

Original Paper

Oxidative Cleavage of Linoleic and Linolenic Acids Followed by Decarboxylation for Hydrocarbon Production

Kiky Corneliasari SEMBIRING, Eiji MINAMI[†], Haruo KAWAMOTO, and Shiro SAKA

(Received July 25, 2019)

Hydrocarbon fuel production from polyunsaturated fatty acids (linoleic and linolenic acids) was studied in a two-step process: oxidative cleavage followed by decarboxylation. In the first step, the effects of oxidizing agent concentration and reaction temperature were investigated. The optimum yield for oxidative cleavage of linoleic acid was 90.3 mol% of hexanoic acid and 53.8 mol% of nonanedioic acid; while that of linolenic acid was 60.0 mol% of nonanedioic acid. In the second step, decarboxylation of hexanoic and nonanedioic acids into hydrocarbons was investigated under different N₂ pressures with a Pd/C catalyst to yield 73.5 mol% of *n*-pentane and 73.1 mol% of *n*-heptane, respectively, which correspond to the carbon number range of gasoline (C4-C10).

Key Words

Hydrocarbons, Linoleic acid, Linolenic acid, Oxidative cleavage, Decarboxylation

酸化開裂及び脱炭酸の2段階反応により、リノール酸及びリノレン酸(多価不飽和脂肪酸)からの炭化水素燃料の製造を検討した。1段階目の酸化開裂の最適化のため酸化剤濃度と反応温度の影響を検討した。その結果、リノール酸から最大で 90.3 mol% のヘキサン酸と 53.8 mol% のノナン二酸が、リノレン酸から最大で 60.0 mol% のノナン二酸が得られた。また、2段階目の脱炭酸を Pd/C 触媒下、様々な N₂ 圧力で検討したところ、ヘキサン酸から 73.5 mol% の *n*-ペンタンが、ノナン二酸から 73.1 mol% の *n*-ヘプタンが得られた。これらの炭化水素はガソリンの炭素数範囲 (C4-C10) に相当する。

キーワード

炭化水素, リノール酸, リノレン酸, 酸化開裂, 脱炭酸

1. Introduction

In recent years, the interest in producing renewable energy from biomass sources has increased significantly. Biomass-based gasoline and diesel fuels, such as bioethanol and biodiesel, have been extensively developed and used as alternatives to fossil fuels. However, the oxygen atoms in their molecules cause low calorific value, corrosion to engine components, and high-water affinities¹⁾. The characteristics of these biofuels are different from petroleum-based fuels, which consist of oxygen-free hydrocarbons. Thus, the production of hydrocarbon fuels attracts high interest. Fatty acid molecules in triglycerides of plant oils have alkyl chains similar to petroleum fuels; therefore, they hold the potential to be converted into hydrocarbons by removing oxygen atoms.

Hydrocarbon production from plant oils has been widely studied by catalytic cracking and hydrotreating. Catalytic cracking is usually conducted at temperatures between 300 and 500 °C at atmospheric pressure with various catalysts, such as NiMo/ γ -Al₂O₃, Ni/SiO₂, Al₂O₃, MgO, and zeolites^{2)~4)}. Hydrotreating is generally conducted between 350 and 450 °C under an H₂ pressure between 4 and 15 MPa with sulfided Ni-Mo and Co-Mo, which are usually supported on Al₂O₃, SiO₂, ZrO₂, TiO₂, and zeolites^{5)~7)}. These processes require high reaction temperatures because of the low reaction rate of triglycerides. Furthermore, reactive double bonds in unsaturated fatty acids of plant oils lead to many side reactions during the high-temperature process, producing a broad range of hydrocarbons^{8)~10)}.

To decrease the reaction temperatures and improve the product yield and selectivity, our research group has investigated hydrocarbon fuel production from saturated and unsaturated fatty acids in plant oils. Fatty acids have

Graduate School of Energy Science, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

[†] Corresponding author: minami@energy.kyoto-u.ac.jp

higher reactivity than triglycerides; therefore, hydrocarbon production can be conducted at lower temperatures than the conventional methods. Sugami *et al.*^{11) 12)} successfully produced renewable diesel by hydrothermal hydrogenation of plant oils followed by Pd/C-catalyzed decarboxylation to yield 91.5 mol% of hydrocarbons from rapeseed oil at 300 °C.

