



# Hydrocarbon production from decarboxylation of fatty acid without hydrogen

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## ABSTRACT

Decarboxylation of oleic acid without hydrogen was carried out using hydrotalcites with three different MgO contents (30, 63 and 70 wt%). Effect of MgO content in hydrotalcites and reaction temperatures on the decarboxylation performance in terms of oleic acid conversion and product distribution were investigated. Also, the stability of hydrotalcites in the decarboxylation reaction was examined by XRD analysis. It was found that MgO content in hydrotalcites and reaction temperature played key roles in decarboxylation reaction. At lower reaction temperature and MgO concentration in hydrotalcite, the conversion of oleic acid scarcely occurred. On the other hand, oleic acid conversions were more than 98% and the oxygen content in the reaction product was less than 1 wt% in the case of decarboxylation with MG63 (63% of MgO) and MG70 (70% of MgO) at 673 K. Solid-like products were formed in the reaction at 623 K, resulting from saponification of oleic acid and MgO. Considering conversion and the stability of catalysts, higher temperature, 673 K, is preferred to prevail decarboxylation over saponification. It was confirmed that most of the oxygen molecules in oleic acid were removed in the form of CO<sub>2</sub> from the elemental and FT-IR analysis of the liquid products. Pure hydrocarbons such as octane, nonane and heptadecene were produced in the case of MG63 and MG70 at 673 K while decanoic acid was additionally observed in case of blank test and MG30 catalyst at 673 K.

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## 1. Introduction

Growing concerns for the depletion of petroleum reserves and greenhouse gas effect have stimulated a research on the utilization of renewable biomass. Especially, the R&D investments in liquid biofuels such as biodiesel and bioalcohol, have been expanded year by year, because they might be the only alternative for conventional transportation fuels. FAME (fatty acid methyl ester) biodiesel made by transesterification is the most popular one and about 6.5 billion liters were produced worldwide in 2006 [1]. However, FAME biodiesel has its own disadvantages. Although its cloud point is dependent on the composition of the esters, it is generally higher than that of petrodiesel [2], which impedes the use in winter season. Free fatty acids remaining in products can cause corrosion problems [3,4]. There is also the issue of energy density. The calorific value of biodiesel is about 33 MJ/l, which is 9% lower than regular petrodiesel. All of these shortcomings, which are mainly attributed to the high oxygen content in FAME biodiesel [5] limit the wide use and much effort has been devoted to improve

the property of biodiesel and to develop additives for blending with biodiesel [2–4].

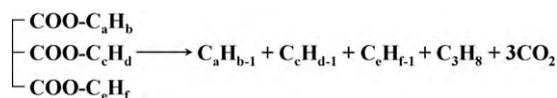
As an effort to solve problems mentioned above, hydrodeoxygenation (HDO) has been developed as an alternative technology [5,6]. HDO is a hydrogenolysis process removing oxygen compounds of lipids in the form of water. HDO uses common hydrotreating catalysts such as NiMo or CoMo supported on gamma alumina [6]. Although HDO guarantees the production of pure hydrocarbons, which are fully compatible with conventional fuels, HDO is an energy intensive process since it requires the use of high-pressure hydrogen stream. At least 2 mol of hydrogen are required for complete deoxygenation of 1 mol of fatty acid. Hydrogen is more expensive than methanol, which is a raw material for FAME biodiesel. Also, the operation with high-pressure hydrogen is not desirable because it requires expensive facilities to make the process explosive-free and safe. Despite the distinct advantages of providing identical liquid fuel to petroleum-based conventional fuel, HDO process still needs to reduce hydrogen consumption in the viewpoint of commercialization.

Decarboxylation of lipids, in the form of carbon dioxide might be an excellent alternative for hydrodeoxygenation (Scheme 1).

Although carbon based yield is low due to CO<sub>2</sub> loss, it does not require hydrogen and could produce pure hydrocarbons. Furthermore, unlike hydrodeoxygenation, water is not produced and deactivation of catalyst, especially in the case of alumina-based

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**Scheme 1.** Decarboxylation of a lipid without hydrogen.

catalyst system could be avoided. Murzin and co-workers reported that catalytic treatment of model lipids such as stearic acid, ethyl stearate, and tristearine by palladium or platinum on carbon support resulted in production of heptadecane even without hydrogen [7–11]. However, use of precious metals such as palladium and platinum, is an economical drawback.

