

Title	Optimization of supercritical dimethyl carbonate method for biodiesel production
Author(s)	Ilham, Zul; Saka, Shiro
Citation	Fuel (2012), 97: 670-677
Issue Date	2012-07
URL	http://hdl.handle.net/2433/156174
Right	© 2012 Elsevier Ltd.
Type	Journal Article
Textversion	author

1 Optimization of Supercritical Dimethyl Carbonate Method for Biodiesel Production

2
3 Zul Ilham and Shiro Saka*

4
5 Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto
6 University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

7 *Corresponding author: Tel/Fax: +81-75-753-4738; E-mail: saka@energy.kyoto-u.ac.jp
8

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

23
24 **Keywords:** biodiesel; optimization; dimethyl carbonate; non-catalytic; supercritical process.
25
26

27 **1. Introduction**

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

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

45 On this line of study, non-catalytic supercritical dimethyl carbonate method for biodiesel

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

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

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

61 **2. Materials and Methods**

62 *2.1 Materials*

63 A commercial refined rapeseed oil supplied by Nacalai Tesque Inc. (Japan), whose fatty acid
64 composition is presented in Table 1, was used in this study. GC analysis for the fatty acid composition

65 was done in accordance to the Standard Method No. 2.3.1 and 2.4.2.1 [31]. Free fatty acid content of
66 the oil was lower than 1wt%. Dimethyl carbonate ($T_c=275^\circ\text{C}$, $P_c=4.63\text{ MPa}$) was used as the solvent
67 and glycerol carbonate, glyoxal, various authentic compounds of oleins, methyl esters and fatty acids
68 such as palmitic, stearic, oleic, linoleic, and linolenic acids were all obtained from Nacalai Tesque Inc.
69 (Japan) and Wako Pure Chemical Industries Ltd. (Japan), all of which were of the highest purity
70 available.

71 *2.2 Experimental Methods*

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

79 In the flow-type reaction system, where temperature and pressure could be constantly
80 controlled, tubular reaction vessel made from Hastelloy C-276 was used and the flow capacity of this
81 system is up to 600mL/h. The working temperature and pressure employed in this study ranged in
82 $270\text{-}400^\circ\text{C}$ and $10\text{-}40\text{MPa}$, respectively, all of which are monitored and controlled by thermocouple
83 and pressure gauge. It should be noted, however, that all the results presented are the ones from

84 flow-type system. Residence time was estimated by dividing the volume of the flow-type reaction
85 vessel tube by the volumetric flow rate at the given conditions [31]. Batch-type was utilized only for
86 initial and preliminary runs to check for the potential of the process. Details have been described in
87 previous works [7-11]. Products from both steps were, then, analyzed by gel permeation
88 chromatography (GPC) (GF-310HQ, 40°C, 1ml/min, mobile phase: acetone, RID 10A) and high
89 performance liquid chromatography (HPLC) (Cadenza CD-C18, 40°C, 1ml/min, mobile phase:
90 methanol, RID 10A). Glycerol carbonate was analyzed by High Performance Liquid Chromatography
91 (HPLC) (Column: Ultrahydrogel 120, oven temperature: 40°C, flow: 1mL/min, mobile phase: water,
92 detector: RID 10A) while water content was measured by Karl-Fischer titration method in accordance
93 to Standard Method No. 2.1.3.4 [32]. For the calibration curve of the authentic standard products,
94 triolein, monoolein, diolein, glycerol carbonate and methyl oleate were used. All sets of experiments
95 were made to at least triplicate for confirmation of the yields by utilizing 42:1 molar ratio of dimethyl
96 carbonate to oil, although not treated statistically. The yield of FAME in weight percent as presented in
97 this study refers to the percentage of yields conversion recovered based on theoretical yield.

98 *2.3 FT-IR Analysis to Detect Isomerization in Biodiesel*

99 As main components of biodiesel, five kinds of FAME (methyl palmitate (16:0), methyl stearate,
100 (18:0), methyl oleate (18:1), methyl linoleate (18:2) and methyl linolenate (18:3)) were, respectively,
101 exposed to supercritical dimethyl carbonate, as previously studied in supercritical methanol [33]. The
102 unsaturated FAME used in this study have only *cis*-type double bonds since in nature, unsaturated

103 fatty acids are all in *cis*-type only. The exposure was made by placing 100 mg of the FAME in 4.9 mL
104 of dimethyl carbonate using a 5 mL batch-type reaction vessel made of Inconel-625 at temperatures
105 between 270°C and 380°C with critical pressures higher than the critical pressure of dimethyl
106 carbonate ($P_c=4.63$ MPa) for a designated reaction time. The reaction vessel is equipped with gas
107 valve, in which air was substituted by N_2 (>99.999%) in advance utilizing the gas charging unit [31] to
108 ensure that the reaction pressure will be constantly at 20MPa during the reaction.

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

113 *2.4 Evaluation of Tocopherol Content*

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

120 *2.5 Evaluation of Fuel Properties*

121 FAME being produced were also subjected to various fuel properties tests to comply with

122 international standards [35-37]. For kinematic viscosity, the test was made at 40°C on Automatic
123 Kinematic Viscosity Measuring System AKV-201 in accordance to ASTM D445. Carbon residue was
124 measured by Micro Carbon Residue Tester ACR-M3 in accordance to ASTM D4530. The pour point
125 and cloud point were measured by a Mini Pour/Cloud Point Tester MPC-102 covering a range from
126 -60°C to 51°C. This tester is in accordance with ASTM D2500 and ASTM D6749. Automated Cold
127 Filter Plugging Point Tester AFP-102 was used to measure cold filter plugging point in accordance to
128 ASTM D637, while Pensky-Martens Closed Cup Automated Flash Point Tester APM-7 was used to
129 determine the ignition point. All of these certified instrumentations [35] were from TANAKA
130 Scientific Ltd., Tokyo. Oxidation stability was also studied in accordance with EN 14112 on Rancimat
131 743 (Methrom, Herisau, Switzerland) [36]. For analyses of acid number, iodine value, the contents of
132 esters, monoglyceride, diglyceride, triglyceride, total glycerol and water, all were made according to
133 the European Standard Methods [36].