In the previous study¹⁾, a two-step process has been proposed for the conversion of monounsaturated fatty acid (oleic acid) to hydrocarbons as renewable gasoline (C4–C10). In the first step, unsaturated fatty acids are treated with KMnO_4 for oxidative cleavage at low temperature (40 °C) to obtain short-chain saturated fatty acids. The obtained short-chain fatty acids without C=C double bonds are beneficial to suppress the side reactions that possibly occur during the following decarboxylation. In the second step, the short-chain fatty acids are selectively decarboxylated into hydrocarbons with Pd/C catalyst under mild reaction conditions (300 °C, 5 MPa). Pd/C catalyst was used in this study because it has been reported to present the best performance for decarboxylation¹³⁾. This reaction process resulted in high yield and selectivity to convert 100 mol oleic acid into 91 mol *n*-octane and 63 mol *n*-heptane. The mild reaction conditions and high product selectivity are the main advantages of the proposed method.

Plant oils consist of both saturated and unsaturated fatty acids, and each plant oil has an intrinsic fatty acid composition depending on plant species. Unsaturated fatty acids are classified into monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA) according to the number of unsaturated double bonds. The most common PUFA in plant oils are linoleic acid and linolenic acid. The difference in chemical structure of unsaturated fatty acid may affect the reaction conditions of the proposed two-step process. In this paper, linoleic and linolenic acids were investigated as model compounds of PUFA for the production of renewable gasoline applying the same method as the previous work for MUFA¹⁾. Combination of the previous and current study will deliver a comprehensive understanding of further application of real plant oils, which contain both MUFA and PUFA.

2. Materials and methods

2.1 Materials

Reagent-grade of linoleic acid, linolenic acid, potassium permanganate (KMnO_4), polyoxyethylene lauryl ether (PLE), sulfuric acid (H_2SO_4), sodium hydrogen sulfite (NaHSO_3), sodium sulfate (Na_2SO_4), diethyl ether, tetrahydrofuran (THF), and *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were purchased from Nacalai Tesque (Kyoto, Japan). Extra-pure hexanoic and nonanedioic acids were

purchased from Tokyo Chemical Industry (Tokyo, Japan). The Pd/C (5%) catalyst was purchased from Nacalai Tesque (Kyoto, Japan).

2.2 Oxidative cleavage of unsaturated fatty acids

Oxidative cleavage was carried out according to the method described in our previous paper¹⁾. An emulsion was prepared by adding linoleic or linolenic acid (0.10 g) to water (2.0 mL) with PLE (0.02 g) as an emulsifier and then ultrasonically agitated at room temperature for 30 min. The emulsion was then mixed with KMnO_4 solution (designated concentration, 4.5 mL) in aqueous H_2SO_4 (0.0225 N) for oxidative cleavage. At the end of the reaction, NaHSO_3 solution was added and the pH was adjusted to 1–2 using 9 N H_2SO_4 to decompose the remaining KMnO_4 . The mixture was heated at 70 °C for 30 min to break the emulsion. It was, then, cooled and the products were extracted with diethyl ether and then dried using anhydrous Na_2SO_4 . The oxidative cleavage product was obtained by removing diethyl ether with a rotary vacuum evaporator.

2.3 Decarboxylation of fatty acids to hydrocarbons

Decarboxylation was conducted according to the method in our previous paper¹⁾. Prior to the experiments, the Pd/C catalyst was dried overnight at 105 °C and reduced by flowing H_2 (15 mL/min) at 200 °C for 2 h. Hexanoic acid (0.18 g) or nonanedioic acid (0.15 g), was placed in a 5-mL batch-type reaction vessel made of Inconel-625 together with the Pd/C catalyst (0.21 g). The vessel was sealed and pressurized with N_2 . The reaction was conducted by immersing the vessel in a molten salt bath at 300 °C under various N_2 pressures, with shaking to agitate the mixture. The reaction was terminated by immersing the vessel into a water bath. The reaction mixture was recovered by dissolving with THF. The catalyst was removed using a centrifugal filtration on a 0.45- μm membrane filter and the products were analyzed by gas chromatography with flame ionization detection (GC-FID) and gas chromatography–mass spectrometry (GC–MS).