In this study, the decarboxylation of oleic acid without using hydrogen was carried out with the aim to convert lipids to hydrocarbon fuels. Hydrotalcites with various MgO contents were tested as the catalyst instead of precious metals. Hydrotalcite is a layered double hydroxide composed of MgO and  $\text{MgAl}_2\text{O}_4$  and is used as absorbents for  $\text{CO}_2$  [12] and catalyst support [13]. It offers sorption selectivity for  $\text{CO}_2$  from other gases at mid-temperatures (658–773 K) and is relatively stable than other solid bases with sufficient decarboxylation activity [14]. Oleic acid, a common fatty acid in vegetable oil was chosen as a model compound. Effects of MgO ratio in hydrotalcites and reaction temperatures on oleic acid conversion and product distribution were investigated. Also, the stability of hydrotalcites in the decarboxylation reaction was examined.

## 2. Experimental

### 2.1. Chemicals and catalysts

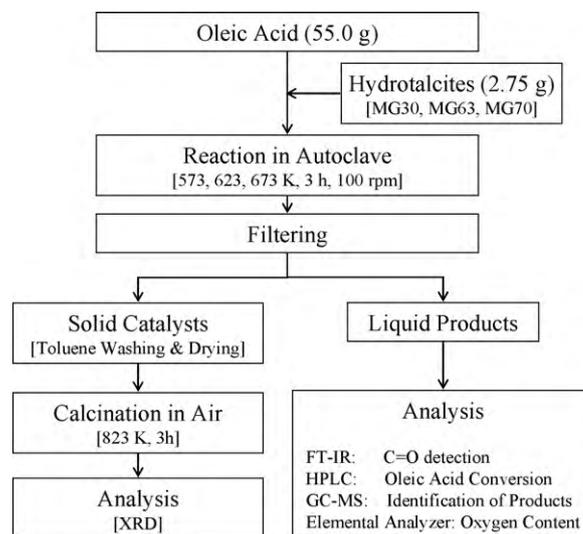
Oleic acid (>90%) was purchased from Aldrich and used without further purification. Three types of hydrotalcites with different magnesium oxide to alumina weight ratio, MG30 (MgO:Al<sub>2</sub>O<sub>3</sub> = 30 wt%:70 wt%), MG63 (63:37), and MG70 (70:30), were provided by Sasol.

### 2.2. Decarboxylation reaction

The decarboxylation tests were performed in a customized autoclave reactor (100 ml) operating in a batch mode. The reactor was designed for operation up to 100 bar and 723 K. A multi-blade impeller was equipped for mixing of liquid reactant and solid catalyst. The particle size of catalysts was less than 45  $\mu\text{m}$ . The temperature was measured with a K-type thermocouple. In a typical batch experiment, 55.0 g of oleic acid, model compounds representing vegetable oils, and 2.75 g of catalysts (reactant:catalyst = 20:1) were placed in the reactor. Hydrotalcite catalysts were activated for 3 h at 823 K under air atmosphere before use. After loading oleic acid and catalyst, the reactor was flushed with nitrogen in order to remove the remaining oxygen. Then, the reactor was heated to 573, 623, and 673 K respectively and maintained for 3 h at that temperature. The stirring speed was maintained to 100 rpm during reaction. The reactor was subsequently cooled down to room temperature. The gas products were collected by tedlar bag if possible. The liquid products were collected after filtering solid phase catalyst. The filtered hydrotalcites were washed with toluene and dried at 393 K for overnight in oven. These were calcined at 823 K for 3 h in air to remove remaining organic impurities.

