Optimization of Supercritical Dimethyl Carbonate Method for Biodiesel Production

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Abstract: Biodiesel could be produced from triglycerides and dimethyl carbonate, instead of the conventional methanol, in this non-catalytic supercritical dimethyl carbonate method. It was demonstrated that, supercritical dimethyl carbonate method successfully converted triglycerides as well as fatty acids to fatty acid methyl esters (FAME) with glycerol carbonate, a higher value by-product compared to the conventional glycerol. The FAME are high in yield, comparable with supercritical methanol method, and satisfy the international standard for use as biodiesel fuel. In this study, therefore, optimization of supercritical dimethyl carbonate method was discussed to include all important key parameters such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the FAME yield, thermal decomposition, degree of denaturation, tocopherol content, oxidation stability and fuel properties. The optimum condition for supercritical dimethyl carbonate method was determined at 300ºC/20MPa/20min/42:1 molar ratio of dimethyl carbonate to oil to have satisfactory yield of FAME at 97.4wt%. Conclusively, this study showed the importance to address all those key parameters in order to produce high quality biodiesel from supercritical dimethyl carbonate method.

Keywords: biodiesel; optimization; dimethyl carbonate; non-catalytic; supercritical process.
1. Introduction

At present, homogenous alkali-catalytic transesterification process is the most common technology used in the industry to produce fatty acid methyl esters (FAME) or generally known as biodiesel, from refined vegetable oil and methanol [1]. This process requires high purity raw materials as feedstock, and separation of the catalyst from the biodiesel at the end of the process is inevitable. Without pre-treatment, this method is not applicable for feedstock with high content of free fatty acids and water, such as the low-grade non-edible oils and waste cooking oils or fats [2]. The catalytic process also requires post-reaction separation of product, by-product and catalyst from the obtained two liquid phases. Most of the catalyst is normally found in the lower by-product layer of glycerol and, therefore, must be removed to produce pure glycerol [3,4]. As biodiesel production grows rapidly in recent years, the overproduction of crude glycerol as the by-product in this process has lead to an oversupply of glycerol in the market [5]. Thus, new non-catalytic production methods of biodiesel without producing glycerol are worth to be explored.

Transesterification under supercritical conditions as means to produce biodiesel in a non-catalytic manner has long been introduced with the establishment of the non-catalytic supercritical methanol method [6-11]. This introduction has triggered many further research works utilizing this method with wide range of raw materials or with certain improvements and modifications in the following years [12-17].

On this line of study, non-catalytic supercritical dimethyl carbonate method for biodiesel
production has been developed previously in one-step [18] and two-step processes [19,20]. By-product such as glycerol carbonate from these processes was found to have higher value than glycerol that is produced in the conventional biodiesel production [18-21]. In addition, catalytic [22] and enzymatic routes [23-25] to produce biodiesel using dimethyl carbonate as reactant have also been studied by some other researchers.

However, it is very crucial to ensure that all the key parameters in the supercritical dimethyl carbonate are properly determined in order to optimize it. Many optimization studies were introduced for biodiesel production [26-28], particularly by non-catalytic supercritical methods, but most of those did not include and describe all important points to produce high quality biodiesel.

In this study, therefore, all important parameters for biodiesel production by non-catalytic supercritical dimethyl carbonate method have been discussed such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, FAME yield, degree of denaturation, thermal decomposition, oxidation stability and fuel properties. Those key parameters were investigated to ensure that only high quality biodiesel, which fulfills the technical regulations and respects the engine technologies [29,30], could be produced by non-catalytic supercritical dimethyl carbonate method.