Some experiments for oxidative cleavage and decarboxylation were performed two or three times, in which case the standard deviation was shown with the results.

2.4 Analytical methods

The oxidative cleavage products were mixtures of monocarboxylic and dicarboxylic acids, and the decarboxylation products were mixtures of hydrocarbons. The carboxylic acids were silylated using BSTFA at 45 °C for 20 min and then analyzed by GC–MS using a GCMS-

QP2010 system (Shimadzu, Kyoto, Japan) with a CP-Sil 8 CB column (30 m $\times$ 0.25 mm i.d., 0.25 μ m thick; Agilent, Wilmington, USA). The column temperature was increased linearly from 45 °C to 250 °C at 3.5 °C/min and then held at 250 °C for 1 min. The injector and detector temperatures were set at 230 °C.

The hydrocarbon products were analyzed by GC-FID using a GC-214 system (Shimadzu) with a CP-FFAP CB column (25 m $\times$ 0.32 mm i.d., 0.30 μ m thick, Agilent). The column temperature was held at 40 °C for 0.2 min, increased linearly to 100 °C at a rate of 15 °C/min, held at 100 °C for 2 min, and then increased linearly to 240 °C at a rate of 7 °C/min. The injector and detector temperatures were set at 270 and 280 °C, respectively.

The volatile products were determined by using a Micro GC CP-4900 (Varian, Middleburg, Netherlands) fitted with two-channel columns. Channel 1 used an MS5A column (10 m $\times$ 0.32 mm i.d., 0.12 μ m thick, Agilent), argon at 100 °C as the carrier gas and a thermal conductivity detector (TCD). Channel 2 used a PoraPLOT Q column (10 m $\times$ 0.32 mm i.d., 0.10 μ m thick, Agilent), helium at 80 °C as the carrier gas and a TCD. All analyses were performed under isothermal conditions.

Fresh and used Pd/C catalysts were scanned by Fourier transform infrared (FTIR) spectrophotometer IRAffinity-1 (Shimadzu, Kyoto, Japan) by KBr method.

3. Results and discussion

3.1 Oxidative cleavage of PUFA

Linoleic acid has two double bonds at carbon numbers 9 and 12, while linolenic acid has three double bonds at carbon numbers 9, 12, and 15. Oxidative cleavage of these double bonds by KMnO_4 will produce monocarboxylic and dicarboxylic acids. The previous study¹⁾ showed that oxidative cleavage of oleic acid proceeded effectively in an emulsified system. In this study, 1 wt% of emulsifier (PLE) was used in oxidative cleavage of linoleic and linolenic

acids. The reaction conditions for oxidative cleavage of PUFA were investigated using various molar ratios of oxidizing agent (KMnO_4) to PUFA and at different reaction temperatures.

3.1.1 Oxidative cleavage of linoleic acid (C18:2)

Table 1 shows the major products from linoleic acid by oxidative cleavage, which are hexanoic [monocarboxylic acid (C6:0)] and nonanedioic [dicarboxylic acid (C9:0)] acids, after the treatment for 60 min. In addition, minor compounds of monocarboxylic acids such as pentanoic (C5:0), heptanoic (C7:0), octanoic (C8:0), nonanoic (C9:0), dodecanoic (C12:0) acids, and dicarboxylic acids such as heptanedioic (C7:0) and octanedioic (C8:0) acids were observed in the reaction products, which might be produced from side reactions occurred during the oxidative cleavage.

The effect of oxidizing agent (KMnO_4) (Entries 1–4) was investigated. In a stoichiometric oxidative cleavage, 16 mol of KMnO_4 is needed to react with 3 mol of linoleic acid (16:3 = 5.3:1). When the amount of KMnO_4 was less than the stoichiometric ratio (Entry 1), the yield of acid products was low. Excess amount of KMnO_4 increased the product yield, and the optimum reaction condition was found when the molar ratio of KMnO_4 to linoleic acid was 8:1 (Entry 3), yielding 90.3 mol% of hexanoic acid and 49.6 mol% of nonanedioic acid. With a more excessive amount of KMnO_4 (Entry 4), the product yield decreased. In this case, the decomposition of products was considered to occur. Therefore, the molar ratio of 8:1 was applied to the following studies for linoleic acid.

