1 **Optimization of Supercritical Dimethyl Carbonate Method for Biodiesel Production**

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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 300ºC/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.

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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

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 (Tc=275ºC, Pc=4.63 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

82 270-400ºC and 10-40MPa, 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: 40ºC, 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 270ºC and 380ºC with critical pressures higher than the critical pressure of dimethyl

106 carbonate (Pc=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 70ºC 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   127ºC and 149ºC. To further investigate this alleged possible decomposition of dimethyl carbonate at

169   low reaction pressure, it was subjected to high temperature (≥270ºC) 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 390ºC,

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 300ºC, 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 300ºC/20MPa. However, when

207   temperature rises up to 350ºC/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 300ºC/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 350ºC/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 300ºC/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 300ºC/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 300ºC/20MPa for 30 min, no significant changes could be observed. Similar observation could be seen

228 when FAME was treated at 270ºC/20MPa for 30 min (Data not presented). King [41], in his findings

229 also showed no fatty acids isomerization at temperatures below 300 ºC.

230 On the other hand, after the exposure at 350ºC/20MPa and 380ºC/20MPa for 30 min,

231 absorption peaks for *cis*-type C=C and $(CH_2)_4$ 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 380ºC/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 270ºC/20MPa and 300ºC/20MPa as presented in

246   Fig. 6, it decreased drastically at severe temperatures of 350ºC/20MPa and 400ºC/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 (300ºC/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 300ºC 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.

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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 300ºC

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) 300ºC/20MPa/30min and c) 380ºC/20MPa/30min

417

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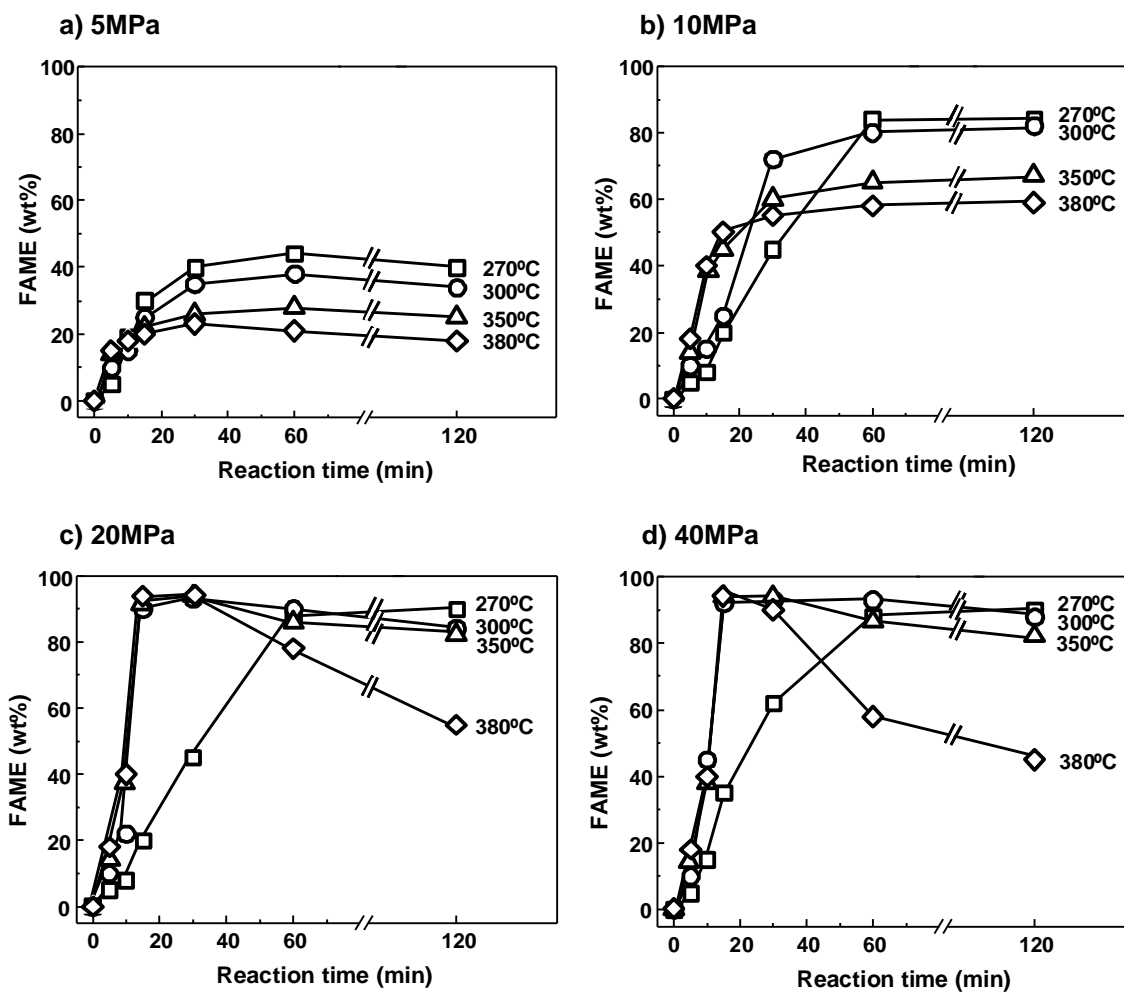
419 20MPa for 30min