### 2.3. Analysis of products and characterization of catalysts

Fig. 1 shows the flow diagram of product analysis in this study. The gas products were analyzed by a gas chromatograph



**Fig. 1.** Experimental procedure.

(Agilent 6890N) equipped with a thermal conductivity detector and a packed column (Carboxen-1000). The liquid products were analyzed by Fourier transform infrared spectrometer Jasco FT/IR-6100 to detect carbonyl group. The elemental analysis of the liquid products was performed on a TruSpec CHN elemental analyzer (Leco Co., USA). In the case of reaction at 573 and 623 K, samples were analyzed by a high performance liquid chromatography (HPLC) (HP1100, Agilent) equipped with refractive index detector (RID) (Agilent 1200, Agilent) and two Supelcosil LC-18 columns (15 cm  $\times$  4.6 mm I.D., 5  $\mu\text{m}$  particles). The mobile phase was acetone of 63.6 vol% and acetonitrile of 36.4 vol%. The flow rate was 1.0 ml/min. In the case of reaction at 673 K, the liquid products were analyzed by a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector and a capillary column (HP-Innowax, 30 m). On the other hand the liquid products were identified by a gas chromatograph-mass spectrometer system (GC HP6890N/MSD HP 5973N) equipped with a 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  UA-5 column (Frontier Lab., Japan). The carrier gas was helium and the flow rate was 1.0 ml/min. The column temperature was programmed to increase from 313 to 553 K at 8 K/min. The final temperature was 553 K and held for 30 min. Samples were dissolved in carbon disulfide before injection.

X-ray diffraction (XRD) patterns for hydrotalcites before and after reaction were obtained in the  $2\theta$  range from  $5^\circ$  to  $80^\circ$  using a Rigaku Diffractometer with  $\text{Cu K}\alpha$  radiation at 40 kV and 126 mA. The XRD patterns were compared with ICDD data for material identification. Also, the X-ray fluorescence (XRF) measurements were performed on Primus-II analyzer from Rigaku.

## 3. Results and discussion

### 3.1. Oleic acid conversion and catalysts stability

The conversion of oleic acid was displayed in Fig. 2. In case of using hydrotalcites as catalysts at a given reaction temperature, oleic acid conversions are higher than those of blank tests. As the MgO concentration in hydrotalcite and reaction temperature increased, oleic acid conversion increased. In blank tests, oleic acid was hardly reacted at 573 K. Oleic acid conversion was only 29% at 623 K, but reached 84% at 673 K. In case of using MG30 as catalyst, all the conversions at given temperature were slightly higher than those without catalyst (blank test). When MG63

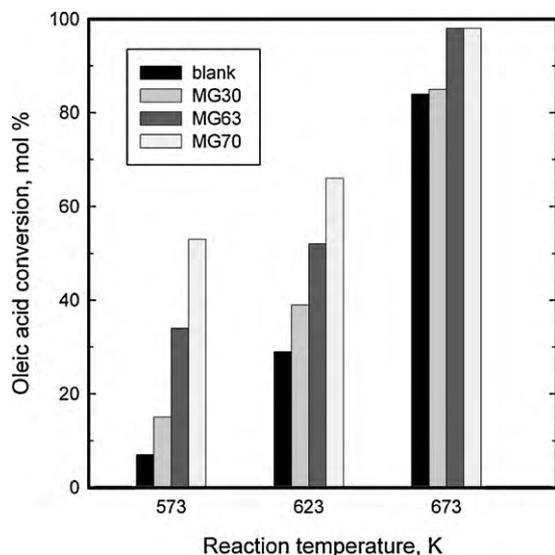
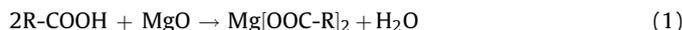


Fig. 2. Oleic acid conversions with hydrotalcites at various reaction temperatures (Blank test means simple heating of oleic acid without catalyst.).

and MG70 were used, MG70 showed better performance than MG63 at 573 and 623 K. To achieve oleic acid conversion higher than 80%, reaction temperature should be higher than 623 K.

Reaction temperature affected not only on the conversion, but also on the physical properties of products, such as phase and fluidity. Reaction products at 573 and 673 K were liquid phase with low viscosity. However, reaction product at 623 K was mostly solid. Considering conversions, liquid product at 573 K seemed to be unreacted oleic acid and that at 673 K was thought to be

hydrocarbon. Solid products obtained at 623 K might come from saponification of oleic acid and MgO as described in Eq. (1).



