

**Title:**

Renewable diesel production from rapeseed oil with hydrothermal hydrogenation and subsequent decarboxylation

**Authors:** Yuitsu Sugami, Eiji Minami and Shiro Saka

**Affiliation:** Graduate School of Energy Science, Kyoto University, Japan

**Address:** Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

**Tel/Fax:** +81 (0) 75 753 4738

**E-mail:** saka@energy.kyoto-u.ac.jp

**Corresponding author:** Shiro Saka

**Highlights**

- Hydrocarbon production from rapeseed oil was studied.
- The process consists of hydrolysis/hydrogenation and subsequent decarboxylation.
- The composition of the obtained hydrocarbons can be foreseen from raw material.
- The product meets the Japanese diesel standard by blending with fossil diesel.

1    **Abstract**

2    Hydrocarbon (renewable diesel) production from rapeseed oil was studied with hydrothermal  
3    hydrogenation and subsequent decarboxylation in a batch-type reaction vessel. An appropriate reaction  
4    condition for hydrothermal hydrogenation was found to be 270 °C/ 5 MPa (H<sub>2</sub> pressure) with water and  
5    Pd/C catalyst for 60 min, under which triglycerides were simultaneously hydrolyzed and hydrogenated  
6    into saturated fatty acids in a yield of 98.4 mol%. The obtained saturated fatty acids were then  
7    decarboxylated to hydrocarbons under the condition of 300 °C/ 1 MPa (H<sub>2</sub> pressure) with Pd/C for 120  
8    min in a yield of 91.5 mol% on rapeseed oil. In addition, the composition of the obtained hydrocarbons  
9    corresponded nearly to that of the fatty acid in rapeseed oil. Such a result indicates that the composition  
10   of hydrocarbons produced in this proposed process can be foreseen from fatty acid composition of the  
11   feedstock triglycerides. By blending the obtained hydrocarbons from rapeseed oil with an adequate  
12   amount of fossil diesel, the blended fuel could satisfy the specification standard of fossil diesel in  
13   Japan.

14

15    **Keywords**

16    Renewable diesel; Plant oil; Hydrolysis; Hydrogenation; Decarboxylation

17

18

19

## 20 **1. Introduction**

21           The fossil fuels are finite resources and their mass consumption has significant impacts on  
22 our environment and society. For these reasons, fatty acid methyl ester (FAME) is being used as an  
23 alternative diesel fuel produced by transesterification of triglyceride, a main component of plant oil,  
24 with methanol. Because FAME is renewable fuel containing no aromatics and sulfur, it can reduce  
25 exhaust emissions [1, 2]. However, FAME has some drawbacks caused by the difference in chemical  
26 structure from petroleum diesel, for example, corrosiveness against certain types of rubber and metal  
27 [3] and poor oxidation stability due to unsaturated double bonds [1-4]. To overcome such drawbacks,  
28 hydrocarbon productions from plant oils with the hydrotreating and catalytic cracking are being  
29 researched worldwide [5-19].

30           The hydrotreatment of plant oils was usually studied in the temperature range between 350  
31 and 450 °C under the pressure between 4 and 15 MPa with H<sub>2</sub> and a catalyst [5-13]. As a catalyst, for  
32 example, sulfided CoMo and NiMo supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and zeolites were used [5-11].  
33 Under the hydrotreating reaction, first, double bonds in fatty acid moieties of triglyceride are  
34 hydrogenated into saturated C-C bonds, followed by the cleavage of ester linkages to produce one  
35 molecule of propane and three molecules of saturated fatty acids [6, 12]. The obtained saturated fatty  
36 acids are then deoxidized into hydrocarbons having carbon numbers mainly between 15 and 18 through  
37 hydrodeoxygenation, decarbonylation and decarboxylation [8, 13]. This reaction also produces  
38 *i*-paraffin and naphthene through isomerization and cyclization of olefin intermediates, which

39 contributes to improving the cold-flow properties. In addition, CO, CO<sub>2</sub>, H<sub>2</sub>O and propane are  
40 produced as byproducts [6].

41 On the other hand, the catalytic cracking of plant oils was usually carried out in the  
42 temperature range between 300 and 500 °C under atmospheric pressure with zeolites, Al<sub>2</sub>O<sub>3</sub> and MgO  
43 as a catalyst [14-17], under which the thermal decomposition is predominant. First, triglycerides are  
44 decomposed to fatty acids, ketones, aldehydes and esters [18]. These products undergo secondary  
45 cracking to form short and long chain paraffins and olefins with CO, CO<sub>2</sub>, H<sub>2</sub>O and alcohols by  
46 breaking C-O and C-C bonds via decarboxylation and decarbonylation. However, this process makes  
47 various hydrocarbons having wide range of carbon numbers with olefins and aromatics.

48 After all, the selectivity of the products is not so high with the conventional hydrotreating and  
49 catalytic cracking mentioned above. It should be caused by the presence of unsaturated fatty acid  
50 moieties, which leads to various side reactions. Actually, Dos Anjos et al. studied the catalytic cracking  
51 of prehydrogenated soybean oil as well as crude one, reporting that prehydrogenated oil yielded  
52 essentially pure hydrocarbon products, while crude oil yielded a mixture of oxygen-containing products  
53 and the lower molecular weight hydrocarbons [20].