134 **3. Results and Discussion**

135 *3.1 Non-catalytic Supercritical Dimethyl Carbonate Method*

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

141 method, by taking the difference in reaction pressure for supercritical methanol method at
142 350°C/43MPa into consideration [7].

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

148 *3.2 Effect of Temperature and Pressure on FAME Yield*

149 Temperature and pressure are crucial parameters in supercritical dimethyl carbonate method
150 because they allow the solvent properties of dimethyl carbonate to be adjusted [18]. Fig. 1 shows the
151 effect of temperature on FAME yield from triglycerides treated in supercritical dimethyl carbonate
152 method at different reaction pressures. Under lower reaction pressures (5MPa and 10MPa) as
153 represented in Figs. 1a and 1b, the yields of FAME are seen not to increase proportionately with
154 increase of temperatures. However, It should be noted here that this is not due to the low reactivity of
155 the reactions done at higher temperatures. Careful observation in the area before 20min in Figs. 1a and
156 1b, showed that an increase of temperature leads to acceleration of the reactivity, leading to higher
157 yield of FAME, respectively.

158 The low yields of FAME from reactions done at higher temperature after 20min in Figs. 1a
159 and 1b are mostly due to the decomposition of dimethyl carbonate as reactant at low reaction pressures.

160 Interestingly, such decomposition of dimethyl carbonate could not be detected at higher reaction
161 pressures. Concomitantly, high FAME yields could be obtained from reactions at high temperatures
162 and pressures although longer treatment time (>30min) leads to thermal deterioration, shown in Figs.
163 1c and 1d. This decomposition phenomenon of dimethyl carbonate at lower reaction pressures is
164 expected to be especially unique to supercritical dimethyl carbonate method due to the thermodynamic
165 properties of dimethyl carbonate itself.

166 Anderson et al. [38] in their study showed that at low pressure condition (0.2MPa), dimethyl
167 carbonate decomposes to carbon dioxide and methanol at reaction temperatures in a range between
168 127°C and 149°C. To further investigate this alleged possible decomposition of dimethyl carbonate at
169 low reaction pressure, it was subjected to high temperature ($\geq 270^\circ\text{C}$) and various pressures at
170 supercritical condition, as presented in Fig. 2. It could be seen that dimethyl carbonate tends to
171 decompose at lower reaction pressures (5MPa and 10MPa), while stable at higher pressures (20MPa
172 and 40MPa), when treated for 30min. These findings were further supported by an earlier findings by
173 Cross et al. [39], showing that dimethyl carbonate does not decompose at temperatures up to 390°C,
174 provided high pressure is employed. This phenomenon might be related to the cage effect of the
175 solvent [40], explaining the enhancement of solvent reaction rate at high temperature and pressure.

176 The influence of reaction pressure on supercritical dimethyl carbonate method has also been
177 investigated in Fig. 3. At a constant temperature of 300°C, this variable was found to show a
178 considerable impact on the reaction yield, especially if low reaction pressure was employed. The

179 FAME yield was only 40wt% at 5MPa and increased to 78wt% at 10MPa after 30min treatment. An
180 additional pressure increases had a positive effect on the FAME yield to be more than 96wt% for both
181 20MPa and 40MPa. However, as in Fig. 3, this is changed if the treatment time has been prolonged to
182 be 60min due to the thermal decomposition. Previous findings also supported this alleged statement
183 [7-9]. These results presented beforehand showed the importance to describe temperature and pressure
184 together in a specific reaction time for optimizing a supercritical process.

185 *3.3 Effect of Molar Ratios and Reaction Time on FAME Yield*

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

197 As presented in Figs. 1 through 3, supercritical dimethyl carbonate method is best to be

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

202 *3.4 Thermal Stability of FAME in Supercritical Dimethyl Carbonate*

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

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

215 The condition is a little bit different for methyl linolenate (18:3) in Fig. 4e, where the
216 decomposition was significant even at 300°C/20MPa and with increase of exposure time, the

217 decomposition is seen to be worst. From these results, it was found that poly-unsaturated FAME are
218 especially vulnerable to thermal decomposition when compared with mono-unsaturated and saturated
219 ones. However, at the temperature of 300°C/20MPa and preferably below, all FAME including the
220 poly-unsaturated FAME were found to be stable as exposed to supercritical dimethyl carbonate
221 method.

222 3.5 Isomerization (Denaturation) of Unsaturated FAME

223 Fig. 5 shows FT-IR spectra of various FAME treated in supercritical dimethyl carbonate
224 method at different reaction conditions. As shown in Fig. 5a, without any treatment, there exists a
225 broad absorption peak for *cis*-type C=C at wavenumber of 690 cm⁻¹, representing the original
226 condition for unsaturated FAME in nature. In Fig. 5b, although various FAME were treated at
227 300°C/20MPa for 30 min, no significant changes could be observed. Similar observation could be seen
228 when FAME was treated at 270°C/20MPa for 30 min (Data not presented). King [41], in his findings
229 also showed no fatty acids isomerization at temperatures below 300 °C.