XRD analysis displayed the structural integrity of hydrotalcite after reaction, as shown in Fig. 3. MgO in MG30 completely

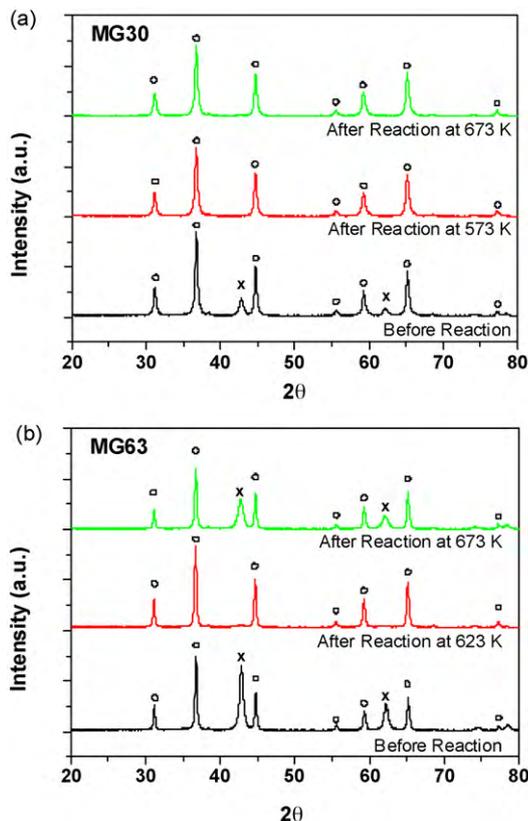


Fig. 3. X-ray diffraction patterns of hydrotalcites before and after reaction: (a) MG30 and (b) MG63 [○: MgAl<sub>2</sub>O<sub>4</sub> (hydrotalcite); ×: MgO].