54 In this study, therefore, hydrocarbon production from plant oil was studied through two-step  
55 reaction with hydrolysis and subsequent decarboxylation. During the hydrolysis step, hydrogenation  
56 was simultaneously conducted to produce stable saturated fatty acids, which may suppress undesirable  
57 side reactions during subsequent decarboxylation [19, 20]. In the literature [5-21], furthermore, an

58 organic solvent such as *n*-dodecane was usually added to enhance the fluidity of the reactants and to  
59 avoid the deactivation of catalyst, even though only a few studies without any solvent can be found [19,  
60 22]. However, the use of such organic solvent requires additional separation and purification steps after  
61 the reaction, and it makes the whole process complicated. Therefore, the reactions of this study were  
62 conducted without any organic solvent so as to simplify the process for production of hydrocarbons as  
63 renewable diesel.

64

## 65 **2. Materials and Methods**

### 66 ***2.1. Experimental procedures***

67 Fig.1 shows the schematic diagram of the saturated hydrocarbon (renewable diesel)  
68 production process in this study via saturated fatty acids from rapeseed oil. Prior to the experiment,  
69 Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 °C and reduced in  
70 H<sub>2</sub> flow (15 ml/min) at 200 °C for 60 min. Rapeseed oil (reagent grade, Nacalai Tesque, Inc.) was, then,  
71 treated in hot-compressed water with H<sub>2</sub> gas and Pd/C catalyst for hydrolysis and hydrogenation to  
72 obtain saturated fatty acids. The obtained saturated fatty acids were then decarboxylated with Pd/C  
73 catalyst to produce saturated hydrocarbons by decarboxylation.

74

75 **2.1.1. Hydrolysis coupled with hydrogenation (Hydrolysis/hydrogenation)**

76 A batch-type reaction vessel (inner volume: 5.0 ml) made of Inconel-625 [23] was used for  
77 the reaction. One gram of rapeseed oil and 1.0 - 3.0 g of ion-exchanged water were placed into the  
78 reaction vessel with 0.05 g of Pd/C. Hastelloy balls (total volume: 0.2 ml) were also placed into the  
79 vessel to agitate the mixture efficiently. After the vessel was sealed, the inside of the vessel was purged  
80 and pressurized to 5 MPa with H<sub>2</sub> gas using a gas-supplying system. The hydrolysis coupled with  
81 hydrogenation (hydrolysis/hydrogenation) reaction was then conducted by immersing the vessel into a  
82 molten salt bath preheated at 270 °C, which is the optimum temperature for hydrolysis of triglycerides  
83 found in previous works [24, 25]. The reaction vessel was swung from side to side to agitate the  
84 mixture during the reaction. After a designated treatment time, the vessel was moved into a water bath  
85 to quench the reaction. The obtained reaction mixture dissolved in tetrahydrofuran (THF, specially  
86 prepared reagent grade, Nacalai Tesque, Inc.) was, then, taken out from the vessel, sonicated for 30 min,  
87 and the catalyst was removed with a filter paper in a micropore of 0.45 μm (Merck Millipore Co.). The  
88 products were, then, warmed up in a water bath at 70 °C for 30 min and separated into THF and water  
89 phases. By removing THF from the THF phase with a rotary vacuum evaporator, the products of the  
90 hydrolysis/hydrogenation reaction were collected and their yield was determined.

91

### 92 **2.1.2. Decarboxylation**

93 For subsequent decarboxylation, approximately 0.9 g of the obtained saturated fatty acids and  
94 0.05 - 0.45 g of Pd/C were placed into the 5 ml reaction vessel with Hastelloy balls. The inside of the  
95 reaction vessel was then purged and pressurized with N<sub>2</sub> or H<sub>2</sub> gas to be 1 MPa which is a favorable  
96 pressure for decarboxylation reaction [26]. The decarboxylation was, then, conducted with the molten  
97 salt bath at 300 °C for 120 min, which is an appropriate condition reported by Lestari *et al.* [27], and  
98 quenched into the water bath in the same way mentioned above. After the reaction, the obtained  
99 products dissolved in THF were taken out from the vessel, sonicated for 30 min, and the catalyst was  
100 removed with the filter paper. After removing THF by the evaporator, the decarboxylated products were  
101 obtained to determine its yield. To clarify the decarboxylation reaction of the saturated fatty acid,  
102 palmitic acid, stearic acid and arachidic acid (all being guaranteed reagent grade from Nacalai Tesque,  
103 Inc.) were also studied.

104

### 105 **2.2. Analytical methods**

106 The fatty acid composition of rapeseed oil used in this work was determined in accordance  
107 with the Japan Oil Chemists' Society standard method [28]. The products, obtained from  
108 hydrolysis/hydrogenation and subsequent decarboxylation, were analyzed by gel permeation  
109 chromatography (GPC, Shimadzu Co. LC-10VP system, column: GF-310 HQ (Showa Denko K.K.),  
110 oven temperature: 40 °C, mobile phase: THF, flow-rate: 1.0 ml/min, detector: refractive index detector

111 RID-10A) and high performance liquid chromatography (HPLC, column: Cadenza CD-C18 (Imtakt  
112 Co.), oven temperature: 40 °C, mobile phase: methanol, flow-rate: 1.0ml/min, detector: RID-10A). By  
113 the GPC analysis, the obtained products from hydrolysis/hydrogenation can be separated into four  
114 peaks, which correspond to the groups of triglycerides, diglycerides, monoglycerides and fatty acids.  
115 The amount of each group was quantified based on the corresponding peak area, using tristearin,  
116 1,3-distearin, 1-monostearin (all being >99% grade from Olbracht Serdary Research Laboratories) and  
117 stearic acid (guaranteed reagent grade from Nacalai Tesque, Inc.) as calibration standards. The HPLC  
118 analysis, by which fatty acids can be separated into single ones, was then conducted to quantify the  
119 amount of each fatty acid. In this way, the yields of the products were determined in mol%. The  
120 obtained product from the decarboxylation reaction was also quantified in a similar manner.