The effect of reaction temperature on oxidative cleavage of linoleic acid (Entries 5–8) was also studied. The product yields were slightly affected by the reaction temperature. Increasing the temperature from 30 to 40 °C (Entries 5–6) slightly increased the acid products. However, further increasing the temperature to 60 °C caused a decrease in acid products because the emulsion system broke to some extent under such high-temperature

Table 1 Yields of the product obtained by oxidative cleavage of linoleic acid with KMnO_4 after 60 min treatment

Entry	Molar ratio of KMnO_4 to linoleic acid	Reaction temperature (°C)	Acids product yield (mol%)		
			Hexanoic acid (C6:0)	Nonanedioic acid (C9:0)	Others
1	4:1	40	64.1 $\pm$ 2.7	32.7 $\pm$ 1.5	5.6 $\pm$ 0.6
2	6:1		74.6 $\pm$ 4.4	46.4 $\pm$ 4.2	12.9 $\pm$ 1.5
3	8:1		90.3 $\pm$ 1.6	49.6 $\pm$ 2.9	17.1 $\pm$ 1.7
4	10:1		73.4 $\pm$ 1.8	53.8 $\pm$ 1.5	13.0 $\pm$ 2.3
5	8:1	30	88.9 $\pm$ 2.3	50.0 $\pm$ 2.8	15.3 $\pm$ 1.0
6		40	90.3 $\pm$ 1.6	49.6 $\pm$ 2.9	17.1 $\pm$ 1.7
7		50	82.5 $\pm$ 3.6	52.9 $\pm$ 1.9	16.3 $\pm$ 2.0
8		60	82.2 $\pm$ 4.7	50.0 $\pm$ 2.1	15.3 $\pm$ 0.5

condition. These results suggest that 40 °C was the optimal temperature for oxidative cleavage of linoleic acid.

The time dependence in oxidative cleavage of linoleic acid was also investigated with 8:1 KMnO_4 at 40 °C and the result is summarized in Fig. 1. When the molar ratio of KMnO_4 to linoleic acid was 8:1 at 40 °C, the product yields (hexanoic, nonanedioic and others) increased rapidly during the initial stage of the reaction until 10 min, then reached plateau to give about 90 mol% hexanoic acid and 50 mol% nonanedioic acid.

In Table 1, the yield of nonanedioic acid was lower than that of hexanoic acid. The possible reason for this difference might be other undesirable reactions. Therefore, the stability of nonanedioic and hexanoic acids was investigated under similar conditions for oxidative cleavage. It was found that nonanedioic acid was partly degraded into other products, such as butanedioic, pentanedioic, heptanedioic, and octanedioic acids, when it was mixed with the KMnO_4 solution at designated conditions. The

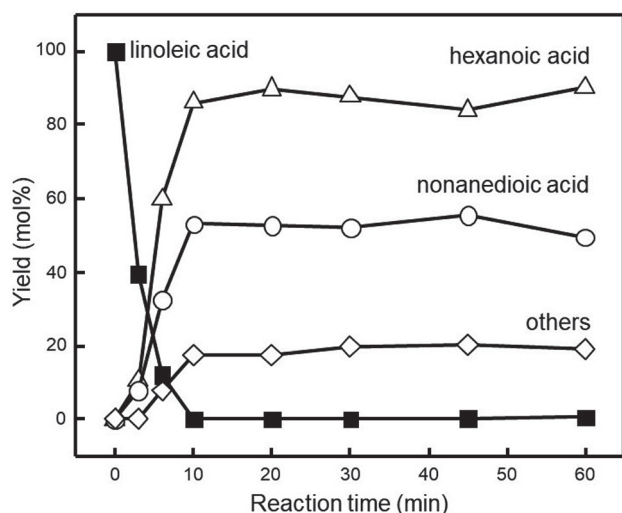


Fig. 1 Yields of hexanoic, nonanedioic, and other acid products obtained by oxidative cleavage of linoleic acid with 8:1 KMnO_4 at 40 °C

higher temperature and concentration of KMnO_4 caused more degraded products. On the other hand, hexanoic acid showed tolerance against further decomposition under the same condition. Although the degradation mechanism remained unclear, these results suggest that KMnO_4 act not only for the oxidative cleavage, but also for the degradation of nonanedioic acid.