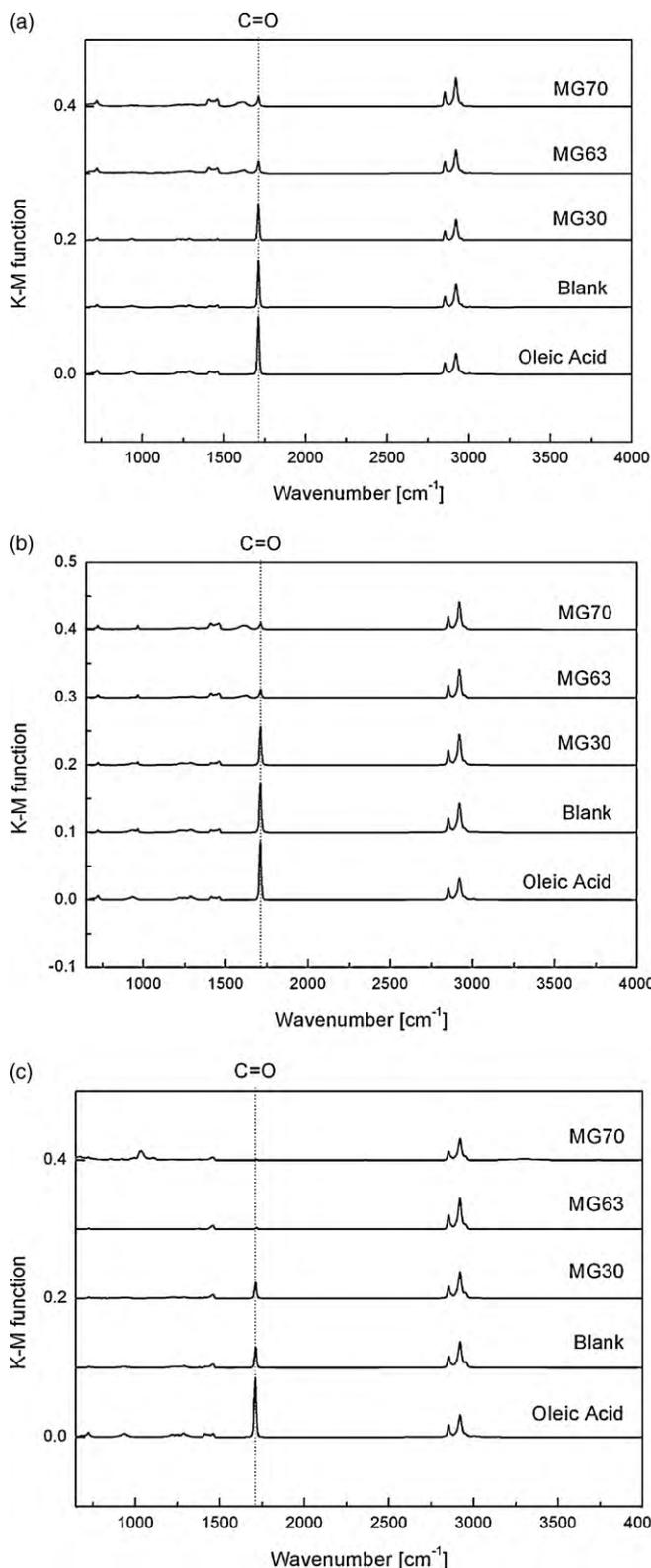


Fig. 4. FT-IR spectra of the reaction products depending on reaction temperatures and catalysts: (a) 573 K, (b) 623 K and (c) 673 K.

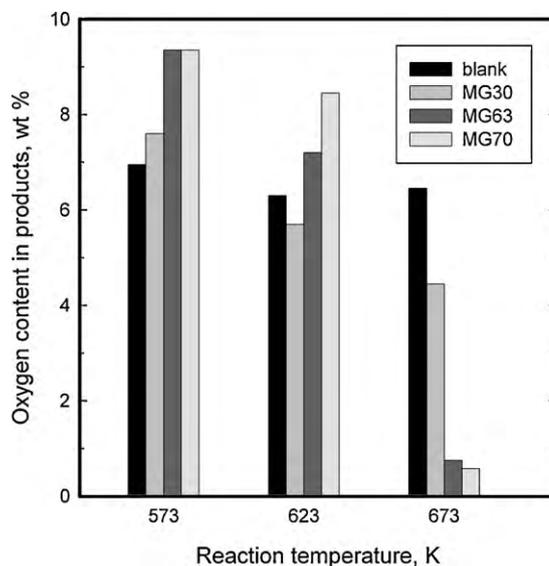
**Table 1**  
Elemental composition of the liquid products.

Catalyst	Temperature (K)	C (wt%)	H (wt%)	O (wt%)	H/C (atomic ratio)
Blank	573	79.75	13.3	6.95	2.00
	623	80.4	13.3	6.3	1.99
	673	80.1	13.45	6.45	2.01
MG30	573	79.1	13.3	7.6	2.02
	623	81.0	13.3	5.7	1.97
	673	81.8	13.75	4.45	2.02
MG63	573	77.8	12.85	9.35	1.98
	623	79.6	13.2	7.20	1.99
	673	84.8	14.4	0.75	2.04
MG70	573	77.8	12.85	9.35	1.98
	623	78.45	13.1	8.45	2.00
	673	85.15	14.27	0.58	2.01
Oleic acid		79.77	13.23	7.00	1.99

disappeared after reaction at 573 and 673 K (Fig. 3(a)). MgO in MG63 almost disappeared after reaction at 623 K. But most of it remained at 673 K (Fig. 3(b)). MgO in MG70 also showed the similar behavior as shown in the case of MG63. Not only decarboxylation, but also saponification is involved in these experimental results. As adsorption and desorption of CO<sub>2</sub> on MgO is the determining step in decarboxylation, structural change is not expected. However, MgO disappeared in saponification reaction because MgO behaves as a reactant. XRD results indicated that saponification was dominant at 623 K and decarboxylation was main at higher than 623 K. Considering conversions and the stability of catalysts, higher temperature, 673 K, is preferred to prevail decarboxylation over saponification.