121           The fuel properties of the renewable diesel were evaluated for flash point, pour point, cold  
122 filter plugging point, kinematic viscosity and density as in Table 2. In addition, the renewable diesel  
123 was blended in various ratios with fossil diesel (#1 diesel of the Japanese Industrial Standard (JIS),  
124 purchased from SHOWA SHELL SEKIYU K.K.), and their fuel properties were also evaluated. The  
125 density was determined in accordance with the ASTM International's standard ASTM D1298 [29],  
126 while the flush point, pour point, cold filter plugging point and kinematic viscosity were measured by  
127 the automated Pensky-Martens closed cup flash point tester (APM-7), the mini pour point tester  
128 (MPC-102), the automated cold filter plugging point tester (AFP-102) and the automatic kinematic  
129 viscosity measuring system (AKV-201), respectively. All of these measuring systems were made by



130 Tanaka Scientific Co. Ltd. The acid and iodine values were determined in accordance with ASTM  
131 D974 and D1959 [30, 31].

132

### 133 **3. Results and Discussion**

134 Table 1 shows the fatty acid composition of rapeseed oil and yields of the products obtained  
135 after hydrolysis/hydrogenation and subsequent decarboxylation. Rapeseed oil used in this study is  
136 composed of saturated and unsaturated fatty acids with 16, 18 and 20 carbon atoms. Through this study,  
137 appropriate reaction conditions for hydrolysis/hydrogenation and decarboxylation were evaluated as  
138 described in the following subsections.

139

#### 140 **3.1. Hydrolysis/hydrogenation**

141 Figure 2(a) and 2(b) show respectively GPC and HPLC chromatograms of the obtained  
142 products through hydrolysis/hydrogenation reaction from 0.9 g of rapeseed oil as treated at 270 °C/ 5  
143 MPa (H<sub>2</sub>) with 3.0 g of water and 0.05 g of Pd/C. In Fig. 2(a), triglycerides (TG) in rapeseed oil are  
144 decreasing as reaction time is prolonged. For 20 and 40 min treatments, diglycerides (DG) and  
145 monoglycerides (MG) are being observed as intermediate compounds, but almost all of them also  
146 disappear after 60 min. Meanwhile, fatty acids (FA) are increasing with reaction time until 60 min  
147 treatment. Incidentally, the retention time of triglycerides in the GPC chart shifts slightly to the shorter  
148 retention time after 20 min treatment. It would imply that the double bonds in fatty acid moieties are

149 converted into saturated ones through hydrogenation, because saturated fatty acids have a slightly  
150 shorter retention time than unsaturated ones on the GPC column used in this study. Actually, only  
151 saturated fatty acids such as palmitic (C<sub>16:0</sub>), stearic (C<sub>18:0</sub>) and arachidic (C<sub>20:0</sub>) acids can be found after  
152 20 min treatment by HPLC analysis as shown in Fig. 2(b). It indicates that hydrogenation is faster than  
153 hydrolysis and completed within 20 min.

154 From the above, an appropriate reaction time for hydrolysis/hydrogenation was found to be  
155 60 min at the given conditions. Based on the HPLC and GPC analyses, the yield of the products from  
156 rapeseed oil was determined as shown in Table 1. Triglycerides in rapeseed oil were converted into  
157 saturated fatty acids and their yield was summed up to be 96.1 (= 4.5 + 89.7 + 1.9) mol%. In addition,  
158 2.3 mol % of glycerides still remained as intermediate compounds. Finally, the total yield of fatty acids  
159 and glycerides was 98.4 mol% and any other products were not observed in the HPLC chart. In  
160 addition, no gaseous products were produced and saturated fatty acids are stable under the given  
161 condition. Thus, no product decomposition would be occurred. Therefore, the rest of 1.6 mol% would  
162 probably be lost through the purification steps. By excluding the lost portion, the molar ratio upon the  
163 obtained products basis was shown in parenthesis in Table 1. As a result, the molar ratio of the obtained  
164 saturated fatty acids (C<sub>16:0</sub> : C<sub>18:0</sub> : C<sub>20:0</sub> = 4.6 : 91.2 : 1.9) is close to the fatty acid composition of  
165 rapeseed oil (C<sub>16:0</sub> + C<sub>16:1</sub> : C<sub>18:0</sub> + C<sub>18:1</sub> + C<sub>18:2</sub> + C<sub>18:3</sub> : C<sub>20:0</sub> + C<sub>20:1</sub> = 4.5 : 94.0 : 1.5). It means that the  
166 selective reaction to be saturated fatty acids has occurred during the hydrolysis/hydrogenation step.

167 With regard to the amount of water, on the other hand, 1.0 g of rapeseed oil was hydrolyzed  
168 with 3.0 g of water. Thus, the weight ratio of water/rapeseed oil was 3.0/1.0 for Table 1 and Fig. 2.  
169 However, when its ratio decreased from 3.0/1.0 to 1.0/1.0, the yield of saturated fatty acids decreased  
170 from 97.7 mol% to 77.2 mol% due to the insufficient hydrolysis of glycerides and fatty acids under the  
171 same reaction condition. From these results, it was concluded that an appropriate  
172 hydrolysis/hydrogenation condition is 270 °C/ 5 MPa (H<sub>2</sub>) with 3.0 g of water and 0.05 g of Pd/C for  
173 1.0 g of rapeseed oil.