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

234 The *cis*- to *trans*- isomerization of FAME, as shown in Fig. 5c, may have a negative effect
235 on cold flow properties of biodiesel, since *trans*-isomer generally has higher melting point than

236 *cis*-isomer [42,43]. A difference between *cis*-type and *trans*-type methyl esters may be reflected in the
237 cold flow properties. Therefore, the effect of *cis*- to *trans*- isomerization of FAME on its cold flow
238 properties is important to be monitored, in order to prevent its denaturation [33].

239 3.6 Tocopherol Content and Oxidation Stability

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

248 3.7 Fuel Properties of FAME from Supercritical Dimethyl Carbonate Method

249 To ensure that the FAME produced from supercritical dimethyl carbonate method are
250 satisfactory as biodiesel, its fuel properties were studied, as presented in Table 2. The FAME were
251 prepared from rapeseed oil treated in supercritical dimethyl carbonate method based on the optimized
252 condition in this study (300°C/20MPa/20min/42:1 molar ratio of dimethyl carbonate to oil). The
253 results were, then, compared with Japanese, EU and US standards [35-37]. Overall, the FAME from
254 this method satisfied all requirements for international biodiesel standards except for the specification

255 stated for oxidation stability. As mentioned earlier, oxidation stability is an important parameter to
256 prevent deterioration and could be improved with addition of antioxidant or by utilizing oils with
257 lower levels of unsaturated fatty acids [34].

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

269 Recently, there have been increasing numbers of publications in the area of biodiesel
270 production via non-catalytic supercritical process [12-17]. Among them are optimization studies
271 [26-28] including an optimization study of supercritical dimethyl carbonate based on minimum sets of
272 experiments and response surface methodology, suggesting 380°C as optimum temperature without
273 describing any pressure [28]. It should be noted that thermal stability of FAME in supercritical

274 dimethyl carbonate is a major concern to produce high quality biodiesel. FAME including unsaturated
275 members were stable in supercritical dimethyl carbonate at the range of 270°C/20MPa to
276 300°C/20MPa. However, at higher temperature and higher pressure, for example, 380°C/20MPa, they
277 were partly decomposed thermally to reduce the FAME yield. It was apparent that the
278 poly-unsaturated FAME (methyl linoleate, 18:2; methyl linolenate, 18:3) were also more vulnerable to
279 thermal decomposition than the mono-unsaturated (methyl oleate, 18:1) and saturated esters (methyl
280 palmitate, 16:0; methyl stearate 18:0). This is also in agreement with a previous study by Imahara et al.
281 [33]. Therefore, it is important that any optimization studies lead to practical applications due to the
282 possible thermal decomposition and deterioration of biodiesel properties, especially if the reaction was
283 preceded at high temperature with low reaction pressure.

284 **4. Conclusions**

285 Based on these lines of evidence, this study stressed the importance to address all key
286 parameters such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the
287 FAME yield, degree of denaturation, thermal decomposition, oxidation stability and fuel properties
288 towards optimization of supercritical dimethyl carbonate method for the production of high quality
289 biodiesel. The optimum condition for supercritical dimethyl carbonate method is preferably in a
290 controlled condition below 300°C and at high pressure more than 20MPa, reaction time less than
291 30min to achieve a high yield of FAME at over 97wt%. Conclusively, this optimization study is very
292 important to produce high quality biodiesel from supercritical dimethyl carbonate method.

293 **Acknowledgements**

294 This study is partially funded by the Japan Science and Technology Agency (JST) (July 2009
295 to March 2010), Kyoto University-University of Malaya AUN-SEED Net JICA Project and
296 Global-COE Program “Energy Science in the Age of Global Warming”, Kyoto University (April 2008

297 to March 2013), as well as Grant-in-Aid for Scientific Research “Challenging Exploratory Research”
298 (April 2011 to March 2013), supported by Ministry of Education, Culture, Sports, Science and
299 Technology, Japan, for all of which the authors greatly acknowledge.

300

301 **References**

302 [1] Mittelbach M, Remschmidt C. Biodiesel: the comprehensive handbook. Vienna: Boersedruck
303 Ges.m.b.H; 2004.

304 [2] Tomasevic AV, Siler-Marinkovic SS. Methanolysis of used frying oil. Fuel Process Technol
305 2003;81:1-6.

306 [3] Hajek M, Skopal F. Treatment of glycerol phase formed by biodiesel production. Bioresour
307 Technol 2010;101:3242-5.

308 [4] Suppes GJ. Glycerol technology options for biodiesel industry. In: Knothe G, Krahl J, Van
309 Gerpen J, editors. The Biodiesel Handbook, Urbana: AOCS Press; 2010, p. 439-55.

310 [5] Johnson DT, Taconi KA. The glycerin glut: Options for the value-added conversion of crude
311 glycerol resulting from biodiesel production. Environ Prog 2007;26:338-48.

312 [6] Saka S. Applications of post-petrochemistry by supercritical fluid. Jasco Report 1999;3:28-31.

313 [7] Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel
314 2001;80:225-31.

315 [8] Kusdiana D, Saka S. Methyl esterification of free fatty acids of rapeseed oil as treated in
316 supercritical methanol. J Chem Eng Japan 2001;34:383-7.

317 [9] Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in
318 supercritical methanol. Fuel 2001;80:693-8.

319 [10] Kusdiana D, Saka S. Two-step preparation for catalyst-free biodiesel fuel production. App
320 Biochem Biotechnol 2004;115:781-91.