### 3.2. Product analysis and decarboxylation activity

FT-IR spectrum was measured to analyze the change of oxygen contents in reactant. Because the oxygen is incorporated in the form of carboxylic group (–COOH), the peak intensity of carbonyl group (C=O), appeared around 1700 cm<sup>-1</sup>, can be a measure for the progress of decarboxylation reaction. In FT-IR spectra of Fig. 4, the peak intensity of C=O reduced as the reaction temperature and MgO concentration in catalysts increased. Especially, C=O almost



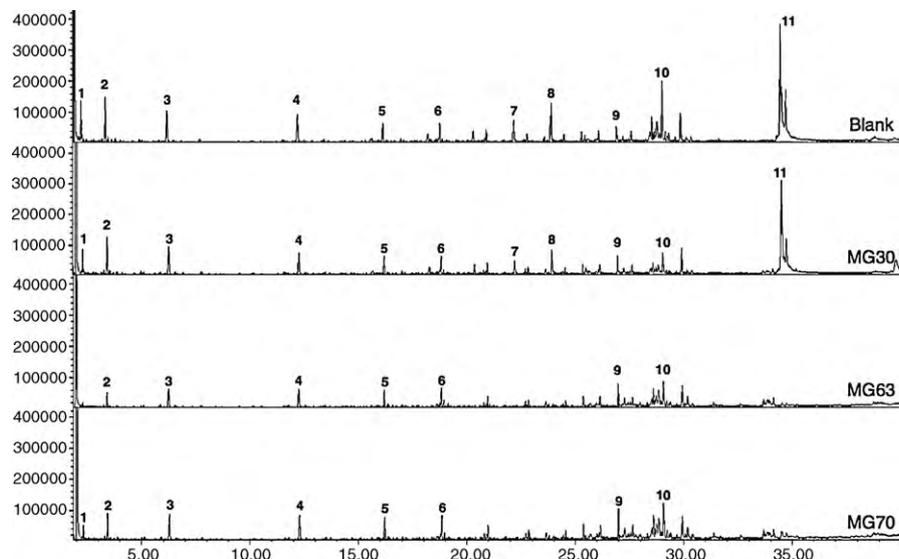
**Fig. 5.** Oxygen contents in liquid products depending on reaction temperatures and catalysts.

disappeared when the reaction temperature was higher than 623 K and MG63 and MG70 were used. FT-IR results strongly suggested that decarboxylation occurred during reaction.

Although decarboxylation was confirmed, oxygen in fatty acid might remain in the form of ether (R–O–R). In order to resolve this issue, total oxygen content in product was measured by elemental analysis to confirm the decrease of oxygen in product (Table 1 and Fig. 5).

In case of blank test, oxygen composition was almost the same as that of oleic acid regardless of reaction temperature. It implies that heating only induced pyrolysis and it did not lead to decarboxylation reaction. In case of using hydrotalcites as catalysts, oxygen content in reaction products decreased as the reaction temperature increased. Especially, the oxygen content decreased to less than 1 wt% when MG63 and MG70 were used as catalysts at reaction temperature of 673 K.

In addition to oxygen content, we focused on hydrogen to carbon ratio (H/C ratio) in the viewpoint of fuel quality (Table 1).



**Fig. 6.** GC/MS chromatograms of the reaction products at 673 K (1: hexane; 2: heptane; 3: octane; 4: nonane; 5: decane; 6: undecane; 7: nonanoic acid; 8: decanoic acid; 9: heptadecene; 10: nonyl cyclohexane; 11: oleic acid).