2. Materials and Methods

2.1 Materials

A commercial refined rapeseed oil supplied by Nacalai Tesque Inc. (Japan), whose fatty acid composition is presented in Table 1, was used in this study. GC analysis for the fatty acid composition
was done in accordance to the Standard Method No. 2.3.1 and 2.4.2.1 [31]. Free fatty acid content of the oil was lower than 1wt%. Dimethyl carbonate (Tc=275°C, Pc=4.63 MPa) was used as the solvent and glycerol carbonate, glyoxal, various authentic compounds of oleins, methyl esters and fatty acids such as palmitic, stearic, oleic, linoleic, and linolenic acids were all obtained from Nacalai Tesque Inc. (Japan) and Wako Pure Chemical Industries Ltd. (Japan), all of which were of the highest purity available.

2.2 Experimental Methods

To study the effect of reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil and thermal stability of FAME, the supercritical biomass conversion system developed previously in our laboratory which includes batch-type and flow-type were the ones utilized. For studies utilizing batch-type, a reaction vessel made of Inconel-625 was charged with dimethyl carbonate and rapeseed oil at various molar ratios and subsequently immersed in the molten tin bath heated at the designated range of temperature and pressure tested. After a fixed reaction time, it was transferred into the water bath to quench the reaction immediately.

In the flow-type reaction system, where temperature and pressure could be constantly controlled, tubular reaction vessel made from Hastelloy C-276 was used and the flow capacity of this system is up to 600mL/h. The working temperature and pressure employed in this study ranged in 270-400°C and 10-40MPa, respectively, all of which are monitored and controlled by thermocouple and pressure gauge. It should be noted, however, that all the results presented are the ones from
flow-type system. Residence time was estimated by dividing the volume of the flow-type reaction vessel tube by the volumetric flow rate at the given conditions [31]. Batch-type was utilized only for initial and preliminary runs to check for the potential of the process. Details have been described in previous works [7-11]. Products from both steps were, then, analyzed by gel permeation chromatography (GPC) (GF-310HQ, 40°C, 1ml/min, mobile phase: acetone, RID 10A) and high performance liquid chromatography (HPLC) (Cadenza CD-C18, 40°C, 1ml/min, mobile phase: methanol, RID 10A). Glycerol carbonate was analyzed by High Performance Liquid Chromatography (HPLC) (Column: Ultrahydrogel 120, oven temperature: 40°C, flow: 1mL/min, mobile phase: water, detector: RID 10A) while water content was measured by Karl-Fischer titration method in accordance to Standard Method No. 2.1.3.4 [32]. For the calibration curve of the authentic standard products, triolein, monoolein, diolein, glycerol carbonate and methyl oleate were used. All sets of experiments were made to at least triplicate for confirmation of the yields by utilizing 42:1 molar ratio of dimethyl carbonate to oil, although not treated statistically. The yield of FAME in weight percent as presented in this study refers to the percentage of yields conversion recovered based on theoretical yield.

2.3 FT-IR Analysis to Detect Isomerization in Biodiesel

As main components of biodiesel, five kinds of FAME (methyl palmitate (16:0), methyl stearate, (18:0), methyl oleate (18:1), methyl linoleate (18:2) and methyl linolenate (18:3)) were, respectively, exposed to supercritical dimethyl carbonate, as previously studied in supercritical methanol [33]. The unsaturated FAME used in this study have only cis-type double bonds since in nature, unsaturated
fatty acids are all in cis-type only. The exposure was made by placing 100 mg of the FAME in 4.9 mL of dimethyl carbonate using a 5 mL batch-type reaction vessel made of Inconel-625 at temperatures between 270°C and 380°C with critical pressures higher than the critical pressure of dimethyl carbonate (Pc=4.63 MPa) for a designated reaction time. The reaction vessel is equipped with gas valve, in which air was substituted by N₂ (>99.999%) in advance utilizing the gas charging unit [31] to ensure that the reaction pressure will be constantly at 20MPa during the reaction.

After the exposure, the obtained product was directly analyzed by HPLC, as described beforehand. The remaining sample was then evaporated at 70°C for 30 min to remove dimethyl carbonate on a rotary evaporator and analyzed by Fourier transform infrared (FT-IR) spectrometry (Shimadzu, FT-IR 8300).