174

### 175 **3.2. Decarboxylation**

176 As a preliminary experiment, the effect of atmospheric gas (N<sub>2</sub> or H<sub>2</sub>) was investigated on  
177 decarboxylation reaction by using stearic acid as a model compound. When N<sub>2</sub> gas was used, no  
178 conversion was observed at the conditions of 300 °C/ 1 MPa/ 0.05 g of Pd/C for 120 min. In the case of  
179 H<sub>2</sub> gas, on the other hand, 16.3 mol% of *n*-heptadecane was obtained at the same condition. Although  
180 H<sub>2</sub> is not essentially required by the decarboxylation reaction, it keeps the catalyst activity [32, 33].  
181 Actually, some researchers have reported that an efficient decarboxylation was observed in the presence  
182 of H<sub>2</sub> [19, 33, 34]. Therefore, H<sub>2</sub> gas was used in the following experiments.

183 Moreover, decarboxylation reaction was carried out for 0.9 g of stearic acid as a model  
184 compound to determine an appropriate amount of the catalyst at the conditions of 300 °C/ 1 MPa (H<sub>2</sub>)  
185 for 120 min. When the two different amounts of Pd/C were studied to be 0.05 and 0.25 g, incomplete

186 conversions were found respectively to be 16.3 and 26.1 mol% from stearic acid into *n*-heptadecane.  
187 On the other hand, 90.3 mol% of *n*-heptadecane was achieved with 0.45 g of Pd/C. Therefore, it was  
188 concluded that 0.45 g of Pd/C is required for the efficient decarboxylation of 0.9 g of fatty acid at the  
189 given conditions. In general, decarboxylation of fatty acids proceeds in three phases, gaseous H<sub>2</sub>, liquid  
190 fatty acids and a solid catalyst, in which the mutual accessibility is an important factor. Although an  
191 organic solvent is usually added to improve its accessibility in the literature [21], decarboxylation was  
192 conducted without any organic solvent in this study to simplify the reaction process. That might be the  
193 reason why such a large amount of Pd/C catalyst was needed. Therefore, an effective agitation would  
194 be required to reduce the amount of the catalyst.

195 On the other hand, Fig.3 shows HPLC chromatograms of rapeseed oil, the obtained fatty  
196 acids by hydrolysis/hydrogenation and hydrocarbons after decarboxylation. Triglycerides in rapeseed  
197 oil are composed of various fatty acids, thus many peaks are found in Fig.3. However, these peaks are  
198 converted mainly into three peaks of saturated fatty acids, palmitic (C<sub>16:0</sub>), stearic (C<sub>18:0</sub>) and arachidic  
199 (C<sub>20:0</sub>) acids, by hydrolysis/hydrogenation of triglycerides. These saturated fatty acids are then  
200 converted into *n*-pentadecane (C<sub>15</sub>H<sub>32</sub>), *n*-heptadecane (C<sub>17</sub>H<sub>36</sub>) and *n*-nonadecane (C<sub>19</sub>H<sub>40</sub>),  
201 respectively, by subsequent decarboxylation. Therefore, the obtained renewable diesel from rapeseed  
202 oil consists of these three kinds of saturated hydrocarbons.

203 Based on the HPLC and GPC analyses, the yields of hydrocarbons were determined as shown  
204 in Table 1. The total yield of hydrocarbons was 91.5 mol% and any other products were not observed.

205 Since hydrocarbons are stable enough under the given condition, no decomposition of the products can  
206 be occurred. Therefore, the rest of 8.5 mol% would probably be lost through the purification steps. The  
207 loss of the products would be caused by using a large amount of catalyst, on which the products were  
208 adsorbed. The molar ratio upon the obtained hydrocarbon basis was shown in parenthesis in Table 1. As  
209 a result, the molar ratio of obtained *n*-pentadecane, *n*-heptadecane and *n*-nonadecane was found out to  
210 be 4.5 : 93.6 : 1.9. This molar ratio is nearly close to the one of saturated fatty acids ( $C_{16:0} : C_{18:0} : C_{20:0}$   
211 = 4.6 : 91.2 : 1.9 in Table 1) obtained after hydrolysis/hydrogenation. Therefore, these saturated fatty  
212 acids seem to be selectively converted without any side reaction into the corresponding hydrocarbons  
213 through decarboxylation. In case of unsaturated fatty acids, however, various side reactions such as  
214 hydrogenation, dehydrogenation, cyclization, ketonization, dimerization and cracking have been  
215 reported to occur concurrently due to the unstable double bonds present [35, 36], which lead to  
216 decrease the degree of the specific production of hydrocarbons. Therefore, unsaturated fatty acids  
217 should be converted into saturated ones before decarboxylation to maintain its high selectivity. For this  
218 specificity, the process shown in Fig. 1 is appropriate and promising.

219 After hydrolysis/hydrogenation, 2.3 mol% of glycerides such as monoglycerides and  
220 diglycerides still remain as shown in Table 1. However, these intermediate compounds are disappeared  
221 after decarboxylation, and converted into hydrocarbons. Actually, when 1-monostearin was treated at  
222 the same condition, it was converted into *n*-heptadecane by decarboxylation treatment with H<sub>2</sub> gas and  
223 Pd/C catalyst even though the reactivity was slightly low, compared with saturated fatty acids.

224 Therefore, the remaining glycerides must be converted to saturated fatty acids during decarboxylation  
225 treatment.

226 The iodine and acid values of the obtained hydrocarbons from rapeseed oil were evaluated  
227 and found out to be zero. This means that the obtained products have neither double bonds nor fatty  
228 acids. It is, therefore, evident that hydrogenation and decarboxylation reactions are successfully  
229 completed during the process.