**Table 2**  
GC/MS percentage peak areas of major liquid products at 673 K.

Name of compound	Percentage peak area (%) (catalysts) <sup>a</sup>			
	Blank	MG30	MG63	MG70
Heptane	4.05	4.18	2.83	3.36
Octane	4.93	5.68	6.56	3.48
Octanoic acid	1.44	1.78		
Nonane	4.75	4.87	6.98	6.00
Nonanoic acid	2.82	2.50		
Nonadecanone			2.83	1.76
Decane	1.98	2.56	4.15	3.48
Decanoic acid	5.27	4.18		
Undecane	1.75	2.19	4.01	3.36
Undecanone		0.75	1.70	1.09
Undecanoic acid	0.70	0.84		
Dodecane	1.04	1.31	2.22	1.89
Tridecane	0.76	0.97	1.65	1.43
Tetradecane	0.68	1.28	1.23	1.17
Pentadecane	0.94	1.03	1.98	1.80
Nonyl cyclohexene	1.83	2.28	4.91	3.02
Hexadecane	0.84	1.09	2.17	2.56
Heptadecene	6.76	3.65	9.76	9.69
Heptadecane	6.71	3.15	6.93	6.50
Undecyl cyclohexane	3.26	3.78	6.42	4.91
Oleic acid	14.38	14.80		

<sup>a</sup> Percentage peak area = individual peak area/total peak area.

Heating of biomass at high temperature without oxygen might bring about pyrolysis and dehydration, which resulted in the increase of olefin and aromatic contents in reaction product. These types of reaction must be minimized because they degrade fuel quality of resultant hydrocarbon products. Unstable olefin compounds reduce long-term stability of fuel and aromatic compounds produce pollutants during combustion. H/C ratio slightly increased in these reaction conditions (reaction temperature of 673 K and MG63/MG70), implying that the generation of olefin and aromatic compound was minimized and hydrotalcites catalyzed decarboxylation reaction selectively. Thus, most of the oxygen in oleic acid was removed in the form of CO<sub>2</sub> by decarboxylation reaction.

Components of reaction product were precisely analyzed and identified by gas chromatography with mass spectrometer (GC-MS). As the reaction temperature increased up to 623 K, the intensity of oleic acid peak decreased regardless of catalysts. But, any other peaks did not appear. On the other hand, various types of reaction products appeared and the intensity of oleic acid decreased when the reaction temperature went up to 673 K. Fig. 6 shows the identified components of the liquid products at 673 K and Table 2 summarizes GC-MS percentage peak areas for major products. In case of blank test and MG30 catalyst at 673 K, not only a series of hydrocarbons, but also low molecular weight fatty acids, such as decanoic acid was presented. Cracking the double bond (9th carbon) in oleic acid explains the production of octane and decanoic acid. It indicates that cracking, instead of decarboxylation, seems to be the dominant reaction pathway in this condition. However, pure hydrocarbons such as octane, nonane and heptadecene were produced only when the reaction temperature was 673 K and catalysts were MG67 and MG70. In

these conditions, cracking and decarboxylation occurred simultaneously. Heptadecene was formed by direct decarboxylation of oleic acid. Decanoic acid, which is detected in the other cases, lost their CO<sub>2</sub> by MG63 and MG70 and then turned into nonane. Based on these product analysis by GC-MS, decarboxylation by hydrotalcites are active when the reaction temperature was the same or higher than 673 K. It is closely related with adsorption-desorption behavior of MgO, considering MgO-CO<sub>2</sub> desorption temperature around 623 K [15,16].

#### 4. Conclusions

To obtain hydrocarbon fuels from vegetable oil, decarboxylation reaction with a series of hydrotalcite catalysts was investigated. It was found that MgO ratio in hydrotalcites and reaction temperature played key roles in decarboxylation reaction. At lower reaction temperature and low MgO concentration in hydrotalcite, the conversion of oleic acid scarcely occurred. On the other hand, oleic acid conversions were more than 98% and the oxygen content in the reaction product was less than 1 wt% in the case of decarboxylation with MG63 and MG70 at 673 K. Also, reaction temperature must be higher than 623 K in order to inhibit saponification with MgO and fatty acid. Previous studies on decarboxylation of fatty acids usually have used high-pressure hydrogen for hydrodeoxygenation or precious metal catalyst system. In this study, hydrotalcites showed the activity of decarboxylation without hydrogen and could produce pure hydrocarbon streams. It was confirmed that most of the oxygen in oleic acid were removed in the form of CO<sub>2</sub> from the elemental and FT-IR analysis of the liquid products. However, selectivity of heptadecene, a product by direct decarboxylation of oleic acid was not very high, implying that the cracking and decarboxylation occurred simultaneously during the reaction by hydrotalcites.

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