321 [11] Warabi Y, Kusdiana D, Saka S. Reactivity of triglycerides and fatty acids of rapeseed oil in
322 supercritical alcohols. Bioresour Technol 2004;91:283-7.

- 323 [12] Varma MN, Madras G. Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids.
324 Ind Eng Chem Res 2006;46:1-6.
- 325 [13] He H, Sun S, Wang T, Zhu S. Transesterification kinetics of soybean oil for production of
326 biodiesel in supercritical methanol. J Am Oil Chem Soc 2007;84:399-404.
- 327 [14] Demirbas A. Studies on cottonseed oil biodiesel prepared in non-catalytic SCF conditions.
328 Bioresour Technol 2008;99:1125-30.
- 329 [15] Tan KT, Lee KT, Mohamed AR. Production of FAME by palm oil transesterification via
330 supercritical methanol technology. Biomass Bioenergy 2009;33:1096-9.
- 331 [16] Valle P, Velez A, Hegel P, Mabe G, Brignole EA. Biodiesel production using supercritical
332 alcohols with a non-edible vegetable oil in a batch reactor. J Sup Flu 2010;54:61-70.
- 333 [17] Olivares-Carrillo P, Quesada-Medina J. Synthesis of biodiesel from soybean oil using
334 supercritical methanol in a one-step catalyst-free process in batch reactor. J Sup Flu
335 2011;58:378-84.
- 336 [18] Ilham Z, Saka S. Dimethyl carbonate as potential reactant in non-catalytic biodiesel production
337 by supercritical method. Bioresour Technol 2009;100:1793-6.
- 338 [19] Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from
339 *Jatropha curcas* oil. Bioresour Technol 2010;101:2735-40.
- 340 [20] Ilham Z, Saka S. Production of biodiesel with glycerol carbonate by non-catalytic supercritical
341 dimethyl carbonate. Lipid Technol 2011;23:10-3.
- 342 [21] Ilham Z, Saka S. Glycerol to value-added glycerol carbonate in the two-step non-catalytic
343 supercritical dimethyl carbonate method. In: Yao T, editor. Zero-Carbon Energy Kyoto 2010,
344 Japan: Springer; 2011, p. 153-8.
- 345 [22] Fabbri D, Bevoni V, Notari M, Rivetti F. Properties of a potential biofuel obtained from soybean
346 oil by transmethylation with dimethyl carbonate. Fuel 2007;86:690-7.
- 347 [23] Su EZ, Zhang MJ, Zhang JG, Gao JF, Wei DZ. Lipase-catalyzed irreversible transesterification of
348 vegetable oils for fatty acid methyl esters production with dimethyl carbonate as the acyl acceptor.

- 349 Biochem Eng J 2007;36:167-73.
- 350 [24] Tian X, Zhou B, Li X. Synthesis of biodiesel from cottonseed oil and dimethyl carbonate
351 catalyzed by immobilized lipase. *Petrochem Technol* 2009;38:677-81.
- 352 [25] Zhang L, Sun S, Xin Z, Sheng B, Liu Q. Synthesis and component confirmation of biodiesel
353 from palm oil and dimethyl carbonate catalyzed by immobilized-lipase in solvent-free system.
354 *Fuel* 2010;89:3960-5.
- 355 [26] Patil PD, Gude VG, Mannarswamy A, Deng S, Cooke P, Munson-McGee S, et al. Optimization of
356 direct conversion of wet algae to biodiesel under supercritical methanol conditions. *Bioresour*
357 *Technol* 2011;102:118-22.
- 358 [27] Sawangkeaw R, Bunyakiat K, Ngamprasertsith S. Continuous production of biodiesel with
359 supercritical methanol: Optimization of a scale-up plug flow reactor by response surface
360 methodology. *Fuel Process Technol* 2011;92:2285-92.
- 361 [28] Tan KT, Lee KT, Mohamed AR. Optimization of supercritical dimethyl carbonate (SCDMC)
362 technology for the production of biodiesel and value-added glycerol carbonate. *Fuel*
363 2010;89:3833-39.
- 364 [29] Fazal MA, Haseeb ASMA, Masjuki HH. Biodiesel feasibility study: An evaluation of material
365 compatibility; performance; emission and engine durability. *Renew Sustain Energy Rev*
366 2011;15:1314-24.
- 367 [30] Tat M, Wang P, Van Gerpen J, Clemente T. Exhaust emissions from an engine fueled with
368 biodiesel from high-oleic soybeans. *J Am Oil Chem Soc* 2007;84:865-9.
- 369 [31] Imahara H, Xin J, Saka S. Effect of CO₂/N₂ addition to supercritical methanol on reactivities and
370 fuel qualities in biodiesel production. *Fuel* 2009;88:1329-32.
- 371 [32] JOCS. Standard methods for fats, oils and related material (in Japanese). Japan: Japan Oil
372 Chemists' Society; 1996.
- 373 [33] Imahara H, Minami E, Hari S, Saka S. Thermal stability of biodiesel in supercritical methanol.
374 *Fuel* 2008;87:1-6.