230

### 231 ***3.3. Fuel properties of saturated hydrocarbons***

232 It is very important to evaluate the fuel properties of the renewable diesel. However, the  
233 prepared renewable diesel is not sufficient in amount to test the fuel properties. As in Table 1, it  
234 consists of the saturated linear hydrocarbons of *n*-pentadecane, *n*-heptadecane and *n*-nonadecane in a  
235 molar ratio of 4.5 : 93.6 : 1.9. In addition, it was confirmed that such a mixture does not contain any  
236 contaminants. Therefore, a mixture of these three kinds of hydrocarbons was prepared from their  
237 chemicals purchased as the renewable diesel and evaluated for the fuel properties.

238 Table 2 shows the evaluated fuel properties of the mixtures of renewable diesel with #1 fossil  
239 diesel in various ratios. In case of 100 vol% renewable diesel, it has a higher flash point than that of the  
240 fossil diesel (0 vol% renewable diesel in Table 2), and satisfies the specification standard of the fossil  
241 diesel in Japan (JIS K2204) [37]. Such a property should be originated from *n*-heptadecane, a main  
242 component of the fuel, which has a relatively high boiling point among the hydrocarbons in petroleum

243 diesel. In addition, the values of kinematic viscosity and density also satisfy the requirements for the  
244 Japanese diesel standard. These values are also close to the ones of *n*-heptadecane. On the other hand,  
245 the cold-flow properties such as pour point and cold filter plugging point are poor due to the presence  
246 of saturated linear hydrocarbons, because these have relatively high melting points, especially in case  
247 of *n*-heptadecane. Therefore, the cold-flow properties should be improved to meet the fossil diesel  
248 standard. Blending the renewable diesel with fossil one is a simple way for this purpose. In case of 20  
249 vol% renewable diesel, as shown in Table 2, the pour point and cold filter plugging point are improved,  
250 and thus, it can satisfy the requirements for the fuel standard. However, when the ratio of renewable  
251 diesel is increased to be 30 vol%, the pour point exceeds the limit of the standard. From such a reason,  
252 the blending ratio would be limited up to around 20 vol% to meet all requirements of the specification  
253 standard in Table 2. This further indicates that the obtained hydrocarbons through this process can be  
254 used as renewable diesel by blending with fossil diesel.

255

#### 256 **4. Concluding Remarks**

257 To produce hydrocarbons from plant oil as renewable diesel fuel, the conventional  
258 hydrotreating and catalytic cracking processes are not really specific for the products selectivity due to  
259 unsaturated double bonds. In this study, therefore, the process composed of hydrolysis/hydrogenation  
260 and subsequent decarboxylation was proposed. In the first treatment, triglycerides in rapeseed oil were  
261 converted into saturated fatty acids through hydrolysis in hot-compressed water and simultaneous

262 hydrogenolysis under the presence of Pd/C catalyst and H<sub>2</sub> gas. In the second treatment, the obtained  
263 saturated fatty acids were decarboxylated into the corresponding hydrocarbons under the presence of  
264 Pd/C. In this process, unsaturated double bonds in fatty acid moieties, which lead to various side  
265 reactions, were hydrogenated into saturated ones prior to the second treatment. Therefore, the selective  
266 conversion was achieved by this two-step treatment without any side reaction. As a result, the  
267 composition of the obtained hydrocarbons corresponded to the fatty acid composition of rapeseed oil.

268           However, the obtained renewable diesel fuel should be improved in cold-flow properties  
269 because saturated linear hydrocarbons have relatively high melting points, whereas other properties  
270 such as flash point, kinematic viscosity and density satisfied the requirements of the fossil diesel. To  
271 satisfy the requirements, a blend of renewable diesel with fossil diesel was found out to weaken the  
272 inferior fuel properties of pour point and cold filter plugging point. Consequently, 20 vol% blend of the  
273 renewable diesel was found out to satisfy the requirements for the Japanese specification standard of  
274 the fossil fuel.

275

## 276 **Acknowledgement**

277           This work was supported by a Grant-in-Aid for Challenging Exploratory Research (No.  
278 25660279, 2013.4-2014.3), supported by the Ministry of Education, Culture, Sports, Science and  
279 Technology, Japan.



280 **References**

- 281 [1] Krawczyk T. BIODIESEL: alternative fuel makes inroads but hurdles remain. Inform  
282 1996;7(8):801-15
- 283 [2] Knothe G, Sharp CA, Ryan TW. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and  
284 alkanes in a new technology engine. *Energ Fuel* 2006;20(20):403–8.
- 285 [3] Haseeb ASMA, Fazal MA, Jahirul MI, Masjuki HH. Compatibility of automotive materials in  
286 biodiesel: A review. *Fuel* 2011;90(3):922-31.
- 287 [4] Moser BR. Biodiesel production, properties, and feedstocks, *In Vitro Cell Dev–Pl*  
288 2009;45(3):229-66.
- 289 [5] Monnier J, Tourigny G, Soveran DW, Alfred Wong, Hogan EN, Stumborg M. Conversion of  
290 biomass feedstock to diesel fuel additive, US patent 5705722, 1998.
- 291 [6] Satyarthi JK., Chiranjeevi T, Gokak DT, Viswanathan PS. An overview of catalytic conversion of  
292 vegetable oils/fats into middle distillate. *Catal Sci Technol* 2013;3(1):70-80.
- 293 [7] Gong S, Shinozaki A, Shi M, Qian EW. Hydrotreating of Jatropha Oil over Alumina Based  
294 Catalysts. *Energ Fuel* 2012;26(4):2394–9.
- 295 [8] Kubička D, Kaluža L. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts.  
296 *Appl Catal A: Gen* 2010;372(2):199–208.
- 297 [9] Madsen AT, Ahmed EH, Christensen CH, Fehrmann R, Riisager A. Hydrodeoxygenation of waste  
298 fat for diesel production: Study on model feed with Pt/alumina catalyst. *Fuel* 2011;90(11):3433–8.

