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Hydrocarbon Fuels from Palm Oil through Hydrolysis Followed by Oxidative Cleavage and Decarboxylation

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Renewable hydrocarbons in the composition ranges of gasoline and diesel were prepared from palm oil through hydrolysis and oxidative cleavage followed by decarboxylation. Hydrolysis was carried out with water in a sub-critical state to obtain saturated and unsaturated fatty acids from palm oil triglycerides. The hydrolysis product was treated with KMnO$_4$ as an oxidizing agent to convert unsaturated fatty acids into short fatty acids by cleaving C=C double bonds. The obtained product was then decarboxylated with Pd/C catalyst under N$_2$ pressure to produce hydrocarbons including gasoline and diesel fractions. This work demonstrated the potential of palm oil as a source of renewable fuels, providing about 21 wt% gasoline hydrocarbons and 48 wt% diesel hydrocarbons based on palm oil as the feedstock.

Keywords
Hydrocarbon, Palm oil, Hydrolysis, Oxidative cleavage, Decarboxylation, Renewable fuel

1. Introduction

Fossil fuel depletion is still a crucial issue in global energy security. The need for renewable biofuels is becoming urgent because of the threat of global climate change. Palm oil is a promising candidate to produce biofuels because of its large-scale production. Driven by high market demand in developing countries, the palm oil industry has grown rapidly. Indonesia and Malaysia dominate the global production of palm oil, accounting for about 85% of world production\(^1\). However, the European Union decided to ban palm oil-derived biofuels because of the deforestation that has accompanied palm oil cultivation\(^2\). Indonesia and Malaysia are thus looking for alternative routes to use palm oil; for example, palm oil producers in Indonesia intend to divert palm oil to domestic biofuel production.

Although biofuels, such as biodiesel and bioethanol, have been widely developed, they are oxygenated fuels, which lead to low calorific values, corrosion of engine components, and high affinities with water. Hydrocarbon biofuels are interesting alternatives to overcome these disadvantages of oxygenated biofuels. Hydrocarbon biofuels can be used in vehicles without engine modification because they are similar to fossil fuels. Hydrocarbons can be produced by removing oxygen atoms from triglycerides (TG) of plant oils through deoxygenation reactions\(^3\)–\(^7\). The number of carbon atoms in a hydrocarbon molecule typically ranges from around C4 to C10 in gasoline and C10 to C20 in diesel derived from fossil fuels.

Conversion of plant oils into hydrocarbons is commonly conducted by catalytic cracking\(^8\)–\(^12\) or hydro-treating\(^13\)–\(^16\). Zeolite-based catalysts, such as HZSM-5 and AlMCM-41/ZSM-5, are extensively used for catalytic cracking because of their acidic properties and large specific surface area\(^17\)–\(^20\). Hydrotreating is typically performed using metal catalysts, such as Pd, Pt, Ni, Rh, Ir, Ru, and Os, supported on activated carbon or metal oxides\(^21\)–\(^26\). However, both catalytic cracking and hydrotreating are low-selectivity processes and yield a variety of hydrocarbons, particularly from unsaturated fatty acids (FA)\(^27\)–\(^30\).

We therefore developed a high-selectivity process, which involves hydrolysis of TG to FA, followed by oxidative cleavage of unsaturated FA and subsequent decarboxylation\(^31\). This process was designed with the intention of producing the diesel fraction (C10-20) from saturated FA, such as palmitic and stearic acids, and the gasoline fraction (C4-10) from unsaturated FA, such as oleic and linoleic acids, by cleaving unsaturated double bonds.

In our previous study, we optimized reaction conditions of oxidative cleavage and decarboxylation for oleic, linoleic, and linolenic acids as model FA\(^31\). Hydrocarbons between C4 and C13 were successfully

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produced from these FA. Based on these results, the current study demonstrates the production of renewable gasoline and diesel from a real plant oil. We used palm oil as the feedstock to produce renewable gasoline and diesel. Because palm oil is composed largely of C16 and C18 saturated and unsaturated FA, it should be possible to produce hydrocarbons in both gasoline and diesel composition ranges.