2.4 Evaluation of Tocopherol Content

The content of tocopherol in the biodiesel produced by supercritical dimethyl carbonate, as one of the main natural antioxidants in vegetable oils [34], was also studied by the HPLC consisting of the column (Asahipak ODP-50, 25 cm in length, 4.6 mm in inner diameter, Shodex Co.) and fluorescence detector (RF-10AXL, Shimadzu) operated under the same conditions as mentioned before. This is in accordance to the Standard Methods for the Analysis of Fats, Oils and Related Materials 2.4.10 and 2.5.2 [32].

2.5 Evaluation of Fuel Properties

FAME being produced were also subjected to various fuel properties tests to comply with
international standards [35-37]. For kinematic viscosity, the test was made at 40°C on Automatic
Kinematic Viscosity Measuring System AKV-201 in accordance to ASTM D445. Carbon residue was
measured by Micro Carbon Residue Tester ACR-M3 in accordance to ASTM D4530. The pour point
and cloud point were measured by a Mini Pour/Cloud Point Tester MPC-102 covering a range from
-60°C to 51°C. This tester is in accordance with ASTM D2500 and ASTM D6749. Automated Cold
Filter Plugging Point Tester AFP-102 was used to measure cold filter plugging point in accordance to
ASTM D637, while Pensky-Martens Closed Cup Automated Flash Point Tester APM-7 was used to
determine the ignition point. All of these certified instrumentations [35] were from TANAKA
Scientific Ltd., Tokyo. Oxidation stability was also studied in accordance with EN 14112 on Rancimat
743 (Methrom, Herisau, Switzerland) [36]. For analyses of acid number, iodine value, the contents of
esters, monoglyceride, diglyceride, triglyceride, total glycerol and water, all were made according to
the European Standard Methods [36].

3. Results and Discussion

3.1 Non-catalytic Supercritical Dimethyl Carbonate Method

Non-catalytic supercritical dimethyl carbonate method was first introduced by Ilham and
Saka [18], based on the direct transesterification of triglycerides with dimethyl carbonate at the
condition of 350°C/20MPa [18]. Without any catalyst applied, triglycerides (rapeseed oil) could be
converted to FAME with glycerol carbonate and more than 94wt% yield of FAME could be obtained
after 12 min reaction at 350°C/20MPa. The FAME yield is comparable with the supercritical methanol
method, by taking the difference in reaction pressure for supercritical methanol method at 350°C/43MPa into consideration [7].

Additionally, to achieve a milder reaction condition, the two-step supercritical dimethyl carbonate method has been explored [19-21]. Details on reaction schemes, by-products, advantages and drawbacks of those methods described above have been discussed earlier [18-21]. Herewith in this study, a thorough outlook on all important key parameters to optimize non-catalytic supercritical dimethyl carbonate method was investigated for high quality biodiesel production.

3.2 Effect of Temperature and Pressure on FAME Yield

Temperature and pressure are crucial parameters in supercritical dimethyl carbonate method because they allow the solvent properties of dimethyl carbonate to be adjusted [18]. Fig. 1 shows the effect of temperature on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at different reaction pressures. Under lower reaction pressures (5MPa and 10MPa) as represented in Figs. 1a and 1b, the yields of FAME are seen not to increase proportionately with increase of temperatures. However, It should be noted here that this is not due to the low reactivity of the reactions done at higher temperatures. Careful observation in the area before 20min in Figs. 1a and 1b, showed that an increase of temperature leads to acceleration of the reactivity, leading to higher yield of FAME, respectively.

The low yields of FAME from reactions done at higher temperature after 20min in Figs. 1a and 1b are mostly due to the decomposition of dimethyl carbonate as reactant at low reaction pressures.
Interestingly, such decomposition of dimethyl carbonate could not be detected at higher reaction pressures. Concomitantly, high FAME yields could be obtained from reactions at high temperatures and pressures although longer treatment time (>30min) leads to thermal deterioration, shown in Figs. 1c and 1d. This decomposition phenomenon of dimethyl carbonate at lower reaction pressures is expected to be especially unique to supercritical dimethyl carbonate method due to the thermodynamic properties of dimethyl carbonate itself.

