



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



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## 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.

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## ABSTRACT

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

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## 1. Introduction

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

The hydrotreatment of plant oils was usually studied in the temperature range between 350 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 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]. Under the hydrotreating reaction, first, double bonds in fatty acid moieties of triglyceride are hydrogenated into saturated C–C bonds, followed by the cleavage of ester linkages to produce one molecule of propane and three molecules of saturated fatty acids [6,12]. The obtained saturated fatty acids are then deoxidized into hydrocarbons having carbon numbers mainly between 15 and 18 through hydrodeoxygenation, decarbonylation and decarboxylation [8,13]. This reaction also produces *i*-paraffin and naphthene through isomerization and cyclization of olefin intermediates, which contributes to improving the cold-flow properties. In addition, CO, CO<sub>2</sub>, H<sub>2</sub>O and propane are produced as byproducts [6].

On the other hand, the catalytic cracking of plant oils was usually carried out in the temperature range between 300 and 500 °C

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under atmospheric pressure with zeolites,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  as a catalyst [14–17], under which the thermal decomposition is predominant. First, triglycerides are decomposed to fatty acids, ketones, aldehydes and esters [18]. These products undergo secondary cracking to form short and long chain paraffins and olefins with  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and alcohols by breaking C–O and C–C bonds via decarboxylation and decarbonylation. However, this process makes various hydrocarbons having wide range of carbon numbers with olefins and aromatics.

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

In this study, therefore, hydrocarbon production from plant oil was studied through two-step reaction with hydrolysis and subsequent decarboxylation. During the hydrolysis step, hydrogenation was simultaneously conducted to produce stable saturated fatty acids, which may suppress undesirable side reactions during subsequent decarboxylation [19,20]. In the literature [5–21], furthermore, an organic solvent such as *n*-dodecane was usually added to enhance the fluidity of the reactants and to avoid the deactivation of catalyst, even though only a few studies without any solvent can be found [19,22]. However, the use of such organic solvent requires additional separation and purification steps after the reaction, and it makes the whole process complicated. Therefore, the reactions of this study were conducted without any organic solvent so as to simplify the process for production of hydrocarbons as renewable diesel.

## 2. Materials and methods

### 2.1. Experimental procedures

Fig. 1 shows the schematic diagram of the saturated hydrocarbon (renewable diesel) production process in this study via saturated fatty acids from rapeseed oil. Prior to the experiment, Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 °C and reduced in  $\text{H}_2$  flow (15 ml/min) at 200 °C for 60 min. Rapeseed oil (reagent grade, Nacalai Tesque, Inc.) was, then, treated in hot-compressed water with  $\text{H}_2$  gas and Pd/C catalyst for hydrolysis and hydrogenation to obtain saturated fatty acids. The obtained saturated fatty acids were then decarboxylated with Pd/C catalyst to produce saturated hydrocarbons by decarboxylation.

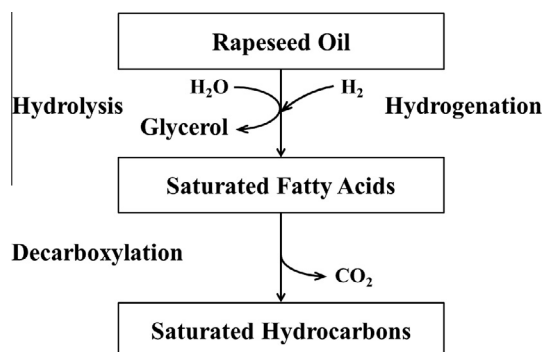


Fig. 1. Schematic diagram of the saturated hydrocarbon production process via saturated fatty acids from rapeseed oil.

#### 2.1.1. Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)

A batch-type reaction vessel (inner volume: 5.0 ml) made of Inconel-625 [23] was used for the reaction. One gram of rapeseed oil and 1.0–3.0 g of ion-exchanged water were placed into the reaction vessel with 0.05 g of Pd/C. Hastelloy balls (total volume: 0.2 ml) were also placed into the vessel to agitate the mixture efficiently. After the vessel was sealed, the inside of the vessel was purged and pressurized to 5 MPa with  $\text{H}_2$  gas using a gas-supplying system. The hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation) reaction was then conducted by immersing the vessel into a molten salt bath preheated at 270 °C, which is the optimum temperature for hydrolysis of triglycerides found in previous works [24,25]. The reaction vessel was swung from side to side to agitate the mixture during the reaction. After a designated treatment time, the vessel was moved into a water bath to quench the reaction. The obtained reaction mixture dissolved in tetrahydrofuran (THF, specially prepared reagent grade, Nacalai Tesque, Inc.) was, then, taken out from the vessel, sonicated for 30 min, and the catalyst was removed with a filter paper in a micropore of 0.45  $\mu\text{m}$  (Merck Millipore Co.). The products were, then, warmed up in a water bath at 70 °C for 30 min and separated into THF and water phases. By removing THF from the THF phase with a rotary vacuum evaporator, the products of the hydrolysis/hydrogenation reaction were collected and their yield was determined.

#### 2.1.2. Decarboxylation

For subsequent decarboxylation, approximately 0.9 g of the obtained saturated fatty acids and 0.05–0.45 g of Pd/C were placed into the 5 ml reaction vessel with Hastelloy balls. The inside of the reaction vessel was then purged and pressurized with  $\text{N}_2$  or  $\text{H}_2$  gas to be 1 MPa which is a favorable pressure for decarboxylation reaction [26]. The decarboxylation was, then, conducted with the molten salt bath at 300 °C for 120 min, which is an appropriate condition reported by Lestari et al. [27], and quenched into the water bath in the same way mentioned above. After the reaction, the obtained products dissolved in THF were taken out from the vessel, sonicated for 30 min, and the catalyst was removed with the filter paper. After removing THF by the evaporator, the decarboxylated products were obtained to determine its yield. To clarify the decarboxylation reaction of the saturated fatty acid, stearic acid (guaranteed reagent grade from Nacalai Tesque, Inc.) was also studied.

### 2.2. Analytical methods

The fatty acid composition of rapeseed oil used in this work was determined in accordance with the Japan Oil Chemists' Society standard method [28]. The products, obtained from hydrolysis/hydrogenation and subsequent decarboxylation, were analyzed by gel permeation chromatography (GPC, Shimadzu Co. LC-10VP system, column: GF-310 HQ (Showa Denko K.K.), oven temperature: 40 °C, mobile phase: THF, flow-rate: 1.0 ml/min, detector: refractive index detector RID-10A) and high performance liquid chromatography (HPLC, column: Cadenza CD-C18 (Imtakt Co.), oven temperature: 40 °C, mobile phase: methanol, flow-rate: 1.0 ml/min, detector: RID-10A). By the GPC analysis, the obtained products from hydrolysis/hydrogenation can be separated into four peaks, which correspond to the groups of triglycerides, diglycerides, monoglycerides and fatty acids. The amount of each group was quantified based on the corresponding peak area, using tristearin, 1,3-distearin, 1-monostearin (all being >99% grade from Olbracht Serdary Research Laboratories) and stearic acid (guaranteed reagent grade from Nacalai Tesque, Inc.) as calibration standards. The HPLC analysis, by which fatty acids can be separated

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