Theoretically, oxidative cleavage of linoleic acid will produce nonanedioic, hexanoic, and propanedioic acids. However, propanedioic acid (C3 dicarboxylic acid) is highly soluble in water, which is used as a medium for this oxidative cleavage reaction. After the reaction, propanedioic acid is expected to remain in the reaction mixture, but it would be difficult to collect propanedioic acid from the water phase. In addition, propanedioic acid has three carbon atoms, which cannot be expected to produce hydrocarbons in the composition range of gasoline (C4-C10).

3.1.2 Oxidative cleavage of linolenic acid (C18:3)

The same experiment was applied for linolenic acid to find out the optimum reaction conditions for oxidative cleavage, and the results are summarized in Table 2. Minor fatty acids were also observed in the products, such as hexanoic, dodecanoic, heptanedioic, octanedioic, and decanedioic acids, which are shown as others in this table. This phenomenon is similar to the oxidative cleavage of linoleic acid. Although the main product is nonanedioic acid, the other fatty acids were produced by side reactions during the oxidative cleavage, or by the decomposition of nonanedioic acid.

Stoichiometrically, 24 mol of KMnO_4 will react with 3 mol of linolenic acid ($24:3 = 8:1$). To determine the optimum ratio of KMnO_4 for linolenic acid, experiments were conducted by changing the ratio from 8:1 to 14:1 (KMnO_4 : linolenic acid) as shown in Table 2 (Entries 1-4). The highest yield was achieved at 10:1 (Entry 2), producing 55.8 mol% of nonanedioic acid. Further trials were conducted at this molar ratio (10:1) to investigate the

Table 2 Yields of the product obtained by oxidative cleavage of linolenic acid with KMnO_4 after 60 min treatment

Entry	Molar ratio of KMnO_4 to linolenic acid	Reaction temperature (°C)	Acid product yield (mol%)	
			Nonanedioic acid (C9:0)	Others
1	8:1	40	35.9 ± 1.2	6.8 ± 1.1
2	10:1	40	55.8 ± 2.2	13.0 ± 2.3
3	12:1	40	47.6 ± 1.1	13.8 ± 2.7
4	14:1	40	44.2 ± 2.1	12.9 ± 1.1
5	10:1	30	51.8 ± 1.7	9.0 ± 1.5
6	10:1	40	55.8 ± 2.2	13.0 ± 2.3
7	10:1	50	60.0 ± 2.6	14.7 ± 2.7
8	10:1	60	51.9 ± 3.4	11.6 ± 1.0

effect of reaction temperature (Entries 4-8). The reaction at 50 °C (Entry 7) gave the highest yield of nonanedioic acid (60.0 mol%).

Fig. 2 shows the effect of reaction time for linolenic acid under the condition with the molar ratio of 10:1 (KMnO_4 : linolenic acid) at 50 °C. The product yields increased sharply at the early stage of the reaction until 30 min, and then slightly increased up to 60 min to yield 56 mol% of nonanedioic acid. Compared to linoleic acid, oxidative cleavage of linolenic acid had a lower reaction rate; therefore, it needed a longer treatment time.

The oxidative cleavage of linolenic acid, which has three double bonds, is theoretically expected to produce nonanedioic, propanedioic, and propionic acids. Propionic acid is also highly soluble in water as well as propanedioic acid as aforementioned. Therefore, propanedioic and propionic acids are difficult to be collected from the water phase. Even if they can be collected, we cannot convert them into renewable gasoline because of too short carbon chain length.

3.2 Decarboxylation of nonanedioic and hexanoic acids

The main products from the oxidative cleavage (nonanedioic and hexanoic acids) were then used to study the decarboxylation behaviors. Because the decarboxylation of nonanedioic acid into hydrocarbons was studied previously¹⁾, the behavior of hexanoic acid was mainly examined in the current study.