- 375 [34] Xin J, Imahara H, Saka S. Oxidation stability of biodiesel fuel as prepared by supercritical
376 methanol. *Fuel* 2008;87:1807-13.
- 377 [35] ASTM. Standard test methods for D445, D4530, D2500, D6371, D93, D6749 and D6751
378 standards. West Conshohocken: American Society for Testing and Materials; 2007.
- 379 [36] CEN. Standard test methods for EN14412, EN14105, ENISO12937, EN14104, EN14111 and
380 EN14214. EU: European Committee of Standardization; 2003.
- 381 [37] JIS. Fatty acid methyl esters (FAME) standards for use as automotive fuel (In Japanese)-JIS
382 K2390. Japan: Japan Industrial Standard Committee; 2008.
- 383 [38] Anderson SA, Manthata S, Root TW. The decomposition of dimethyl carbonate over copper
384 zeolite catalyst. *App Catal A: General* 2005;280:117-24.
- 385 [39] Cross JTD, Hunter R, Stimson R. The thermal decomposition of simple carbonate esters. *Aust J*
386 *Chem* 1976;29:1477-81.
- 387 [40] Turro NJ. Molecular structure as a blueprint for supramolecular structure chemistry in confined
388 spaces. *Proc Nat Aca Sci* 2005;102:10766-70.
- 389 [41] King JW. Critical fluid technology for the processing of lipid-related natural products, *Comptes*
390 *Rendus Chimie* 2004;7:647-59.
- 391 [42] Musavi A, Cizmeci M, Tekin A, Kayahan M. Effects of hydrogenation parameters on trans
392 isomer formation, selectivity and melting properties of fat. *Eur J Lipid Sci Technol*
393 2008;110:254-60.
- 394 [43] Valenzuela A, Morgado N. Trans fatty isomers in human health and in the food industry. *Biol Res*
395 1999;32:273-87.
- 396 [44] Gunstone F. Vegetable oils. In: Shahidi F, editor. *Bailey's Industrial Oil and Fat Products*, New
397 York: John Wiley and Sons Inc; 2005, p. 217-8.
- 398 [45] Knothe G. Improving biodiesel fuel properties by modifying fatty ester composition. *Energy*
399 *Environ Scie* 2009;2:759-66.

400

401 **Figure captions:**

402

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

405

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

408

409 Fig. 3 Effect of pressure on FAME yield from triglycerides treated in supercritical dimethyl carbonate
410 method at 300°C

411

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

414

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

417

418 Fig. 6 Effect of temperature on tocopherol content in supercritical dimethyl carbonate method at
419 20MPa for 30min

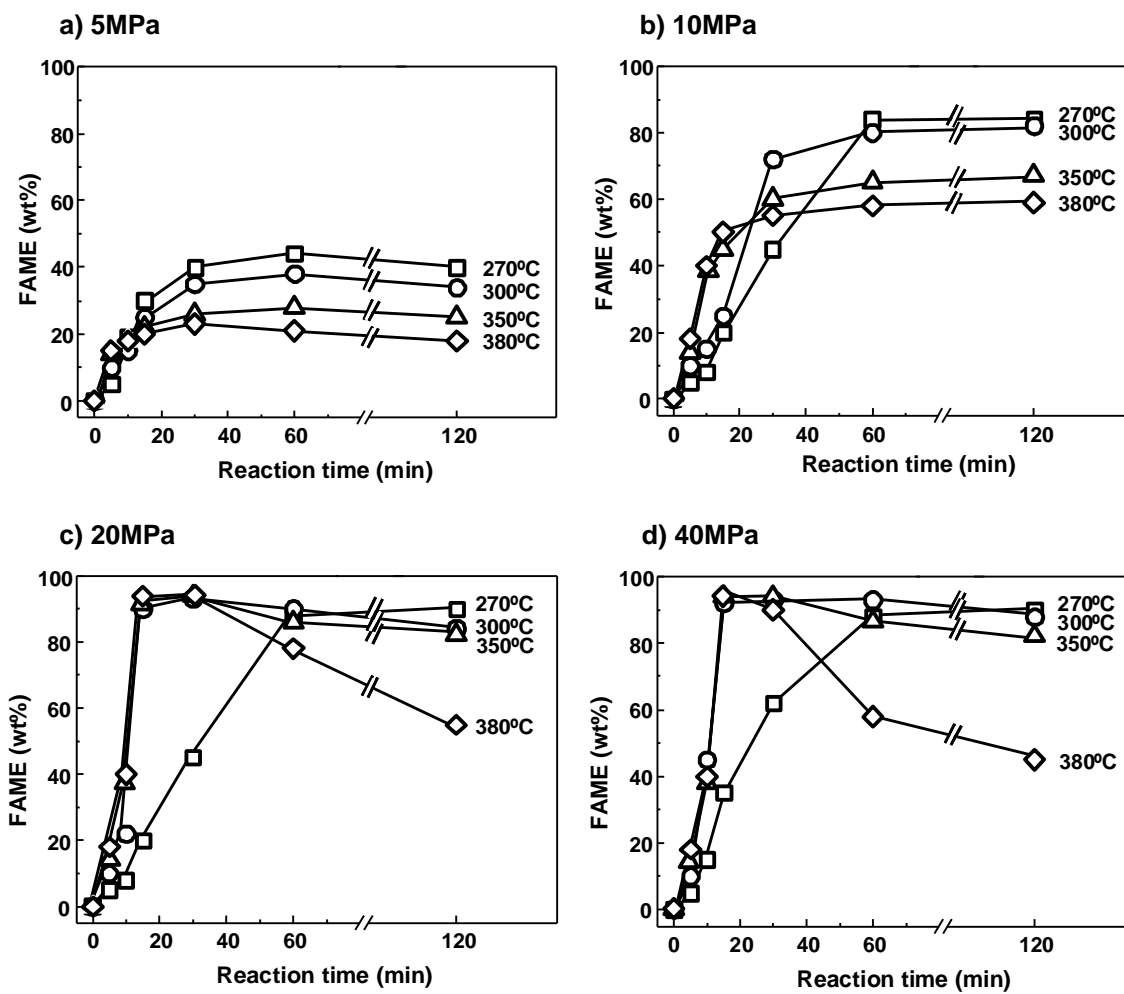


Fig. 1 Effect of temperature on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at different reaction pressures