Fig. 1 Effect of temperature on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at different reaction pressures
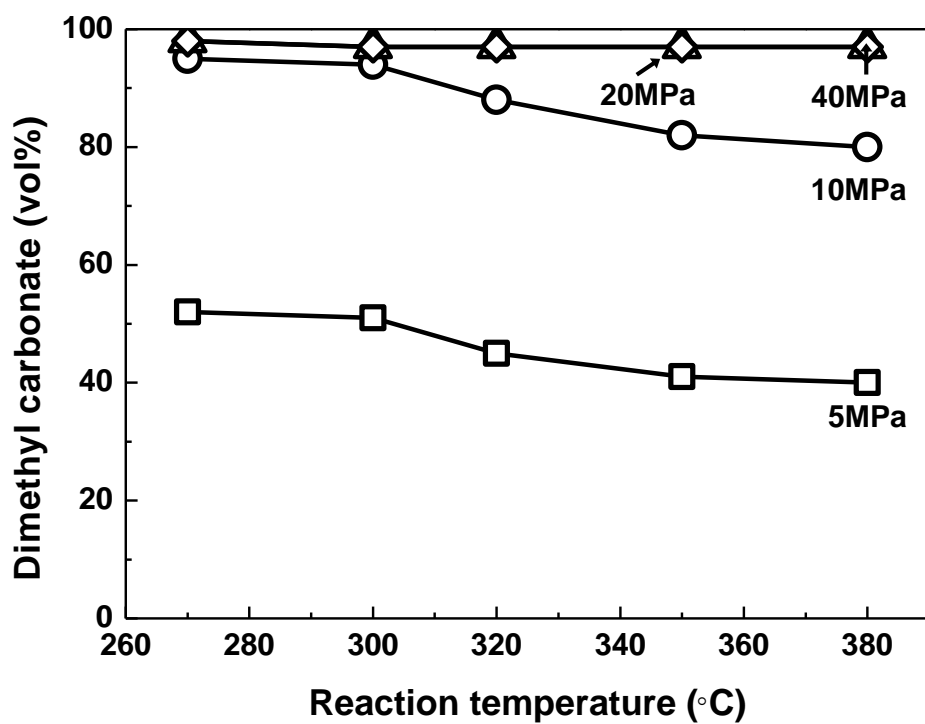
Fig. 2 Effect of various temperatures and pressures at supercritical conditions to dimethyl carbonate as a solvent after 30min treatment
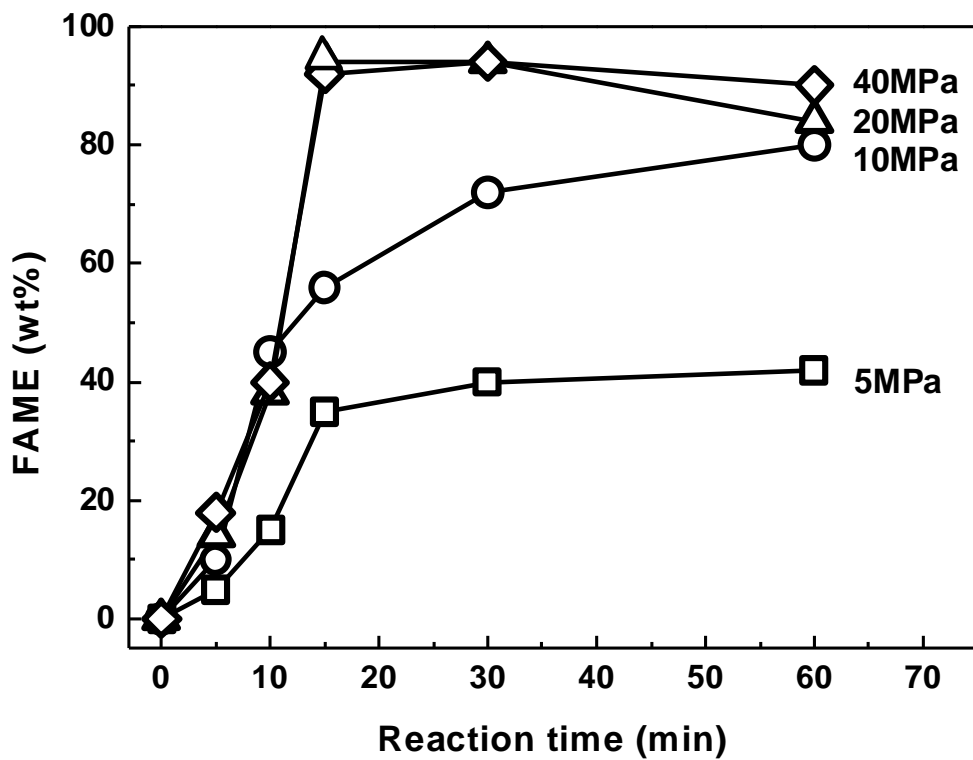