- 299 [10] Krár M, Kovács S, Kalló D, Hancsók J. Fuel purpose hydrotreating of sunflower oil on  
300 CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. *Bioresource Technol* 2010;101(23):9287–93.
- 301 [11] Huber GW, O’Conno P, Corma A. Processing biomass in conventional oil refineries: Production of  
302 high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Appl Catal A:*  
303 *Gen* 2007;329(1):120–9.
- 304 [12] Watanabe M, Iida T, Inomata H. Decomposition of a long chain saturated fatty acid with some  
305 additives in hot compressed water. *Energ Convers Manage* 2006;47(18-19):3344-50.
- 306 [13] Mikulec J, Cvengroš J, Joríková L, Banič M, Kleinová A. Second generation diesel fuel from  
307 renewable sources. *J Clean Prod* 2010;18(9):917–26.
- 308 [14] Tani H, Shimouchi M, Haga H, Fujimoto K. Development of Direct Production Process of Diesel  
309 Fuel from Vegetable Oils. *J Jpn Inst Energy* 2011;90:466-70.
- 310 [15] Maher KD, Bressler DC. Pyrolysis of triglyceride materials for the production of renewable fuels  
311 and chemicals. *Bioresource Technol* 2007;98(12):2351–68.
- 312 [16] Rao KVC. Production of hydrocarbons by thermolysis of vegetable oils. US patent 4102938 A,  
313 1978.
- 314 [17] Twaiq FA, Zabidi NAM, Bhatia S. Catalytic Conversion of Palm Oil to Hydrocarbons:  
315 Performance of Various Zeolite Catalysts. *Ind Eng Chem Res* 1999;38(9):3230-7.
- 316 [18] Taufiqurrahmi N, Bhatia S. Catalytic cracking of edible and non-edible oils for the production of  
317 biofuels. *Energy Environ Sci* 2011;4:1087-112.

- 318 [19] Snåre M, Kubičková I, Mäki-Arvela P, Chichova D, Eränen K, Murzin DY. Catalytic  
319 deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons.  
320 Fuel 2008;87(6):933-45.
- 321 [20] Dos Anjos JRS, Gonzalez WDA, Lam YL, Frety R. Catalytic decomposition of vegetable oil. Appl  
322 Catal 1983;5(3):299-308.
- 323 [21] Wang WC, Thapaliya N, Campos A, Stikeleather LF, Roberts WL. Hydrocarbon fuels from  
324 vegetable oils via hydrolysis and thermo-catalytic decarboxylation. Fuel 2012;95:622-9.
- 325 [22] Theilgaard MA, Rosmyslowicz B, Mäki-Arvela P, Simakova IL, Eränen K, Murzin DY, Fehrmann,  
326 R., Deactivation in Continuous deoxygenation of C18-fatty feedstock over Pd/Sibunit, Top Catal  
327 2013;56(9) 714-24.
- 328 [23] Saka S, Dadan K. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel  
329 2001;80:225-31.
- 330 [24] Kusdiana D, Saka S. Two-Step Preparation for Catalyst-Free Biodiesel Fuel Production. Appl  
331 Biochem Biotech 2004;115(1-3):781-91.
- 332 [25] Minami E, Saka S. Kinetics of hydrolysis and methyl esterification for biodiesel production in  
333 two-step supercritical methanol process. Fuel 2006;85(17-18):2479-83.
- 334 [26] Marker TL, Kokayeff P, Abdo SF, Baldiraghi F, Sabatino LMF. Production of diesel fuel from  
335 biorenewable feedstocks with lower hydrogen consumption. US patent 2009/0193709 A1, 2009.

- 336 [27] Lestari S, Simakova I, Tokarev A, Mäki-Arvela P, Eränen K, Murzin DY. Synthesis of Biodiesel  
337 via Deoxygenation of Stearic Acid over Supported Pd/C Catalyst. *Catal Lett* 2008;122:247–51.
- 338 [28] Standard Methods for the Analysis of Fats, Oils and Related Materials, 2.4.2.2-2013, Fatty acids  
339 composition (FID temperature programmed gas chromatography), Japan Oil Chemists' Society,  
340 Tokyo, 2013.
- 341 [29] ASTM D1298-99 Standard test method for density, or API gravity of crude petroleum and liquid  
342 petroleum products by hydrometer method.
- 343 [30] ASTM D974-06 Standard Test Method for Acid and Base number by color-indicator titration.
- 344 [31] ASTM D1959-97 Standard test method for iodine value of drying oils and fatty acids.
- 345 [32] Maier W, Roth W, Thies I, van Ragué Schleyer P. Gas phase decarboxylation of carboxylic acids.  
346 *Chem Ber* 1982;115:808-812.
- 347 [33] Mäki-Arvela P, Kubičková I, Snåre M, Eränen K, Murzin DY. Catalytic deoxygenation of fatty  
348 acids and their derivatives. *Energ Fuel* 2007;21:30-41.
- 349 [34] Kubičková I, Snåre M, Eränen K, Mäki-Arvela P, Murzin DY. Hydrocarbons for diesel fuel via  
350 decarboxylation of vegetable oils. *Catal Today* 2005;106:197–200.
- 351 [35] Simakova I, Rozmysłowicz B, Simakova O, Mäki-Arvela P, Simakov A, Murzin DY. Catalytic  
352 Deoxygenation of C18 Fatty Acids Over Mesoporous Pd/C Catalyst for Synthesis of Biofuels. *Top*  
353 *Catal* 2011;54(8-9):460–6.