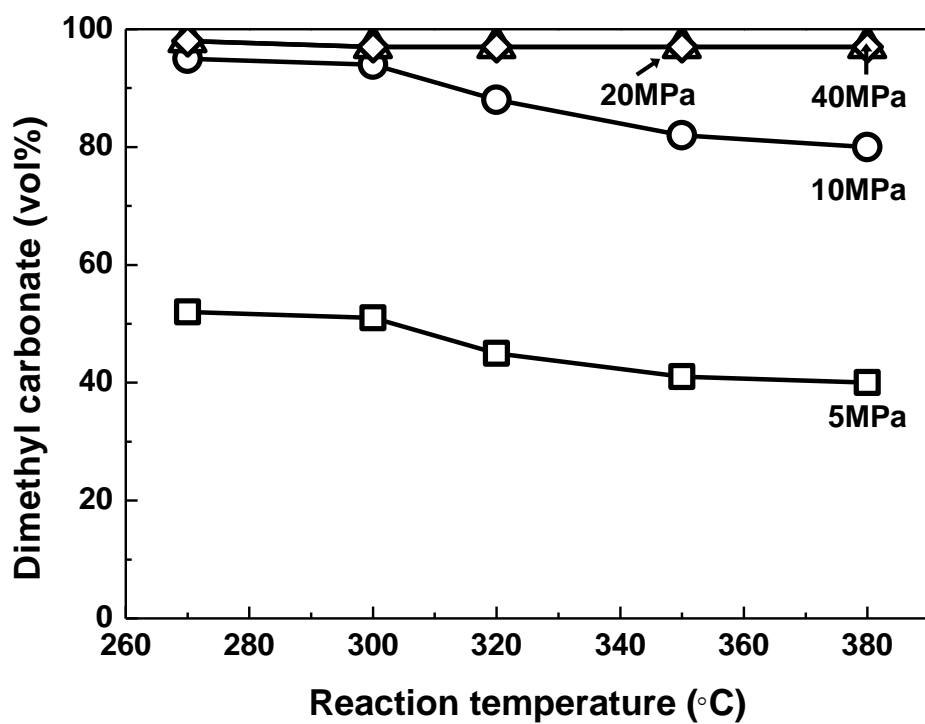


Fig. 2 Effect of various temperatures and pressures at supercritical conditions to dimethyl carbonate as a solvent after 30min treatment

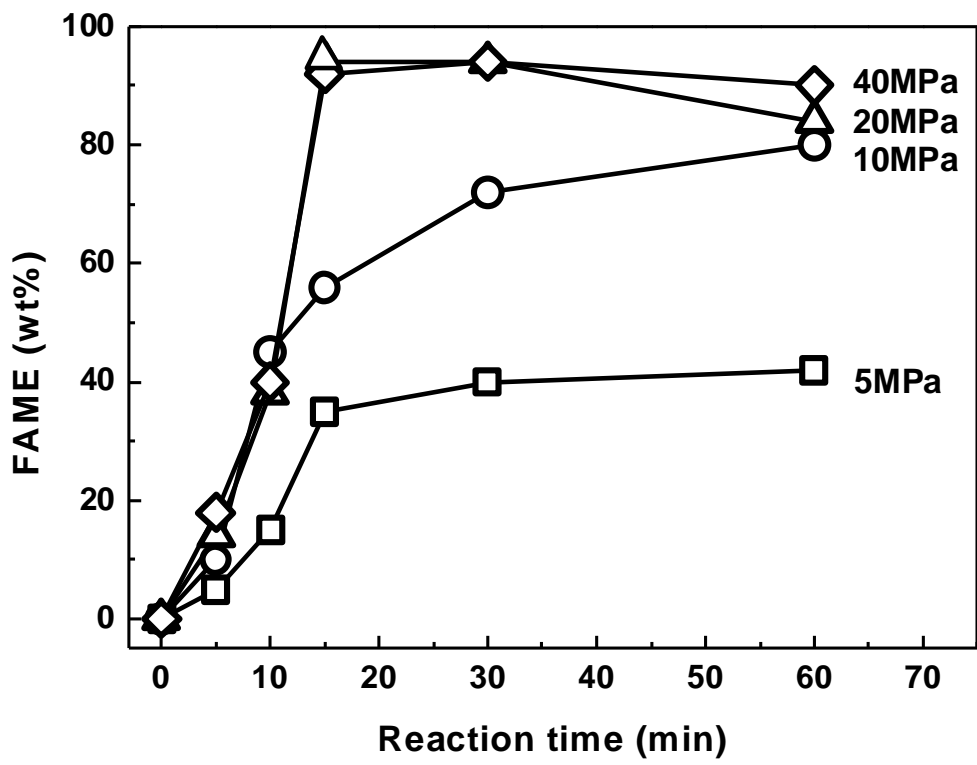


Fig. 3 Effect of pressure on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at 300°C