In the previous work¹⁾, we understood that decarboxylation of nonanedioic and nonanoic acids was more successful under N_2 atmosphere. For the current study, N_2

was used to pressurize the reaction vessel (0.1–10 MPa) for the decarboxylation of hexanoic acid. Fig. 3 shows the N_2 pressure dependence of the hydrocarbon yield for decarboxylation of nonanedioic and hexanoic acids to *n*-heptane and *n*-pentane, respectively, with Pd/C catalyst at 300 °C for 6 h. The data of nonanedioic acid is taken from our previous work¹⁾.

Fig. 3 revealed that N_2 pressure did not significantly affect the yield of *n*-heptane (C7) from nonanedioic acid. The yield of *n*-heptane was around 70 mol% under wide range of the N_2 pressure. For decarboxylation of hexanoic acid, the increase in N_2 pressure from 0.1 to 1 MPa increased the *n*-pentane (C5) yield from 44.2 to 73.7 mol%. One difference between hexanoic and nonanedioic acids is the number of carboxyl groups; hexanoic acid is mono-, and nonanedioic acid is dicarboxylic acid. At the applied reaction temperature (300 °C), hexanoic acid is most likely in gas phase when the pressure is less than 1 MPa, because its boiling point is 205 °C at 0.1MPa and 310 °C at 1 MPa, which was estimated by using a steady-state process simulator Pro/II, ver 10.1 (Schneider Electric, Rueil-Malmaison, France). If the reactant becomes gas, the accessibility to the Pd/C catalyst will become poor compared with the liquid reactant. The low hydrocarbon yield from hexanoic acid at low pressures might be because of the low boiling point. However, the hydrocarbon yield from hexanoic acid decreased when the reaction pressure increased more than 1 MPa. Although the reason remained unclear, it is considered that a part of *n*-pentane might be volatilized and lost when recovering the reaction product, because the boiling point (36 °C at atmospheric pressure) is close to room temperature.

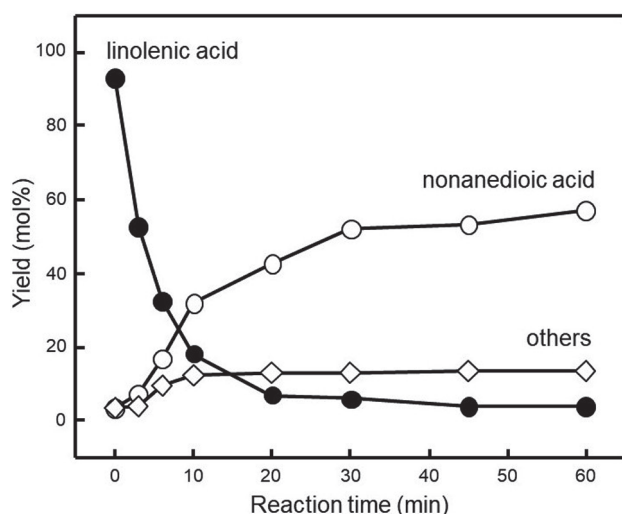


Fig. 2 Yields of nonanedioic and other acid products obtained by oxidative cleavage of linolenic acid with 10:1 KMnO_4 at 50 °C

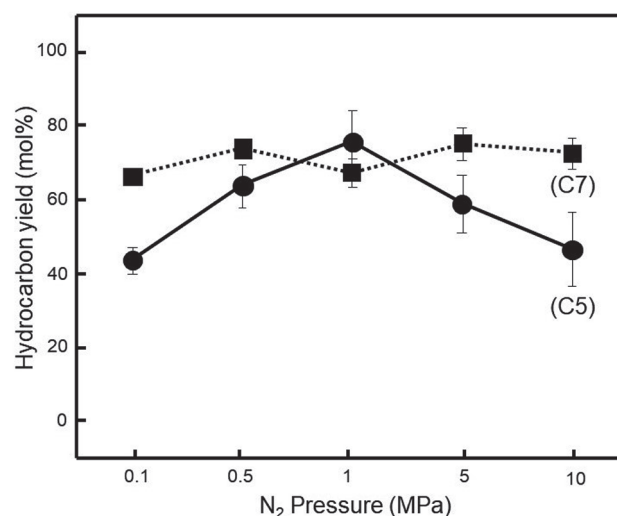


Fig. 3 The effect of N_2 pressure on product yields for decarboxylation of nonanedioic¹⁾ and hexanoic acids into *n*-heptane (C7) and *n*-pentane (C5), respectively, as treated with Pd/C at 300 °C for 6 h