Fig. 3 Effect of pressure on FAME yield from triglycerides treated in supercritical dimethyl carbonate method at 300ºC
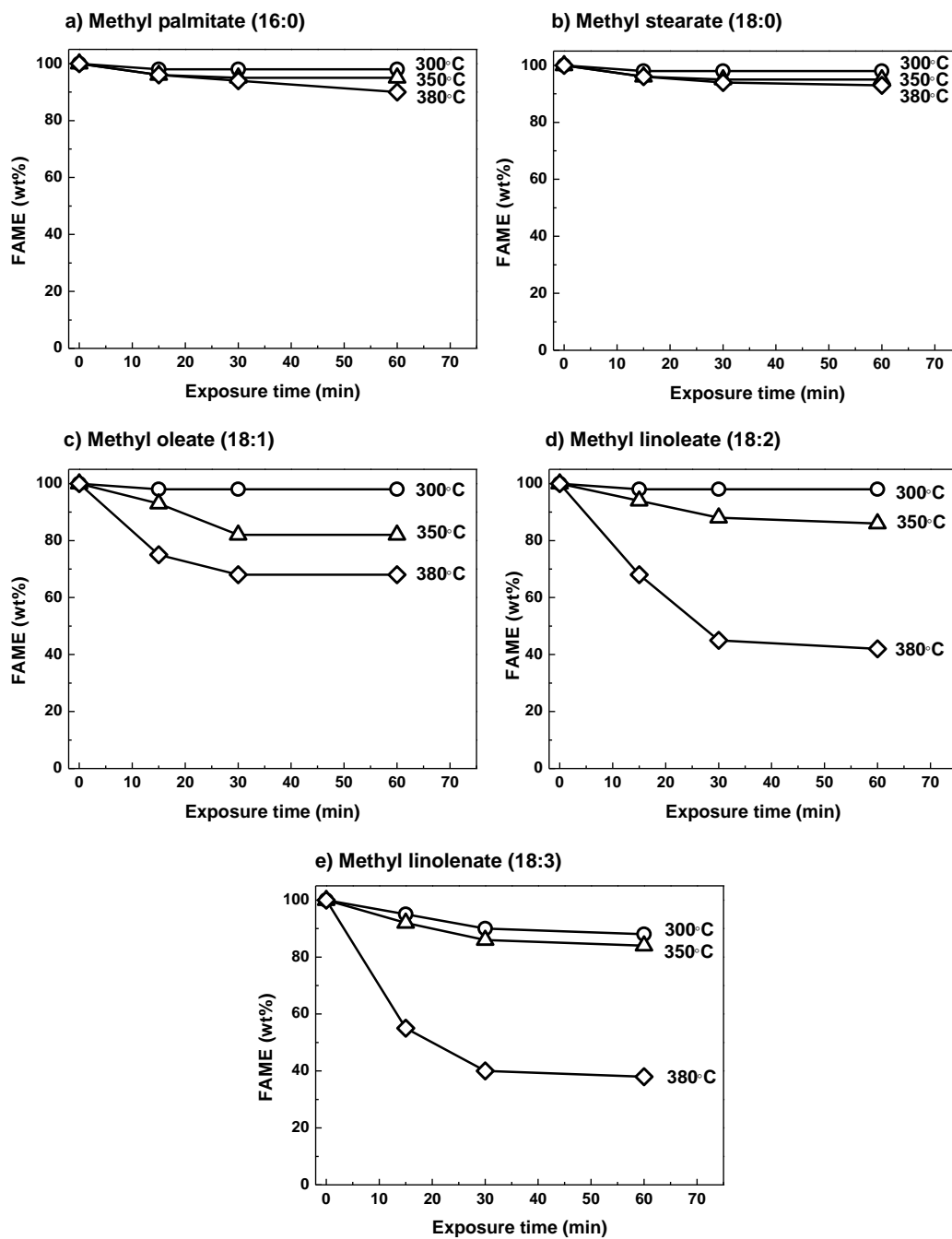
Fig. 4 Thermal stability of various FAME in supercritical dimethyl carbonate method under different temperatures at 20MPa
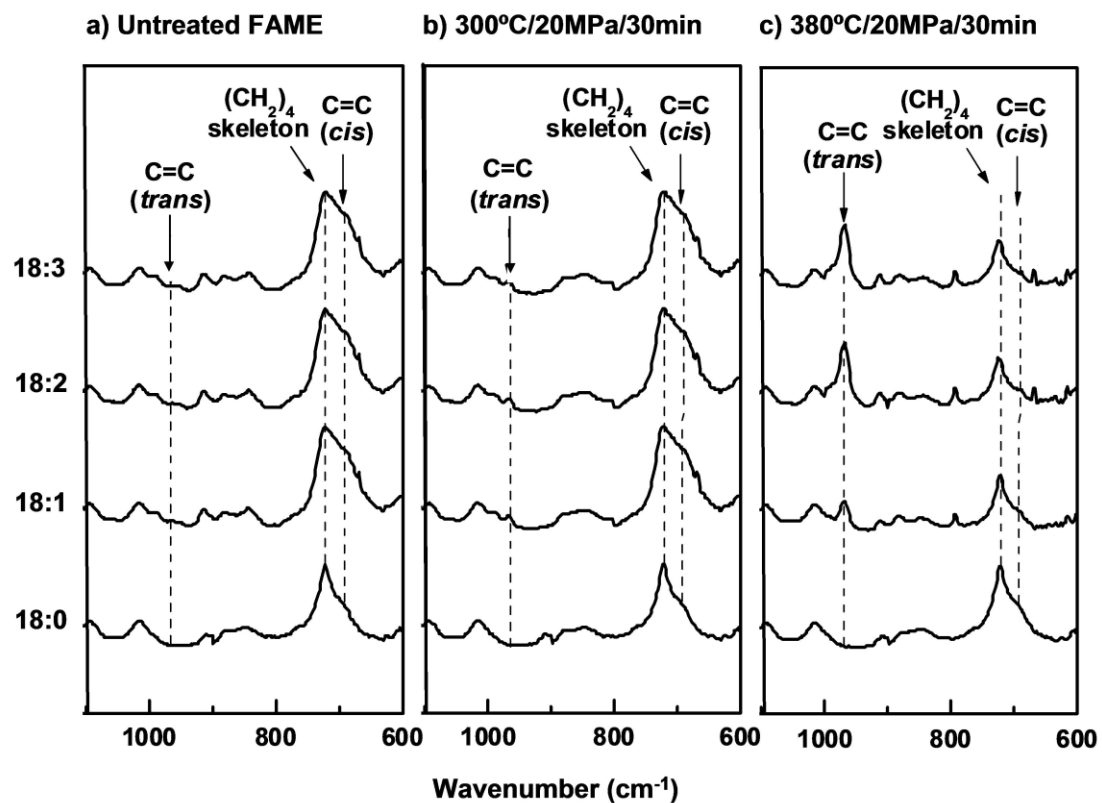
