



Full Length Article

Hydrocarbon production from coconut oil by hydrolysis coupled with hydrogenation and subsequent decarboxylation



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HIGHLIGHTS

- Hydrocarbon production from coconut oil was studied.
- The process consists of hydrolysis/hydrogenation and subsequent decarboxylation.
- The comparison between coconut and rapeseed oils with this process was discussed.
- The product meets the Japanese diesel standard by blending with fossil diesel.

ARTICLE INFO

Article history:

Received 27 December 2016
 Received in revised form 3 February 2017
 Accepted 14 February 2017
 Available online 23 February 2017

Keywords:

Renewable diesel
 Coconut oil
 Hydrolysis
 Hydrogenation
 Decarboxylation

ABSTRACT

Hydrocarbon production from coconut oil for use as a renewable diesel was studied by a two-step process: hydrolysis coupled with hydrogenation and subsequent decarboxylation. In the first step, coconut oil was treated in subcritical water at 270 °C/5 MPa (H₂) with a Pd/C catalyst for 60 min, in which triglycerides were hydrolyzed and hydrogenated into saturated fatty acids with a yield of 91.2 mol%. In the second step, the obtained saturated fatty acids were decarboxylated into hydrocarbons as renewable diesel at 300 °C/1 MPa (H₂) with Pd/C for 360 min. However, its yield was only 53.3 mol% based on coconut oil. Although the reaction time for the hydrolysis/hydrogenation of coconut oil was the same as that of rapeseed oil that was studied in previous work, the complete decarboxylation conversion took three times longer. Such differences in reaction time and final hydrocarbon yield are related to the shorter coconut oil chains. The obtained renewable diesel was evaluated and their cold-flow properties were satisfactory, but the flash point and kinematic viscosity were out of the fossil diesel specification standard range, unlike those from rapeseed oil. The renewable diesel properties could be improved by blending an adequate amount of fossil diesel to satisfy the specification.

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1. Introduction

Fatty acid methyl ester (FAME) is used as an alternative fossil diesel with no or minor engine modification. In general, FAME is produced by triglyceride transesterification, and is the main component of plant oil along with methanol. Because plant oil includes no aromatics and sulfur, the use of FAME can reduce exhaust emissions [1,2]. However, FAME exhibits some disadvantages that are caused by differences in chemical structure from fossil diesel, such as a corrosiveness to certain rubbers and metals, a poor oxidation stability because of its unsaturated double bonds and poor cold-flow properties because saturated compounds have a high melting point [1,3,4].

In recent years, hydrocarbon production, which is often termed green diesel or renewable diesel, has been researched globally by hydrotreatment or catalytic cracking of plant oils to resolve these disadvantages. Hydrotreatment has been studied typically between 300 and 450 °C under a H₂ pressure of between 4 and 15 MPa with sulfide or noble metal catalysts [5–11]. This process involves the concurrent hydrogenation of unsaturated double bonds and cleavage of ester linkages in triglycerides, followed by deoxygenation such as hydrodeoxygenation, decarboxylation and decarbonylation to produce hydrocarbons, mainly between C15 and C18 [11]. Catalytic cracking is usually carried out between 350 and 500 °C under atmospheric pressure with a catalyst such as zeolite, Al₂O₃ and MgO [12–15]. In this case, thermal decomposition dominates, and produces various hydrocarbons with a wide range of carbon numbers. However, the product yield and selectivity of these conventional processes may be low. The first reason is the presence of unstable double bonds in fatty acid moieties, which

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leads to various side reactions [16]. The second reason is the relatively severe reaction conditions that are required to convert triglycerides to hydrocarbons [17]. In particular, a high temperature may lead to a low selectivity because of undesirable reactions [6].

To improve the product yield and selectivity, our research group has proposed a hydrocarbon production process from plant oils by a two-step reaction [9]. In the first step, plant oil is treated in subcritical water with H₂ gas and a Pd/C catalyst to produce saturated fatty acids. In subcritical water, the cleavage of ester linkages proceeds through hydrolysis at ~270 °C [18], which is lower than the conventional processes. Concurrently, unsaturated double bonds are hydrogenated to saturated bonds because of the presence of Pd/C and H₂. Thus, saturated fatty acids are produced selectively from triglycerides. In the second step, the obtained saturated fatty acids are decarboxylated into saturated hydrocarbons with a Pd/C catalyst at 300 °C. The temperature is relatively low compared with the conventional processes, because fatty acids are more easily decarboxylated than triglycerides [17], and this results in a high yield and selectivity.

In the previous study, the proposed two-step process achieved an excellent conversion of rapeseed oil to hydrocarbons with a high selectivity [9]. In this process, all C16 fatty acid (palmitic acid) and C18 fatty acid (stearic, oleic, linoleic and linolenic acids) moieties in the triglyceride were converted completely to the corresponding saturated hydrocarbons, *n*-pentadecane (C15) and *n*-heptadecane (C17), respectively, without any side reaction. This result indicates that the hydrocarbon composition in the proposed process can be predicted from the fatty-acid composition of the feedstock triglycerides.