In contrast, two carboxylic groups in nonanedioic acid have more extensive association of intermolecular hydrogen bonding. Hence the boiling point of nonanedioic acid is high (360 °C at atmospheric pressure), so nonanedioic acid is always in the liquid phase at the given condition. That may be the reason why the hydrocarbon yield from nonanedioic acid did not depend on the pressure.

The possible pathway in the decarboxylation of carboxylic acids has been proposed by Lu and Behtash as follows¹⁴: Fatty acid molecules are first adsorbed on the Pd/C surface followed by O-H scission to produce $C_xH_{2x+1}COO$ and H. Direct $C_xH_{2x+1}CO_2$ scission is then occurred to release CO_2 . Meanwhile, C_xH_{2x+1} will associate with H to produce hydrocarbon.

Fig. 4 shows the time dependence of nonanedioic¹⁾ and hexanoic acids decarboxylation to *n*-heptane and *n*-pentane, respectively, as treated at 300 °C and 1 MPa (N_2). The reaction rate of nonanedioic acid (C9 dicarboxylic acid) was rapid in the first 3 h and then plateaued to produce about 69.0 mol% *n*-heptane (C7). In contrast, hexanoic acid (C6 monocarboxylic acid) showed a steady reaction rate until almost all hexanoic acid had been consumed in 6 h to give about 73.5 mol% *n*-pentane (C5). The decarboxylation rate of nonanedioic acid was higher than that of hexanoic acid.

Kipling and Wright¹⁵, Jeffrey *et al.*¹⁶, and Mohite *et al.*¹⁷ reported that the lower decarboxylation rate was observed in the decarboxylation of shorter carbon chain acids. They found that fatty acids with shorter carbon chain have poorer adsorption onto the activated carbon support. In general, the number of methylene groups in

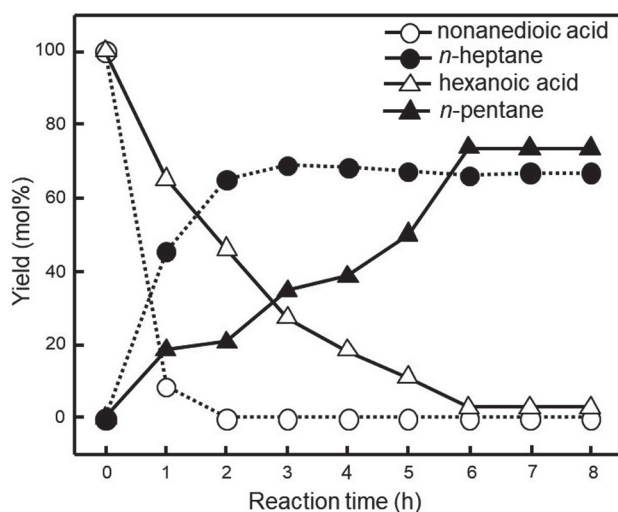


Fig. 4 Time dependence of the product yield for decarboxylation of nonanedioic¹⁾ and hexanoic acid into *n*-heptane and *n*-pentane, respectively, as treated with Pd/C at 300 °C and 1MPa

the molecule is an important factor, but the polarity of the reactant would also play a role. In addition, as the estimated boiling point of hexanoic acid at 1 MPa (310 °C) is close to the reaction temperature (300 °C), there is a possibility that a part of hexanoic acid may be still in gas phase. If the gas phase existed, the reactivity would decrease as aforementioned.

Furthermore, significant differences were observed between the theoretical and practical yields for the decarboxylation of nonanedioic and hexanoic acids; the product yields were not close to 100 mol% (Fig. 4). In this case, decomposition reactions and deposition of the hydrocarbon products on the catalyst surface were likely considered.