First, palm oil is hydrolyzed in subcritical water to obtain FA. The hydrolysis product is treated with potassium permanganate (KMnO₄) as an oxidizing agent to cleave double bonds in unsaturated FA, followed by decarboxylation with Pd/C to produce hydrocarbons including gasoline and diesel fractions. Moreover, if separation of saturated and unsaturated FA after hydrolysis is possible, it could allow separate production of gasoline and diesel fractions. We attempt a separation step using the difference in melting points between saturated and unsaturated FA, and compare the results for cases with and without the separation process.

2. Materials and Methods

2.1. Materials

Refined palm oil was purchased from Fluka (Buchs, Switzerland) and used without purification. Reagent-grade KMnO₄, polyoxyethylene lauryl ether (PLE), sulfuric acid (H₂SO₄), sodium hydrogen sulfite (NaHSO₃), sodium sulfate (Na₂SO₄), diethyl ether, tetrahydrofuran (THF), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), and Pd/C catalyst (5 wt% Pd) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan).

2.2. Hydrolysis of Palm Oil

Palm oil (1 mL) and water (4 mL) were charged into a 5-mL batch-type reaction vessel made of Inconel-625. Hydrolysis was conducted by immersing the vessel in a molten salt bath at the desired temperature (270-300 °C) for 20 min. Subsequently, the vessel was cooled in a water bath (25 °C) to terminate the reaction. The obtained product was extracted using hexane and then kept until the two phases separated. The upper portion containing FA was then evaporated by a rotary vacuum evaporator to remove hexane. The obtained hydrolysis product was analyzed by Fourier transform infrared (FTIR) spectroscopy using an IRAffinity-1 spectrometer (Shimadzu Corporation, Kyoto, Japan) in reflection mode with a GladiATR attachment (Pike Technologies, Wisconsin, US). The FA composition was determined by GC-MS using an IRAffinity-1 spectrometer (Shimadzu Corp., Kyoto, Japan) in reflection mode with a GladiATR attachment (Pike Technologies, Wisconsin, US). Quantitative analysis of the hydrolysis product was conducted by GPC using an LC-10VP system (Shimadzu) under the following conditions. Column: GF-310 HQ (Showa Denko K. K., Tokyo, Japan), oven temperature: 40 °C, eluent: acetone, flow rate: 1.0 mL/min, detector: refractive index detector (RID).

2.3. Separation of the Hydrolysis Product

The hydrolysis product (1.0 g) was added to 90 vol% aqueous acetonitrile (10 mL). The mixture was ultrasonically heated at 80 °C for 10 min to melt fully, and then cooled at −15 °C for 20 h to recrystallize saturated FA, which have higher melting points than unsaturated ones. The solid fraction, which was expected to be rich in saturated FA, was collected by using a 0.45-μm centrifugal filter (Nanosep, Pall Corp., New York, US). The aqueous acetonitrile was removed from the filtrate by vacuum evaporation to obtain the liquid fraction rich in unsaturated FA.

2.4. Oxidative Cleavage of Unsaturated FA

Oxidative cleavage was carried out according to the method described in our previous paper31. A sample (0.10 g of whole or separated hydrolysis product) was added to water (2 mL) containing PLE (0.02 g) as an emulsifier and then ultrasonically agitated at room temperature for 30 min to form an emulsion. The emulsion was mixed with KMnO₄ solution (designated concentration, 4.5 mL) in aqueous H₂SO₄ (0.0225 N). Oxidative cleavage was conducted at 40 °C for 30 min. Aqueous NaHSO₃ solution was added and then the pH was adjusted to 1-2 using 9 N H₂SO₄. The mixture was heated at 70 °C for 30 min to break the emulsion. The mixture was cooled and the products were extracted with diethyl ether and then dried using anhydrous Na₂SO₄. The oxidative cleavage product was obtained by removal of diethyl ether using the rotary vacuum evaporator.