- 354 [36] Snåre M, Kubičková I, Mäki-Arvela P, Eränen K, Murzin DY. Heterogeneous Catalytic  
355 Deoxygenation of Stearic Acid for Production of Biodiesel. Ind Eng Chem Res  
356 2006;45(16):5708-15.
- 357 [37] JIS K2204, Japanese industrial standards committee. Diesel fuel; 2007 [in Japanese].

358 **List of figures**

359

360 Figure 1: Schematic diagram of the saturated hydrocarbon production process via saturated fatty acids  
361 from rapeseed oil.

362

363 Figure 2: GPC (a) and HPLC (b) chromatograms of the obtained saturated fatty acids by  
364 hydrolysis/hydrogenation from rapeseed oil at 270 °C/ 5 MPa (H<sub>2</sub>) with 3.0 g of water and 0.05 g of  
365 Pd/C.

366

367 Figure 3: HPLC chromatograms of rapeseed oil, the obtained saturated fatty acids by  
368 hydrolysis/hydrogenation (270 °C/ 5 MPa (H<sub>2</sub>) with 3.0 g of water and 0.05 g of Pd/C for 60 min) and  
369 the saturated hydrocarbons by decarboxylation (300 °C/ 1 MPa (H<sub>2</sub>) with 0.45 g Pd/C for 120 min).

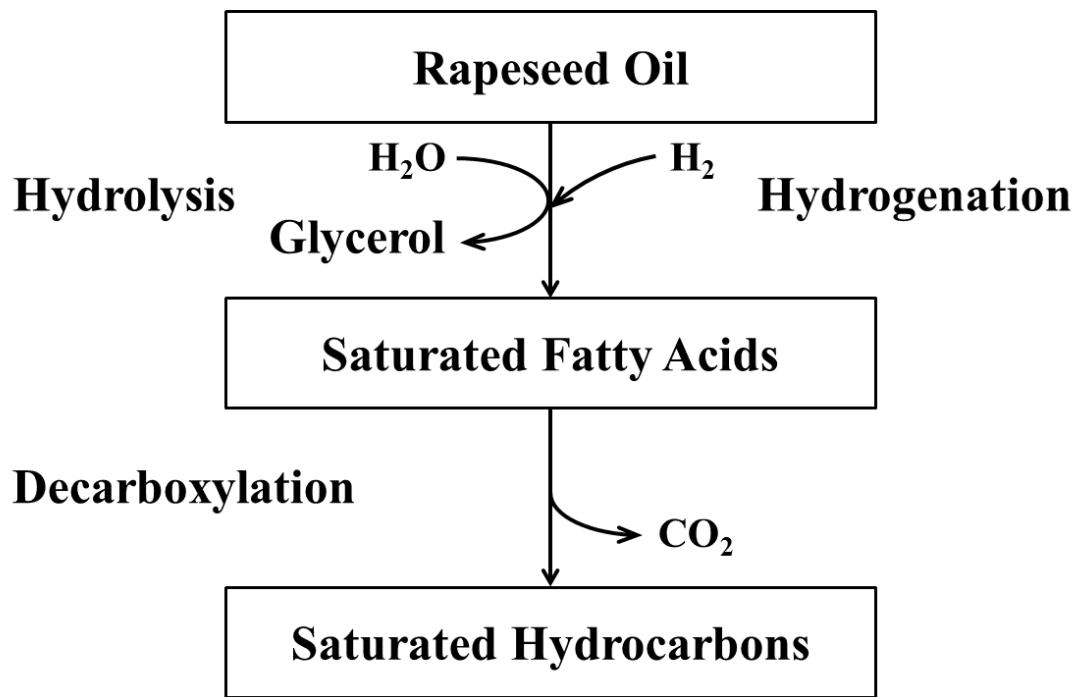
370 **List of tables**

371

372 Table 1: Fatty acid composition of rapeseed oil, the obtained saturated fatty acids by  
373 hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation.

374

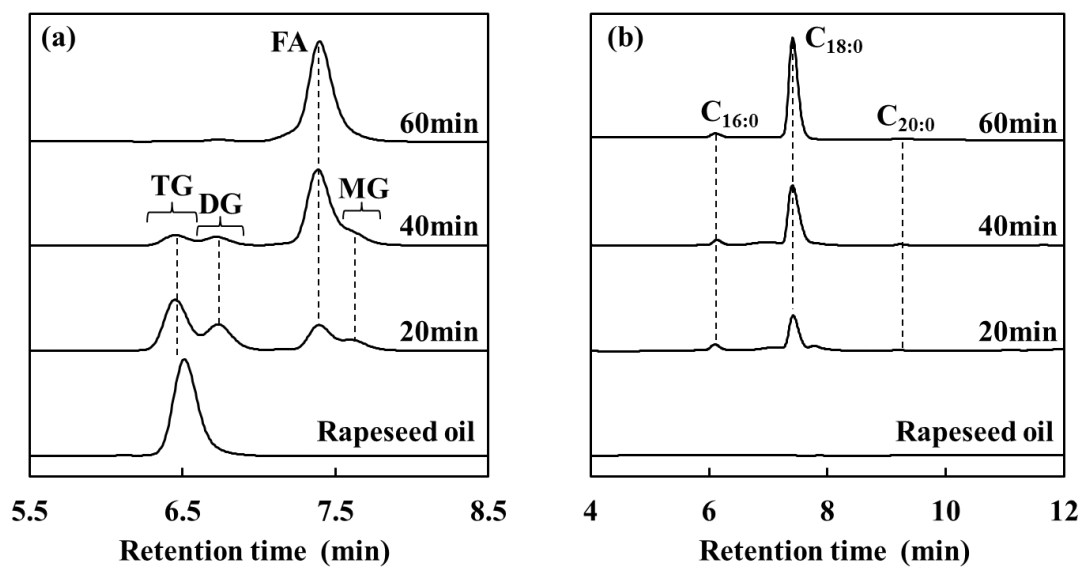
375 Table 2: The fuel properties of renewable diesel blended with fossil diesel in various ratios compared  
376 with Japanese #1 diesel standard (JIS K2204) [37].