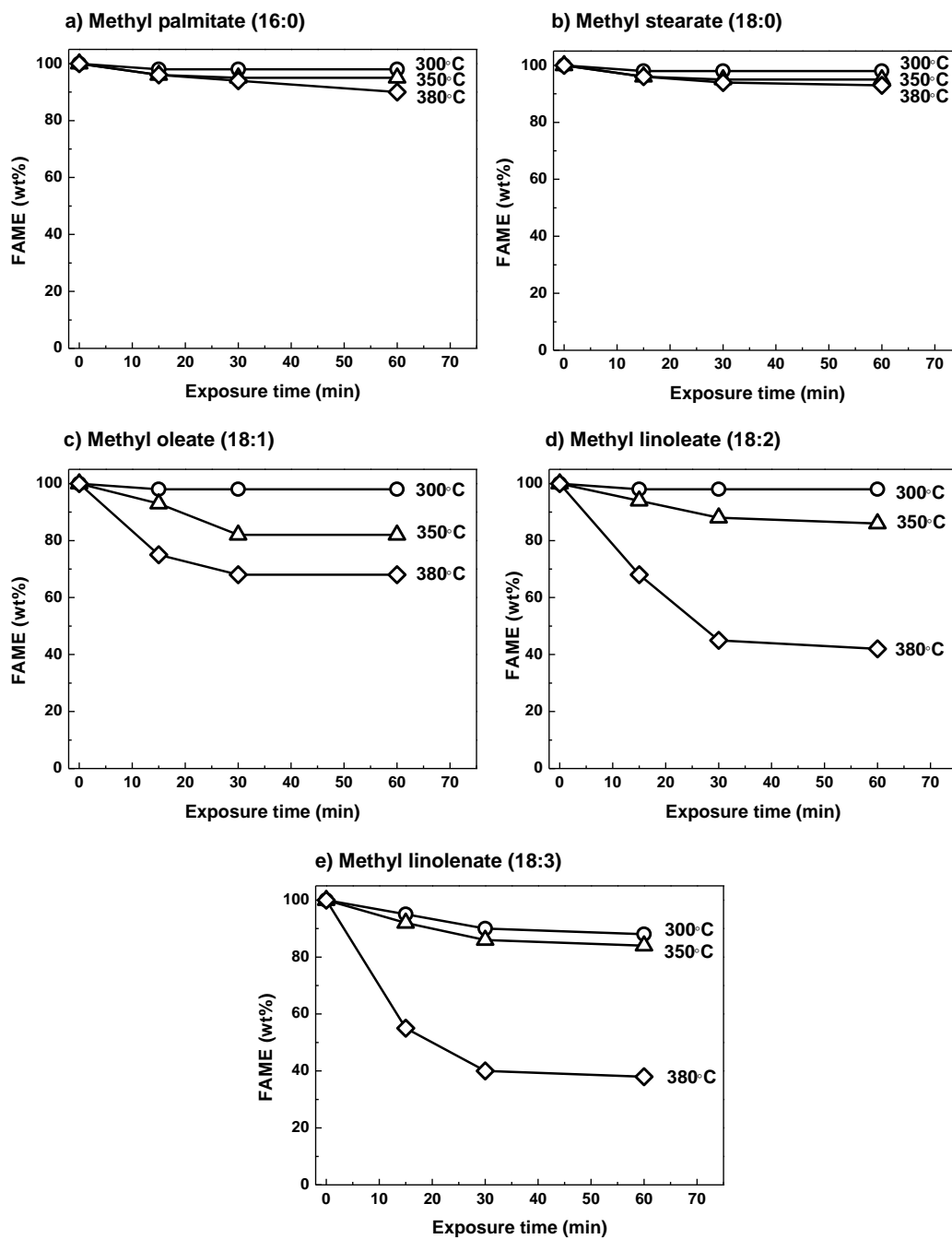


Fig. 4 Thermal stability of various FAME in supercritical dimethyl carbonate method under different temperatures at 20MPa

