the slurry
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55 of DMC and NaOCH_3 was mixed with vegetable oil and transesterification was
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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 NaOCH_3 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 molar 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 NaOCH_3 (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 NaOCH_3 purchased as a reagent. For the reaction, NaOCH_3 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

1 wt%. This indicates that powdered NaOCH_3 is unsuitable for industrial use for the
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3 production of DMC–biodiesel because of its low activity.
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5 A high conversion was established by increasing the molar ratio of DMC to oil even
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7 when the amount of catalyst was reduced. In a previous study (Panchal et al., 2013), high
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9 conversion could be established by increasing the molar ratio of DMC to oil above 30
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11 when KOH was used. However, since DMC dissolves in FAMES and more energy is
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13 required to remove unreacted DMC from the produced fuels, the use of excessive
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15 amounts of DMC is undesirable.
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20 Usually the reaction rate can be increased by increasing reaction the temperature.
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22 However, the temperature could not be increased over 90 °C under atmospheric pressure,
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24 because the boiling point of DMC is 90 °C. Fabbri et al. (2007) mentioned that pure
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26 NaOCH_3 is inactive for transesterification with DMC because NaOCH_3 is solid and does
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28 not dissolve in vegetable oils and DMC. This may be the reason that there are very few
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30 reports concerning DMC–biodiesel production via alkali-catalyzed transesterification.
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37 **3.2 Crystallized catalyst**

38 **3.2.1 Preparation of catalyst by crystallization**

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40 The reaction rate of liquid–solid catalyst reactions generally increases with increasing
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42 surface area of solid catalysts. Therefore, reaction activity will be increased by producing
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44 very fine particles of NaOCH_3 . In this study, a fine powder of NaOCH_3 was prepared by
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46 the crystallization of NaOCH_3 after it was dissolved into methanol as described in the
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48 experimental section. The size of the crystallized catalyst was less than 10 μm , and the
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50 size of the powdered catalyst was between 40 and 300 μm .
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57 As shown in Fig. 1, the conversion after 2 h was only 33% for the unprocessed
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powdered catalyst when the molar ratio of DMC to oil was 3:1 and catalyst weight was 5 wt% at 85 °C. On the other hand, the activity of the crystallized catalyst was very high under the same conditions. The conversion after 1 h was approximately 100% even though the temperature was decreased to 65 °C. Thus, catalytic activity was dramatically increased by the crystallization method.

3.2.2 Effects of molar ratio of DMC to oil

The conversion increases when the ratio of DMC to oil is increased. Fig. 2 (a) shows the change in conversion when the catalyst weight was 1.5 wt% at 65 °C. As described above, one of the purposes of this study was to reduce excessive amounts of DMC. Therefore, the molar ratio range was set below 4:1. This figure shows that the conversion increased with the molar ratio. Oil conversion was more than 90% after 1.5 h when the molar ratio was 4:1. Considering that the catalyst amount was 1.5 wt%, the activity of the crystallized catalyst was sufficient.

3.2.3 Effect of catalyst amount

It is better to decrease the catalyst weight for practical use from a cost standpoint. The effect of catalyst weight on the conversion was studied. The maximum catalyst amount was 5 wt% in the experiment. The molar ratio of DMC to oil was 3:1, and the reaction temperature was 65 °C. As shown in Fig. 2 (b), the conversion increased with increasing catalyst weight, and the conversion was more than 96% after 2 when the catalyst amount was more than 2.0 wt%.

3.2.4 Effect of temperature

The effect of temperature on the conversion was evaluated when the catalyst amount was 1.5 wt% and the molar ratio of DMC to oil was 3:1. Since the intrinsic reaction rate generally increased with temperature, the conversion at the initial stage of the reaction increased with reaction temperature. However, the conversion after 1 h did not increase with temperature when the reaction temperature was 85 °C. On the other hand, when the reaction temperature was 45 °C, the conversion gradually increased with time and exceeded the conversion at 85 °C after 6 h.

A liquid phase was observed inside the upper part of the reactor and condenser. Since the amount of this condensed liquid increased with reaction temperature, this must be DMC that escaped as vapor from the reaction solution. Therefore, the DMC concentration in the liquid phase decreased with increasing temperature, and consequently reduced the reaction rate at higher temperatures. Therefore, high temperature near the boiling point of DMC (90 °C) was unsuitable to establish high conversion of oils when the reaction was performed under atmospheric pressure in an open system. Considering these results, the optimum conditions were a molar ratio of DMC to oil of 3:1, 2.0 wt% catalyst, and 65 °C.

3.2.5 Effects of moisture content and acid value

NaOCH_3 forms methanol and NaOH by reaction with water. As described above, since the catalytic activity of NaOH is very small, this reaction is undesirable. However, the raw material usually contains a small amount of water in addition to free fatty acids (FFAs). Therefore, the effects of moisture content and acid value on the conversion were measured with 2.0 wt% catalyst.

The results showed that the conversion was not affected by the moisture content when it was below 0.1 wt%. In addition, when the acid value was lower than 2.0 mg KOH/g oil,

the effect of FFAs was insignificant. The conversion was above 96% when moisture content was 0.13 wt% and the acid values were 2.0 mg KOH/g oil.

3.2.6 Deactivation of NaOCH₃ catalyst

Since the NaOCH₃ catalyst is in the solid state, it can be separated from the liquid mixture by filtration after the reaction. The activity of the used catalyst was measured to confirm whether the catalyst can be used repeatedly. The reactions using the fresh catalyst were performed using 1.5 wt% of the crystallized NaOCH₃ catalyst at 85 °C for 2 h and at 45 °C for 5 h. The ratio of DMC to oil was 3:1. After filtration under reduced pressure, the solid on the filter was collected using a spatula and used for a second reaction. The temperature of the second batch reactions was 85 °C in both cases.

The conversions of the reactions using the used catalyst were very low. This result means that the activity of the used catalyst sharply decreased during the first reaction regardless of the difference in the reaction temperature, and catalyst deactivation cannot be prevented by decreasing the reaction temperature.

On the other hand, when the used catalyst was dissolved in methanol and crystallized by a method proposed in this study, only a small decrease in catalytic activity was observed. Since the color of the catalyst changed from white to light brown during the reaction, deactivation could be caused by the adsorption of other components on the catalyst surface or transformation of NaOCH₃ in contact with the reactant mixtures.

4. Conclusions

Fine and active catalyst particles were formed by the crystallization of NaOCH₃ to produce biodiesel from canola oil and DMC. This method allowed the reaction to occur under mild conditions, but the catalyst could not be used repeatedly. Methanol

conversion was above 96% when the catalyst amount was 2.0 wt%, the molar ratio of DMC to oil was 3:1, and the reaction temperature was 65 °C. The conditions to establish high conversion were not affected by moisture when it was below 0.13 wt% or the acidic value when it was below 2.0 mg KOH/g oil.

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Figure captions

Fig. 1. Effect of catalyst amount on oil conversion for powdered sodium methoxide catalyst. Molar ratio of DMC to oil: 3, temperature: 85 °C.

Fig. 2. Effect of molar ratio of DMC to oils on oil conversion (a), and effect of catalyst amount on conversion (b) for crystallized sodium methoxide catalyst.

Figures

Fig. 1 Effect of catalyst amount on the conversion of oil for powdered sodium methoxide catalyst. Molar ratio of DMC to oil: 3, temperature: 85°C.

Fig. 2 Effect of molar ratio of DMC to oils on the oil conversion (a), and effect of catalyst amount on the conversion (b) for crystallized sodium methoxide catalyst.