2.5. Decarboxylation of FA to Form Hydrocarbons

Decarboxylation was conducted according to the method in our previous paper31. Prior to use, the Pd/C catalyst was dried overnight at 105 °C and reduced in an H₂ flow (30 mL/min) at 200 °C for 2 h. The oxidative cleavage product (0.15 g) was placed in the 5-mL reaction vessel with the Pd/C catalyst (approximately 15 mol% of Pd relative to FA). The vessel was sealed and pressurized to 5 MPa by supplying N₂ gas with a compressor. The reaction was conducted by immersing the vessel in a molten salt bath at 300 °C with shaking to agitate the mixture. The reaction was terminated by cooling the vessel in the water bath. The reaction mixture was collected from the vessel by dissolving in THF. The catalyst was removed using the 0.45-μm centrifugal filter. The product was analyzed by gas chromatography with flame ionization detection (GC-FID) and GC-MS.

2.6. Analytical Methods

The hydrolysis product was examined by FTIR spectroscopy using an IRAffinity-1 spectrometer (Shimadzu Corp., Kyoto, Japan) in reflection mode with a GladiATR attachment (Pike Technologies, Wisconsin, US). Quantitative analysis of the hydrolysis product was conducted by GPC using an LC-10VP system (Shimadzu) equipped with a CP-Sil 8 CB column (30 m × 0.25 mm i.d., 0.25 μm thick; Agilent, Wilmington, US). The column temperature was increased linearly from 45 to 250 °C at a rate of 3.5 °C/min and then held at 250 °C.
for 1 min. The injector and detector temperatures were set at 230 °C. The sample was injected with a split ratio of 10/1 after silylation using BSTFA at 45 °C for 20 min.

The hydrocarbon product was analyzed by GC-FID using a GC-214 system (Shimadzu) equipped with a CP-FFAP CB column (25 m × 0.32 mm i.d., 0.30 μm thick, Agilent). The column temperature program was: initial temperature of 40 °C for 0.2 min, linear increase to 100 °C at a rate of 15 °C/min, 2 min at 100 °C, linear increase to 240 °C at a rate of 7 °C/min. The injector and detector temperatures were set at 270 °C and 280 °C, respectively.

The volatile products were determined using a Micro GC CP-4900 chromatograph (Varian, Middelburg, the Netherlands) fitted with two-channel columns. Channel 1 used an MS5A column (10 m × 0.32 mm i.d., 0.12 μm 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 × 0.32 mm i.d., 0.10 μm thick, Agilent), helium at 80 °C as the carrier gas, and a TCD. The analyses were performed under isothermal conditions.

3. Results and Discussion

3.1. Hydrolysis of Palm Oil

The hydrolysis reaction of palm oil was carried out at temperatures from 270 to 300 °C, and the FTIR spectra of the resulting hydrolysis products are shown in Fig. 1. For untreated palm oil, the absorption band at 1743 cm⁻¹ originates from the C=O stretching vibration of ester groups. After hydrolysis, the absorption at this wavelength decreased, and a new band at 1712 cm⁻¹ appeared that was assigned to the C=O stretching of carboxylic groups. A peak at 1166 cm⁻¹ from the O-H bending of ester groups was observed for untreated palm oil; the intensity of this peak decreased gradually with rising reaction temperature. Absorption bands at 1292 cm⁻¹ from C-O stretching and 941 cm⁻¹ from O-H bending of carboxylic acid groups appeared in the FTIR spectra of hydrolysis products. The changes in the FTIR spectra indicate the effective formation of FA when hydrolysis was performed above 290 °C for 20 min.

Figure 2 shows GPC results for palm oil treated in subcritical water at 270-300 °C for 20 min. The products were separated into three peaks; TG, diglycerides (DG), and a mixture of monoglycerides (MG) and FA. The results of GPC analysis are consistent with those of FTIR analysis. A higher hydrolysis temperature gave lower yields of unreacted TG and DG. The GPC data were used to quantify the hydrolysis products. However, because the peak from MG was overlapped with that from FA, the yields of MG and FA were determined by GC-MS analysis. The yield of each product is shown in Table 1. When the reaction temperature was increased from 270 to 300 °C, TG yield decreased from 13.2 to 0.5 wt%. The yields of DG and MG also decreased to only 1.1 wt% and 2.0 wt%, respectively when the reaction temperature was raised from 270 to 300 °C. In contrast, FA yield increased monotonically from 52.2 to 88.8 wt% based on palm oil. The theoretical maximum yield of FA from palm oil is calculated to be 96.6 wt%; the decrease from 100 wt% is caused by the formation of glycerol as by-product. The FA yield of 88.8 wt% corresponds to about 92 % conversion based on the theoretical maximum. The composition of FA obtained from the hydrolysis of palm oil is also listed in Table 1. The major saturated and un-
saturated FA were palmitic and oleic acids, respectively. Hydrolysis of palm oil at 300 °C for 20 min gave the best results, so the product obtained under these conditions was used in the next step.