Fig. 5 FT-IR spectra of various FAME as treated in supercritical dimethyl carbonate method at different reaction conditions a) Untreated FAME, b) 300°C/20MPa/30min and c) 380°C/20MPa/30min
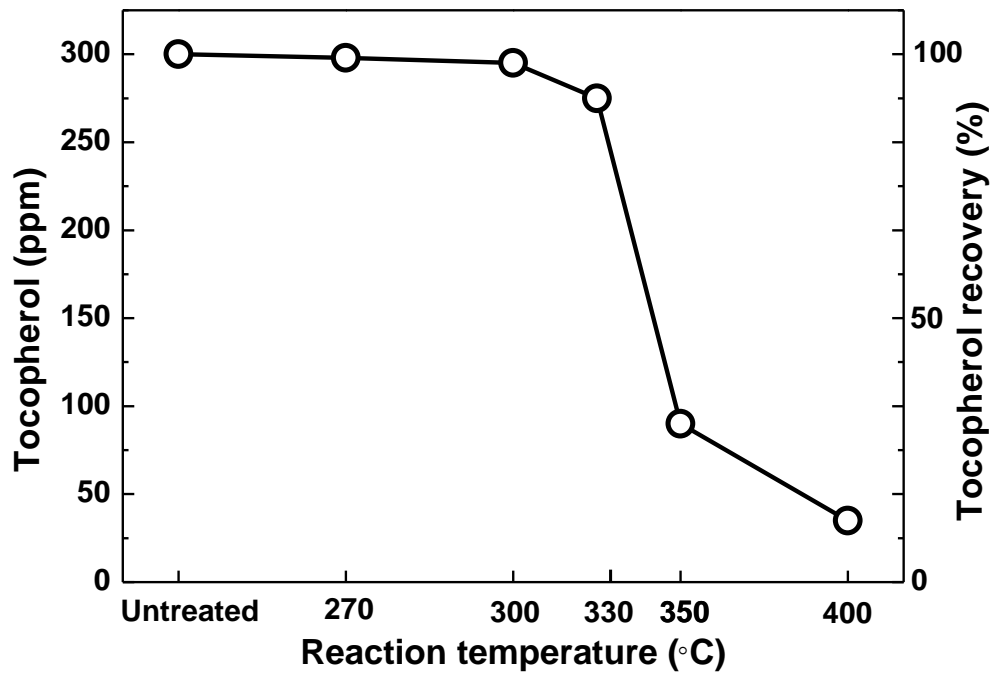
Fig. 6 Effect of temperature on tocopherol content in supercritical dimethyl carbonate method at 20MPa for 30min

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	$\leq$ 0.30	$\leq$ 0.30	$\leq$ 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	$\geq$ 120	$\geq$ 101	$\geq$ 130
Cloud point	ASTM D6749	°C	-7.0	-	-	-
Oxidation stability	EN 11442	h	5.5	-	$\geq$ 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.