Fuel

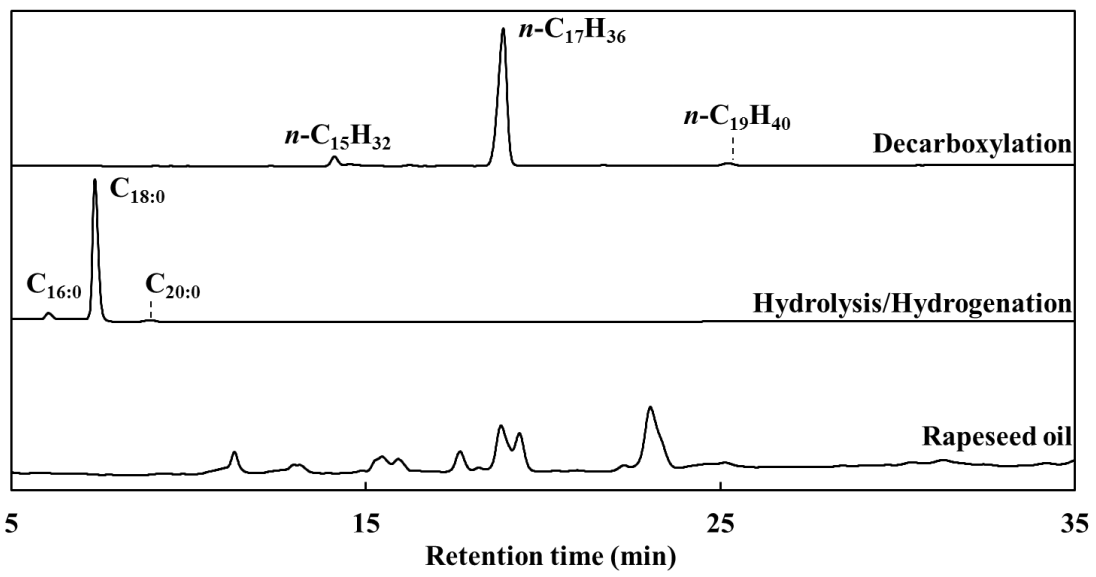
Figure 1





Fuel

Figure 2



Fuel

Figure 3

Table 1: Fatty acid composition of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation.

Fatty acid composition of rapeseed oil (mol%)		Yield (mol%)*1		
		Saturated fatty acids by hydrolysis/hydrogenatio n*2	Saturated hydrocarbons by decarboxylation*3	
C <sub>16:0</sub>	4.3	4.5 (4.6)	4.1 (4.5)	C <sub>15</sub> H <sub>32</sub>
C <sub>16:1</sub>	0.2	0.0	-	
C <sub>18:0</sub>	0.7	89.7 (91.2)	85.7 (93.6)	C <sub>17</sub> H <sub>36</sub>
C <sub>18:1</sub>	66.4	0.0	-	
C <sub>18:2</sub>	19.4	0.0	-	
C <sub>18:3</sub>	7.5	0.0	-	
C <sub>20:0</sub>	0.5	1.9 (1.9)	1.7 (1.9)	C <sub>19</sub> H <sub>40</sub>
C <sub>20:1</sub>	1.0	0.0	-	
Glycerides	-	2.3 (2.3)	0.0	
<b>Total</b>	<b>100</b>	<b>98.4 (100)</b>	<b>91.5 (100)</b>	

\*1: The values in parenthesis indicate the mol% on the total yield basis of rapeseed oil.

\*2: 270 °C/ 5 MPa (H<sub>2</sub>) with 3.0 g of water and 0.05 g of Pd/C for 60 min

\*3: 300 °C/ 1 MPa (H<sub>2</sub>) with 0.45 g Pd/C for 120 min

Table 2: The fuel properties of renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204) [37].

Property	Ratio of renewable diesel <sup>*1</sup> to #1 fossil diesel (vol%)					#1 diesel standard
	100	30	20	5	0 <sup>*2</sup>	
	Flash point (°C)	153	75.0	69.5	64.5	63.5
Pour point (°C)	20	3.0	-2.5	-7.0	-8.0	≤ -2.5
Cold filter plugging point (°C)	22	-2.0	-6.0	-3.0	-5.0	≤ -1
Kinematic viscosity at 30 °C ( mm <sup>2</sup> /s)	4.5	3.7	3.6	3.6	3.5	≥ 2.7
Density at 15 °C ( g/cm <sup>3</sup> )	0.77	0.82	0.83	0.83	0.83	≤ 0.86

\*1: The renewable diesel is prepared by mixing pure hydrocarbons with the same molar ratio as in

Table 1.

\*2: Renewable diesel 0 vol% corresponds to fossil diesel 100 vol%.