### 3.2. Separation of Saturated and Unsaturated FA

The product obtained from palm oil hydrolysis at 300 °C consisted of saturated and unsaturated FA with ratios of 47.4 wt% and 41.4 wt%, respectively, as calculated from Table 1. Saturated FA are expected to be converted into renewable diesel, whereas the unsaturated ones are anticipated to provide the gasoline fraction. Therefore, the separation of saturated and unsaturated FA by recrystallization from aqueous acetonitrile was studied.

From 1.0 g of the hydrolysis product, 43.0 wt% solid and 49.5 wt% liquid fractions were recovered; the remaining 7.5 wt% was lost during the separation process. The solid fraction was rich in saturated FA as expected; the ratio of saturated to unsaturated FA was 89.8 : 10.2 (w/w) according to GC-MS analysis. The liquid fraction included a higher proportion of unsaturated FA; the ratio of saturated to unsaturated was 26.3 : 73.7 (w/w). Thus, only a rough separation was achieved by our recrystallization method even though several conditions and solvents were examined (data not shown). Because unsaturated FA remained in the solid fraction, both liquid and solid fractions were subject to oxidative cleavage.

### 3.3. Oxidative Cleavage of Hydrolysis Products

Double bonds in oleic and linoleic acids can be oxidatively cleaved with KMnO₄ to give monocarboxylic (pelargonic and caproic acids) and dicarboxylic acid (azelaic acid). Our previous study[1] showed that oxidative cleavage proceeded effectively in an emulsified system (1 wt% aqueous PLE) and the appropriate molar ratios of KMnO₄ to unsaturated FA were found to be 4 : 1 and 8 : 1 for oleic (monounsaturated) and linoleic (diunsaturated) acids, respectively. In theory, linoleic acid requires twice as much oxidant as oleic acid because the number of double bond is twice; therefore, this result was reasonable.

In the current study, the oxidative cleavage of the liquid fraction was first examined with various molar ratios of KMnO₄ at 40 °C for 30 min. When the molar ratios of KMnO₄ to unsaturated FA were 4 : 1, 6 : 1, and 8 : 1, the quantified total yields of FA were 115.1, 112.8, and 114.0 wt%, respectively, based on reactant FA; values higher than 100 wt% are caused by the introduction of oxygen atoms. Theoretically, 120.3 wt% yield is expected for the liquid fraction if complete oxidative cleavage occurs. These results indicated that a 4 : 1 molar ratio of KMnO₄ to unsaturated FA is sufficient to achieve a high conversion ratio of 95.7 % (115.1/120.3 wt%). Although the liquid fraction included both oleic and linoleic acids, it required only 4 : 1 of KMnO₄ to FA, which is the same ratio for oleic acid; this is because that oleic acid is dominant and the amount of linoleic acid is very small in palm oil. Furthermore, the high conversion might mean that saturated FA in the liquid fraction did not affect the oxidative cleavage of unsaturated FA.

Oxidative cleavage was therefore conducted with 4 : 1 of KMnO₄ to unsaturated FA for the separated liquid and solid fractions and crude hydrolysis product (without separation); the results are summarized in Table 2. The solid fraction exhibited a high conversion ratio above 90 %, like the liquid fraction. In contrast, the crude hydrolysis product showed only 81.8 % conversion. The low conversion might result from the oxidative degradation of long-chain FA, such as palmitic (C16:0) and stearic (C18:0) acids, by KMnO₄. Actually, C16:0 and C18:0 in the crude hydrolysis product (Table 1, 300 °C) decreased after oxidative cleavage (Table 2, without separation), and other short fatty acids were found; for example, pentanoic acid. A part of such short dicarboxylic acids can be solved in water phase and hard to be recovered after the reaction. That may be the reason of low conversion from the crude hydrolysis product. In the cases of liquid and solid fractions, the influence of the degradation of long-