Anderson et al. [38] in their study showed that at low pressure condition (0.2MPa), dimethyl carbonate decomposes to carbon dioxide and methanol at reaction temperatures in a range between 127°C and 149°C. To further investigate this alleged possible decomposition of dimethyl carbonate at low reaction pressure, it was subjected to high temperature (≥270°C) and various pressures at supercritical condition, as presented in Fig. 2. It could be seen that dimethyl carbonate tends to decompose at lower reaction pressures (5MPa and 10MPa), while stable at higher pressures (20MPa and 40MPa), when treated for 30min. These findings were further supported by an earlier findings by Cross et al. [39], showing that dimethyl carbonate does not decompose at temperatures up to 390°C, provided high pressure is employed. This phenomenon might be related to the cage effect of the solvent [40], explaining the enhancement of solvent reaction rate at high temperature and pressure.

The influence of reaction pressure on supercritical dimethyl carbonate method has also been investigated in Fig. 3. At a constant temperature of 300°C, this variable was found to show a considerable impact on the reaction yield, especially if low reaction pressure was employed. The
FAME yield was only 40wt% at 5MPa and increased to 78wt% at 10MPa after 30min treatment. An additional pressure increases had a positive effect on the FAME yield to be more than 96wt% for both 20MPa and 40MPa. However, as in Fig. 3, this is changed if the treatment time has been prolonged to be 60min due to the thermal decomposition. Previous findings also supported this alleged statement [7-9]. These results presented beforehand showed the importance to describe temperature and pressure together in a specific reaction time for optimizing a supercritical process.

3.3 Effect of Molar Ratios and Reaction Time on FAME Yield

One of the most important parameters affecting supercritical dimethyl carbonate method is the molar ratio of dimethyl carbonate to oil. Stoichiometrically, 3 moles of dimethyl carbonate are required to react with 1 mole of triglycerides. In practice, however, excess amount of dimethyl carbonate is needed to drive the reaction in favor of the product in producing higher yield of FAME. In supercritical dimethyl carbonate, as more dimethyl carbonate is used, higher FAME yield can be obtained, but eventually a plateau region is reached where more dimethyl carbonate does not help to increase the reaction rate. The point for esterification was found at the molar ratio of 14, while for transesterification, the optimum molar ratio was 42. This result is in good agreement with previous finding [19], showed a similar trend with supercritical methanol [7-9] and suggested that high molar ratio of dimethyl carbonate to oil helps to facilitate the batch and flow-type supercritical dimethyl carbonate processes for high yield of FAME.

As presented in Figs. 1 through 3, supercritical dimethyl carbonate method is best to be
operated at high temperature and high pressure with high molar ratio of dimethyl carbonate to reach the optimum yield in a short reaction time. The ideal range of reaction time for supercritical dimethyl carbonate method is determined to be less than 30 min as in Fig. 3 in order to prevent potential thermal deterioration of the FAME.

3.4 Thermal Stability of FAME in Supercritical Dimethyl Carbonate

In order to study the thermal stability of the biodiesel, individual FAME itself was evaluated for its stability against an exposure to supercritical dimethyl carbonate method at various exposure conditions. It can be clearly seen in Figs. 4a and 4b that saturated FAME, methyl palmitate (16:0) and methyl stearate (18:0), are stable and recovered quantitatively at 300ºC/20MPa. However, when temperature rises up to 350ºC/20MPa, they were becoming unstable and slightly decomposed by increasing exposure time, with approximately 95 wt% in yield after 60 min.

For unsaturated FAME, however, decomposition behavior was more severe. In Fig. 4c, methyl oleate (18:1) was stable at 300ºC/20MPa as observed for saturated FAME in Figs. 4a and 4b, but gradually became unstable with increase in temperature and exposure time. In the case of methyl linoleate (18:2), a monotonous decrease was getting more obvious with increase in temperature as shown in Fig. 4d. For example, at 350ºC/20MPa, approximately 85 wt% of methyl linoleate was only recovered after a 30 min exposure.