The decomposition reaction was confirmed by analyzing the gas phase of the decarboxylation products by Micro GC. For the nonanedioic acid decarboxylation, H_2 and short-chain hydrocarbons, such as methane, ethane, and propane were detected. For the hexanoic acid decarboxylation, H_2 and methane were observed. These observations suggest that some hydrocarbon products decompose into H_2 and short-chain hydrocarbons during the decarboxylation reaction. These volatile hydrocarbons are not in the composition range of gasoline (C4–C10), and will be lost to the atmosphere together with H_2 .

To confirm the deposition of the product on the catalyst, FTIR analysis was performed with fresh and used catalysts. Several absorption bands appeared in the spectra of the used catalysts that were not observed for the fresh catalyst (Fig. 5). A strong absorption band at about 1384 cm^{-1} was assigned to the skeleton vibration of CH in CH, CH_2 , or CH_3 in aliphatic groups¹⁸. Another band at about 1716 cm^{-1} was assigned to the C=O stretching peak

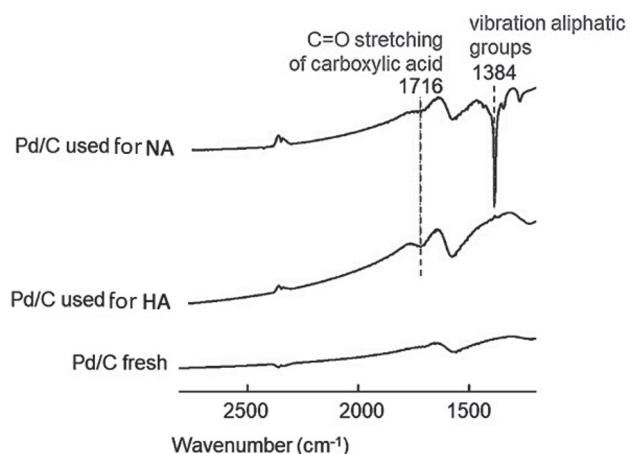


Fig. 5 FTIR spectra of catalysts: Pd/C fresh, Pd/C used for decarboxylation of hexanoic acid (HA) and nonanedioic acid (NA)

of carboxylic acid groups¹⁹. Based on these lines of evidence, in decarboxylation of nonanedioic and hexanoic acids, some unreacted carboxylic acid and hydrocarbon products did not diffuse out of the catalyst, resulting in a coke formation.

About 17 mol% of other fatty acids from the oxidative cleavage of linolenic acid (Fig. 1) are also expected to be decarboxylated into hydrocarbons in the gasoline range. Similarly, 12 mol% of other fatty acids from linolenic acid (Fig. 2) will be converted into renewable gasoline. Therefore, the yields of hydrocarbons from linoleic and linolenic acids should be more than those mentioned above. When applying the proposed method to real plant oil, the yield of hydrocarbons will be higher because many plant oils are rich in monounsaturated fatty acid.

The two-step process for renewable gasoline production has several advantages; the reaction temperature is milder compared with the catalytic cracking and hydrotreating, and the selectivity for alkane hydrocarbons is very high without paraffin, isoparaffin, olefin, naphthenes and aromatics compounds in the product.

4. Concluding remarks

The proposed method for hydrocarbon production from PUFA, which involves oxidative cleavage and decarboxylation, was successfully demonstrated. Oxidative cleavage of PUFA produced sufficient yields of target products (nonanedioic and hexanoic acids) even though propanedioic and propionic acids were also produced and lost. The hydrocarbon yield from nonanedioic and hexanoic acids by decarboxylation was around 70 mol% because of the decomposition and deposition of hydrocarbon products on the catalyst. Nevertheless, this method shows considerable potential for the production of hydrocarbons in the gasoline fraction from PUFA, which are found in abundance with MUFA in natural sources. For further application, unsaturated fatty acids can be obtained from biomass by hydrolyzing the plant oils and then separated from its saturated fatty acids. Then, the unsaturated fraction, which contains MUFA and PUFA, can be treated with the proposed method to get hydrocarbons in the gasoline range.

Acknowledgment

The first author is thankful to the Indonesia Endowment Fund for Education (LPDP) from the Ministry of Finance, Republic of Indonesia, for the financial support during her study at Kyoto University.

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