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**Table 1** Yields of the Products Obtained by Subcritical Water Treatment of Palm Oil for 20 min at Different Temperatures

| Composition       | Yield (wt% on palm oil) |
|-------------------|-------------------------|
|                   | 270 °C | 280 °C | 290 °C | 300 °C |
| Triglycerides     | 13.2   | 2.6    | 0.4    | 0.5    |
| Diglycerides      | 10.6   | 9.0    | 2.5    | 1.1    |
| Monoglycerides    | 14.1   | 10.0   | 7.6    | 2.0    |
| Fatty acids       | 52.2   | 68.7   | 77.7   | 88.8   |
| Myristic acid (C14:0) | 1.2   | 0.0    | 1.8    | 2.1    |
| Palmitic acid (C16:0) | 22.9  | 30.6   | 33.8   | 38.9   |
| Stearic acid (C18:0) | 3.5   | 4.8    | 5.4    | 5.8    |
| Arachidic acid (C20:0) | 0.3   | 0.4    | 0.5    | 0.6    |
| Oleic acid (C18:1)  | 20.1   | 27.3   | 30.5   | 35.9   |
| Linoleic acid (C18:2) | 4.2   | 5.6    | 5.8    | 5.5    |
chain FA by KMnO₄ is thought to be limited. This is because the amounts of C₁₆:0 and C₁₈:0 in the liquid fraction were small; in addition, the solid fraction, which was low in unsaturated FA, only required a small amount of KMnO₄ to achieve effect oxidative cleavage.

3.4. Decarboxylation

In our previous work, the decarboxylation of model FA (caproic, pelargonic, and azelaic acids) was studied with Pd/C under 5 MPa of N₂, and the results showed a shorter FA needed a longer reaction time. Caproic acid (C₆:0) required 6 h for decarboxylation, whereas pelargonic acid (C₉:0) took only 3 h. In this study, the reaction time for the oxidative cleavage product from the liquid fraction was examined; the results are depicted in Fig. 3. The hydrocarbons obtained were a mixture of gasoline and diesel fractions. In this study, C₅, C₇, and C₈ hydrocarbons were assigned to the gasoline fraction and longer ones were assigned to diesel fraction.

Figure 3 shows that the yields of both fractions increased with the reaction time until they reached a plateau after 8 h. The maximum yields were about 47 wt% of gasoline fraction and 31 wt% of diesel fraction after reaction for 8 h. The long reaction time might be related to the presence of short FA in the reactant. A reaction time of 8 h was then used for the other oxidative cleavage products; the results are summarized in Table 3.

The major hydrocarbons in the gasoline fraction were n-heptane (C₇H₁₆) and n-octane (C₈H₁₈), whereas the main component of the diesel fraction was n-pentadecane (C₁₅H₃₂). Furthermore, micro-GC analysis revealed the formation of gaseous products such as H₂, methane (CH₄), ethane (C₂H₆), and propane (C₃H₈). The formation of gaseous products indicates that hydrocarbon decomposition occurred during decarboxylation to form lower hydrocarbons.

Although the solid fraction (after separation) and crude hydrolysis product (without separation) exhibited high conversion ratios of 86.4 wt% and 86.9 wt%, respectively, the sample from the separated liquid fraction showed slightly lower conversion. The reason for this remained unclear, but it is feasible that part of the gasoline fraction was lost during the experiment because the liquid fraction was rich in hydrocarbons in the gasoline fraction, which are volatile.

3.5. Comparison of the Processes with and without Separation

Figure 4 shows the schemes and product yields of the whole process from 100 g of palm oil, which were based on the conversion ratio of each reaction step. The process with the separation step produced 23.7 g of gasoline and 15.9 g of diesel from the liquid fraction and 0.04 g of gasoline and 30.9 g of diesel from the solid fraction (Fig. 4(a)). Therefore, 23.74 g of gasoline and 46.8 g of diesel are expected from 100 g of palm oil. Because the products are still mixtures of gasoline