The condition is a little bit different for methyl linolenate (18:3) in Fig. 4e, where the decomposition was significant even at 300ºC/20MPa and with increase of exposure time, the
decomposition is seen to be worst. From these results, it was found that poly-unsaturated FAME are especially vulnerable to thermal decomposition when compared with mono-unsaturated and saturated ones. However, at the temperature of 300ºC/20MPa and preferably below, all FAME including the poly-unsaturated FAME were found to be stable as exposed to supercritical dimethyl carbonate method.

3.5 Isomerization (Denaturation) of Unsaturated FAME

Fig. 5 shows FT-IR spectra of various FAME treated in supercritical dimethyl carbonate method at different reaction conditions. As shown in Fig. 5a, without any treatment, there exists a broad absorption peak for cis-type C=C at wavenumber of 690 cm⁻¹, representing the original condition for unsaturated FAME in nature. In Fig. 5b, although various FAME were treated at 300ºC/20MPa for 30 min, no significant changes could be observed. Similar observation could be seen when FAME was treated at 270ºC/20MPa for 30 min (Data not presented). King [41], in his findings also showed no fatty acids isomerization at temperatures below 300 ºC.

On the other hand, after the exposure at 350ºC/20MPa and 380ºC/20MPa for 30 min, absorption peaks for cis-type C=C and (CH₂)₄ skeleton tremendously decreased for poly-unsaturated FAME, while an absorption peak for trans-type C=C appeared for methyl linoleate (18:2) and methyl linolenate (18:3). Data for 380ºC/20MPa is depicted in Fig. 5c.

The cis- to trans- isomerization of FAME, as shown in Fig. 5c, may have a negative effect on cold flow properties of biodiesel, since trans-isomer generally has higher melting point than
cis-isomer [42,43]. A difference between cis-type and trans-type methyl esters may be reflected in the cold flow properties. Therefore, the effect of cis- to trans- isomerization of FAME on its cold flow properties is important to be monitored, in order to prevent its denaturation [33].

3.6 Tocopherol Content and Oxidation Stability

As a main natural antioxidant in vegetable oils, the tocopherols play an important role in preventing oxidation in biodiesel. Rapeseed oil in its crude form contains mostly α- (5,7,8- trimethyl) and γ- (7,8- dimethyl) tocopherol, with the latter almost doubled in amount and greater in its potential as antioxidant [44]. The significant decrease in tocopherol content could, thus, affect the oxidation stability of biodiesel, reducing its capability to be stored for a longer time [34]. While tocopherols remained almost unchanged at milder conditions of 270°C/20MPa and 300°C/20MPa as presented in Fig. 6, it decreased drastically at severe temperatures of 350°C/20MPa and 400°C/20MPa, therefore, possibly deteriorating the oxidation stability of biodiesel in such high temperature conditions.

3.7 Fuel Properties of FAME from Supercritical Dimethyl Carbonate Method

To ensure that the FAME produced from supercritical dimethyl carbonate method are satisfactory as biodiesel, its fuel properties were studied, as presented in Table 2. The FAME were prepared from rapeseed oil treated in supercritical dimethyl carbonate method based on the optimized condition in this study (300°C/20MPa/20min/42:1 molar ratio of dimethyl carbonate to oil). The results were, then, compared with Japanese, EU and US standards [35-37]. Overall, the FAME from this method satisfied all requirements for international biodiesel standards except for the specification
stated for oxidation stability. As mentioned earlier, oxidation stability is an important parameter to prevent deterioration and could be improved with addition of antioxidant or by utilizing oils with lower levels of unsaturated fatty acids [34].