Various plant oils such as rapeseed, soybean, sunflower and olive oils are available as a feedstock for renewable diesel. These plant oils are composed mainly of C16 and C18 fatty acids. However, several plant oils, for example, coconut and palm kernel oils, have unique fatty-acid compositions with shorter carbon chains, such as C10 (capric acid), C12 (lauric acid) and C14 (myristic acid). The difference in carbon-chain length may affect the reaction conditions of the proposed two-step process. The fuel properties of hydrocarbons that are produced from coconut and palm kernel oils may differ from those that are produced from typical plant oils.

In this study, therefore, hydrocarbon production as a renewable diesel from coconut oil by the two-step process was investigated, and is compared with that from rapeseed oil. In addition, the fuel properties of the obtained renewable diesel from coconut oil were evaluated.

2. Materials and methods

2.1. Experimental procedures

Renewable diesel production from coconut oil was conducted based on a previous study [9]. Prior to the experiment, a Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 °C, and reduced in H₂ (15 ml/min) at 200 °C for 60 min.

2.1.1. Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)

For the hydrolysis/hydrogenation reaction, 1.0 g coconut oil (reagent grade, Nacalai Tesque, Inc.), 3.0 g ion-exchanged water and 0.05 g Pd/C were placed in a 5-mL batch-type Inconel-625 reaction vessel [19] with Hastelloy balls (total volume: 0.2 ml) to agitate the mixture efficiently. The vessel was sealed, purged and pressurized to 5 MPa with H₂ gas using a gas-supply system. The vessel was immersed into a molten-salt bath that was preheated

at 270 °C and agitated. After a designated treatment time, the vessel was moved into a water bath to quench the reaction.

The reaction mixture was removed from the vessel by its dissolution in tetrahydrofuran (THF, specially prepared reagent grade, Nacalai Tesque, Inc.) and sonicated for 30 min to detach products that had adsorbed on the catalyst surface. The catalyst was removed by using 0.45- μ m filter paper (Merck Millipore Co.). The obtained mixture was separated into THF and water phases, and the water phase, including glycerol, was removed. By removing THF from the THF phase with a rotary vacuum evaporator, a hydrolysis/hydrogenation product was obtained and weighed by using an electronic balance. The chemical composition of the product was determined by gas chromatography with a flame ionization detector (GC-FID), and the fatty acid yield was estimated based on the product mass and its chemical composition.

2.1.2. Decarboxylation

Subsequent decarboxylation was conducted in the same manner as the hydrolysis/hydrogenation step. Approximately 0.8 g of the products obtained by hydrolysis/hydrogenation was treated at 300 °C with 0.40 g Pd/C, H₂ gas (1 MPa) and Hastelloy balls. Although H₂ is not required for decarboxylation, sometimes it maintains the catalyst activity [6]. Therefore, H₂ was used in this study as was used in previous work [9]. After a designated reaction time, the obtained reaction mixture, which is expected to contain volatile hydrocarbons such as *n*-pentane (C5), was removed from the vessel by its dissolution in 50 ml of 2-propanol (extra pure reagent grade, Nacalai Tesque, Inc.). To analyze the chemical composition of the product, 2-propanol solution was centrifuged at 5000 rpm for 10 min, and 1.0 μ l of the clear supernatant was used in GC-FID analysis to prevent short-chain hydrocarbon volatilization. The 2-propanol solution (~50 ml) with catalyst was sonicated for 30 min to detach those products that remained on the catalyst surface. The catalyst and 2-propanol were removed by using filter paper and a rotary vacuum evaporator, respectively. The decarboxylation product was weighed by using the electronic balance. During the purification steps short-chain hydrocarbons such as *n*-pentane were partially lost. Therefore, the absolute yield was estimated by adding the lost part, which was calculated from the chemical compositions and the masses before and after the purification.

2.2. Analytical methods

The fatty-acid composition of the coconut oil was determined according to the Japan Oil Chemists' Society standard method [20]. Hydrolysis/hydrogenation and decarboxylation products were analyzed by GC-FID (GC-2014, Shimadzu Co.). For the glycerides and hydrocarbons, CP-TAP CB for triglycerides (Agilent Technology; length, 25 m; diameter, 0.25 mm; thickness, 0.10 μ m) was used as a column under the following conditions: injector temperature, 350 °C; detector temperature, 370 °C; column temperature, 30 °C (7 min), 30 °C \rightarrow 80 °C (5 °C/min), 80 °C \rightarrow 120 °C (10 °C/min), 120 °C \rightarrow 230 °C (5 °C/min), 230 °C \rightarrow 350 °C (27 °C/min), 350 °C (40 min); carrier gas, He; flow rate, 27.7 ml/min. For fatty acids and short-chain hydrocarbons, CP-FFAP CB (Agilent Technology; length, 25 m; diameter, 0.32 mm; thickness, 0.30 μ m) was used under the following conditions: injector temperature, 270 °C; detector temperature, 280 °C; column temperature, 50 °C (0.2 min), 50 °C \rightarrow 150 °C (22 °C/min), 150 °C \rightarrow 240 °C (6 °C/min), 240 °C (20 min); carrier gas, He; flow rate, 65.7 ml/min.

The fuel properties of the obtained renewable diesel were evaluated by using the automated Pensky–Martens closed-cup flash point tester (APM-7), the mini pour point tester (MPC-102), the automated cold-filter-plugging point tester (AFP-102) and the

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