**Table 2  Yields of Fatty Acids Obtained by Oxidative Cleavage of the Hydrolysis Products with KMnO₄ (KMnO₄ : fatty acid molar ratio of 4 : 1) at 40 °C for 30 min**

| Composition                    | Yield (wt% on reactant fatty acids) |
|-------------------------------|------------------------------------|
|                               | with separation                    |
|                               | liquid fraction | solid fraction |
| Caproic acid (C₆:0)           | 3.7               | 0.2            | 2.1           |
| Azelaic acid (C₉:0)           | 39.3              | 4.1            | 21.3          |
| Pelargonic acid (C₉:0)        | 28.8              | 3.3            | 17.1          |
| Palmitic acid (C₁₆:0)         | 20.8              | 73.6           | 34.1          |
| Stearic acid (C₁₈:0)          | 3.1               | 9.7            | 3.8           |
| Other fatty acids             | 19.4              | 2.7            | 11.2          |
| (a) Total fatty acids         | 115.1             | 93.6           | 89.6          |
| (b) Theoretical maximum        | 120.3             | 101.7          | 109.5         |
| Conversion (a/b, %)           | 95.7              | 92.0           | 81.8          |

\( a) \) The theoretical maximum is the yield if all unsaturated fatty acids in the reactant are oxidatively cleaved.

![Fig. 3](image-url) Yields of Hydrocarbons from the Oxidative Cleavage Product of the Liquid Fraction by Decarboxylation with Pd/C at 300 °C/5 MPa (N₂)

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and diesel fractions, a distillation step is necessary to completely refine the products into gasoline and diesel fractions.

In the case without separation (Fig. 4(b)), 21.2 g of gasoline and 48.0 g of diesel were produced, giving a total hydrocarbon weight of 69.2 g, which is almost the same as the case with separation. When the separation was conducted, the conversion ratio in oxidative cleavage was high, but 7.5 wt% of the sample was lost during the separation, as mentioned in Section 3.2. Therefore, at least for palm oil, the separation step might not be meaningful, because complete separation was not achieved and the hydrocarbon yield was not improved. Thus the simple process without separation (Fig. 4(b)) is suitable for palm oil. However, the effect of separation remains unclear for other oil feedstocks because the separation behavior will depend on the FA composition. If an efficient separation process were developed, it would benefit the production of renewable gasoline and diesel fuels.

4. Concluding Remarks

A proposed hydrocarbon production method involving hydrolysis, oxidative cleavage, and subsequent decarboxylation was successfully demonstrated using palm oil as the feedstock. All the reaction steps worked well for palm oil, producing hydrocarbons in gasoline and diesel fractions with yields of 21.2 wt% and 48.0 wt%, respectively. Although a separation process of saturated and unsaturated FA after hydrolysis was studied, the separation was not high enough, and the total hydrocarbon yield was not improved compared to the case without the separation step. Further investigations using highly unsaturated plant oils, such as sunflower, safflower, and soybean oils to produce gasoline-rich hydrocarbons should be conducted. In this study, we used KMnO₄ as the oxidant for oxidative cleavage, but it was consumed during the reaction. Thus, non-consumed and heterogeneous solid catalysts would be more preferable than KMnO₄ for oxidative cleavage, although such a prospect is challenging.

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要 旨
加水分解、酸化開裂および脱炭酸反応によるバーム油からの炭化水素燃料生産
Kicy Corneliasari SEMBIRING, 南 英治, 河本 晴雄, 坂 志朗
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バーム油の加水分解、酸化開裂および脱炭酸反応により、ガソリンおよびディーゼル留分を含む炭化水素燃料の生産を検討した。加水分解は蒸煮水処理により行い、バーム油のトリグリセリッドから飽和および不飽和脂肪酸を生成した。得られた加水分解物を過マンガン酸カリウム（酸化剤）により処理し、不飽和脂肪酸の二重結合を酸化開裂することで短鎖の脂肪酸を得た。さらに、飽和脂肪酸および短鎖の脂肪酸をパラジウム触媒（Pd/C）を用いて脱炭酸することにより、ガソリンおよびディーゼル留分の炭化水素を得た。本研究で提案したプロセスにより、バーム油から21 wt%のガソリン留分と48 wt%のディーゼル留分が得られ、再生可能燃料の原料としてのポテンシャルが示された。