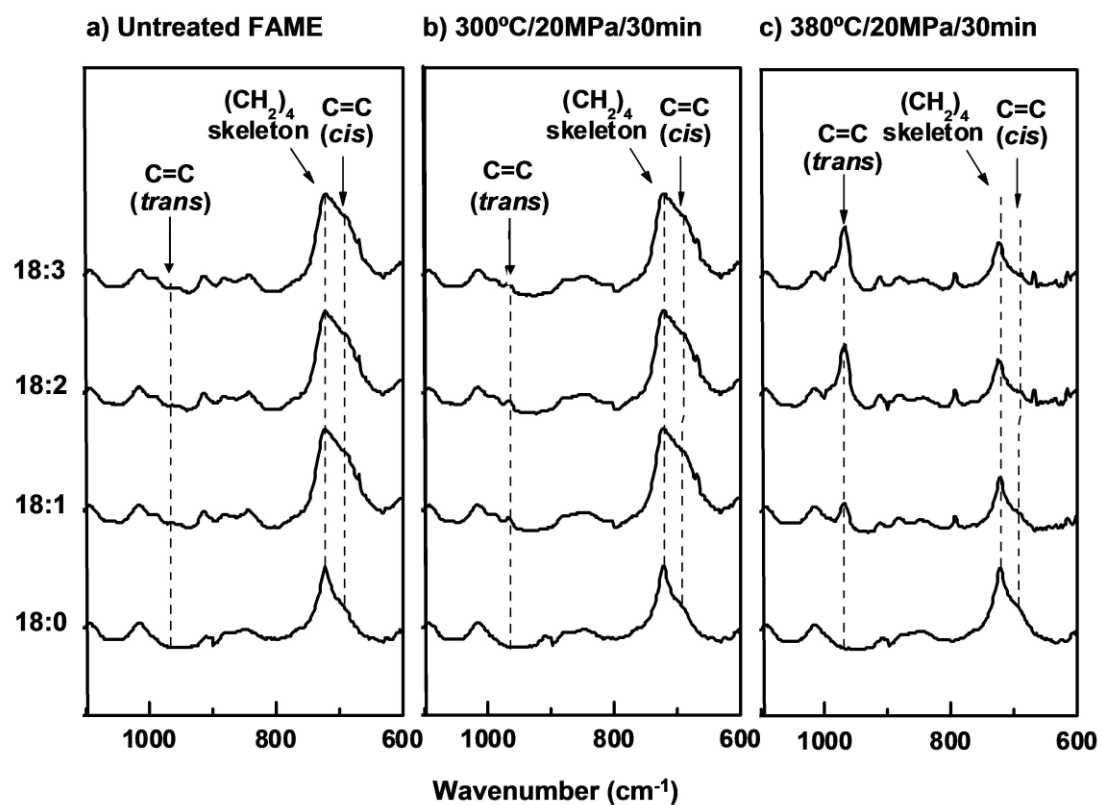


Fig. 5 FT-IR spectra of various FAME as treated in supercritical dimethyl carbonate method at different reaction conditions a) Untreated FAME, b) 300°C/20MPa/30min and c) 380°C/20MPa/30min

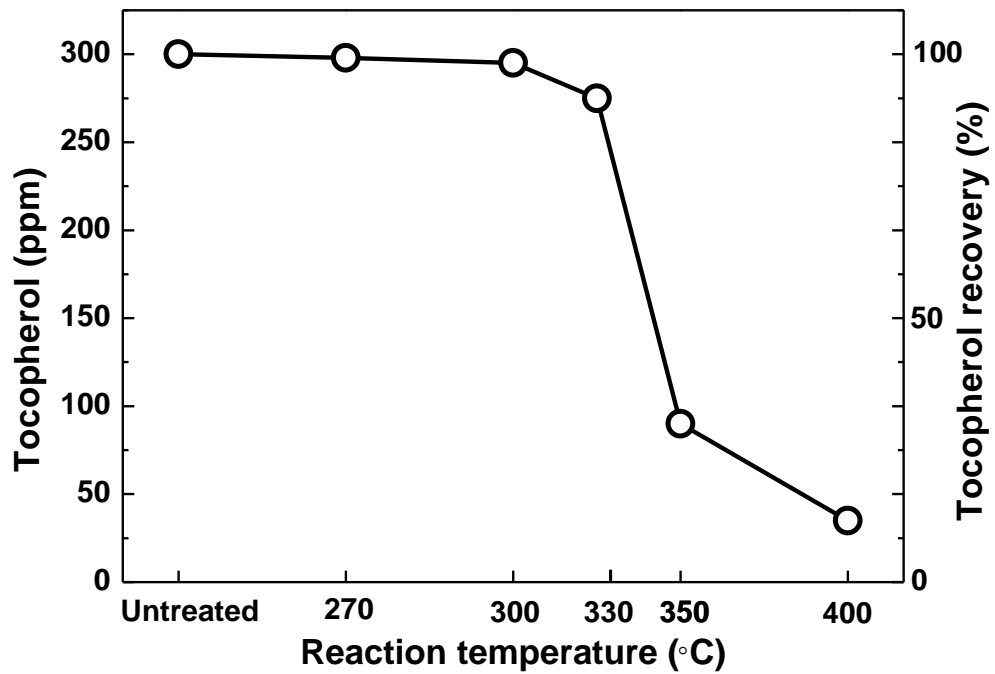


Fig. 6 Effect of temperature on tocopherol content in supercritical dimethyl carbonate method at 20MPa for 30min

Table 1 Total fatty acid composition of rapeseed oil used in this study

Fatty acid ^a		Composition (wt%)
Palmitic acid	16:0	6.0
Stearic acid	18:0	1.4
Oleic acid	18:1	57.6
Linoleic acid	18:2	23.8
Linolenic acid	18:3	11.2

^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 2 Fuel properties of fatty acid methyl esters (FAME) from rapeseed oil as treated in supercritical dimethyl carbonate method compared with international standards

Properties	Method	Unit	FAME (Biodiesel)	International standards ^a		
				Japan (JIS K2390)	EU (EN 14214)	US (ASTM D6751-07)
Kinematic viscosity (40°C)	ASTM D445	mm ² /s	4.3	3.5-5.0	3.5-5.0	1.9-6.0
Carbon residue	ASTM D4530	wt%	0.08	≤ 0.30	≤ 0.30	≤ 0.05
Pour point	ASTM D2500	°C	- 7.0	-	-	-
Cold filter plugging point	ASTM D6371	°C	- 7.2	-	-	-
Ignition point	ASTM D93	°C	162.5	≥ 120	≥ 101	≥ 130
Cloud point	ASTM D6749	°C	-7.0	-	-	-
Oxidation stability	EN 11442	h	5.5	-	≥ 6	-
Ester content	EN 14103	wt%	97.4	>96.5	>96.5	-
Monoglyceride	EN 14105	wt%	0.1	<0.80	<0.80	-
Diglyceride	EN 14105	wt%	0.06	<0.20	<0.20	-
Triglyceride	EN 14105	wt%	n.d. ^b	<0.20	<0.20	-
Total glycerol content	EN 14105	wt%	0.02	<0.25	<0.25	<0.24
Water content	EN ISO12937	mg/kg	255	<500	<500	<500
Acid number	EN 14104	mg(KOH)/g	0.14	<0.50	<0.50	<0.50
Iodine value	EN 14111	g(I ₂)/100g	102	<120	<120	-

^a JIS (2008); CEN (2003); ASTM (2007).

^b n.d., not detectable.