In the supercritical process, it should also be noted that the FAME could be reduced in quality, especially if a reaction takes place at a very severe temperature under low reaction pressure, i.e., 380°C/5MPa. Problems in quality could be resulted from the physical and chemical properties of FAME itself as the major components of biodiesel, as well as minor fuel constituents arising due to poor transesterification condition [45]. This emphasizes the necessity to evaluate the biodiesel properties according to the international standards and to define a supercritical condition by stating both temperature and pressure of the reaction. In addition, it is crucial to monitor the temperature and pressure due to the marked effect of supercritical condition on the stability of dimethyl carbonate itself. If dimethyl carbonate subjected to high temperature and high pressure below or beyond the real optimum supercritical condition, dimethyl carbonate could decomposes as in Fig. 2 to reduce the yield of both FAME and value-added by-products [18-21].

Recently, there have been increasing numbers of publications in the area of biodiesel production via non-catalytic supercritical process [12-17]. Among them are optimization studies [26-28] including an optimization study of supercritical dimethyl carbonate based on minimum sets of experiments and response surface methodology, suggesting 380°C as optimum temperature without describing any pressure [28]. It should be noted that thermal stability of FAME in supercritical
dimethyl carbonate is a major concern to produce high quality biodiesel. FAME including unsaturated members were stable in supercritical dimethyl carbonate at the range of 270°C/20MPa to 300°C/20MPa. However, at higher temperature and higher pressure, for example, 380°C/20MPa, they were partly decomposed thermally to reduce the FAME yield. It was apparent that the poly-unsaturated FAME (methyl linoleate, 18:2; methyl linolenate, 18:3) were also more vulnerable to thermal decomposition than the mono-unsaturated (methyl oleate, 18:1) and saturated esters (methyl palmitate, 16:0; methyl stearate 18:0). This is also in agreement with a previous study by Imahara et al. [33]. Therefore, it is important that any optimization studies lead to practical applications due to the possible thermal decomposition and deterioration of biodiesel properties, especially if the reaction was preceded at high temperature with low reaction pressure.

4. Conclusions

Based on these lines of evidence, this study stressed the importance to address all key parameters such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the FAME yield, degree of denaturation, thermal decomposition, oxidation stability and fuel properties towards optimization of supercritical dimethyl carbonate method for the production of high quality biodiesel. The optimum condition for supercritical dimethyl carbonate method is preferably in a controlled condition below 300°C and at high pressure more than 20MPa, reaction time less than 30min to achieve a high yield of FAME at over 97wt%. Conclusively, this optimization study is very important to produce high quality biodiesel from supercritical dimethyl carbonate method.

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References


Figure captions:

Fig. 1 Effect of temperature on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at different reaction pressures.

Fig. 2 Effect of various temperatures and pressures at supercritical conditions to dimethyl carbonate as a solvent after 30min treatment.

Fig. 3 Effect of pressure on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at 300ºC.

Fig. 4 Thermal stability of various FAME in supercritical dimethyl carbonate method under different temperatures at 20MPa.

Fig. 5 FT-IR spectra of various FAME as treated in supercritical dimethyl carbonate method at different reaction conditions a) Untreated FAME, b) 300ºC/20MPa/30min and c) 380ºC/20MPa/30min.

Fig. 6 Effect of temperature on tocopherol content in supercritical dimethyl carbonate method at 20MPa for 30min.
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Fig. 6 Effect of temperature on tocopherol content in supercritical dimethyl carbonate method at 20MPa for 30min
Table 1 Total fatty acid composition of rapeseed oil used in this study

<table>
<thead>
<tr>
<th>Fatty acid</th>
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<tr>
<td>Palmitic acid</td>
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<td>Oleic acid</td>
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<td>Linolenic acid</td>
<td>18:3, 11.2</td>
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\( ^a \) The former number represents the one of the carbons in the hydrocarbon chain while the latter the number of the double bond in fatty acid
<table>
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<tr>
<th>Properties</th>
<th>Method</th>
<th>Unit</th>
<th>FAME (Biodiesel)</th>
<th>International standards(^a)</th>
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\(^a\) JIS (2008); CEN (2003); ASTM (2007).

\(^b\) n.d., not detectable.