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Selective catalytic decarboxy-cracking of triglyceride to middle-distillate hydrocarbon

H. Tani, T. Hasegawa, M. Shimouchi, K. Asami, K. Fujimoto*

Department of Chemical Processes and Environments, Faculty of Environmental Engineering, University of Kitakyushu, 1-1, Hibikino, Wakamatsu, Kitakyushu 808-0135, Japan

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ABSTRACT

It was found that MgO supported catalysts gave liquid hydrocarbons and CO_2 selectively, from palm oil and other vegetable oil at around 703 K. The hydrocarbon product was composed of paraffins and olefins, whose carbon number was C_3 and C_{10}–C_{20} hydrocarbons whose peak located at C_{15}. Chemical structure of the products was the mixture of straight chain and branched chain hydrocarbons. The fluid point of the product was about 253 K. Supported MgO promoted the di-carboxylation of triglyceride or free fatty acid. The products showed lower acid value and iodine value. The product was successfully used for the diesel engine.

1. Introduction

Conversion of vegetable oil or animal fat to diesel fuel is one of the promising technologies to make renewable fuel, especially the petroleum alternatives for transportation fuel. The most popular technology for this purpose is the transesterification of triglycerides with methanol to give methyl esters of fatty acids and glycerine [1–7]. They are largely industrialized to make biodiesel. Other methods are is hydrocracking or catalytic, non-catalytic cracking to hydrocarbon and water [8–10].

The former one is operated at 310–360 K with excess methanol and alkali compounds such as NaOH, KOH, $NaOCH_3$, or alkaline earth oxide. This process can be operated under atmospheric pressure and the reaction proceeds almost quantitatively. The product is separated into two phases. One is oily phase (methyl ester, target product) and another is the aqueous phase which contains glycerine, spent catalyst, free acid and water. The crude methyl ester must be purified with several steps to clear the commercial fuel standard.

Another one is the hydrocracking of triglyceride with transition metal catalyst under high hydrogen pressure [8,11,12]. This process is operated in the hydrocarbon solvent and gives straight chain paraffins composed of the same chemical structure to that of the triglyceride, propane and waster. The product shows high cetane number (80–90) but high fluid point. It consumes hydrogen and makes water as by product.

The last one is the cracking reactions at high temperature such as 673–773 K. The non-catalytic reaction of triglyceride proceeds via the free radical mechanism and gives a liquid product which is rich in naphtha and gases as well as CO and CO_2 [9]. Liquid product contains hydrocarbons and oxygen-containing compounds and tarry matter. The reactions involved are quite complicated. The catalytic cracking is conducted at around 723 K over solid acid catalyst such as USY, REY, HZSM-5, MCM-41 and SBA-5 [13–21]. The main product is the gasoline-range hydrocarbons which contain paraffins (mainly balanced), olefins and aromatic hydrocarbons. Other byproducts are water and CO_2. These reactions are not suitable for making middle-distillate hydrocarbon.

The present study report a new catalytic cracking process for a variety of triglycerides which aimed at the selective production of diesel fuel.

2. Experimental

Catalysts were prepared by impregnating a commercially available silica gel (Fujisilicia, Q-10, specific surface area 313 m^2/g) and active carbon (wood made 1100 m^2/g) with magnesium oxide from aqueous solution of magnesium nitrate, drying at 393 K and the calcinating it under N_2 atmosphere at 823 K for 3 h MgO loading was 10% by weight. Reactions were conducted in a agitated flow reaction systems, at around 703 K under atmospheric pressure as shown in Fig. 1. The precise figure of the reactor is shown in Fig. 2 reactor size. The catalyst used was a powder with the average diameter of 1.2 mm. Into the agitated catalyst (50 ml) bed feed oil was directly introduced (5–20 ml liquid/h) after being preheated with the carrier gas (50 ml/min). The product which came out of the reactor was cooled with a 2-stage condenser which was kept at 273 K and 193 K, respectively. The uncondensed gaseous products were exhausted after being analyzed with on-line GC (TCD and FID).

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* Corresponding author. Tel.: +81 93 695 3387; fax: +81 93 695 3387.
E-mail address: fujimoto@env.kitakyu-u.ac.jp (K. Fujimoto).

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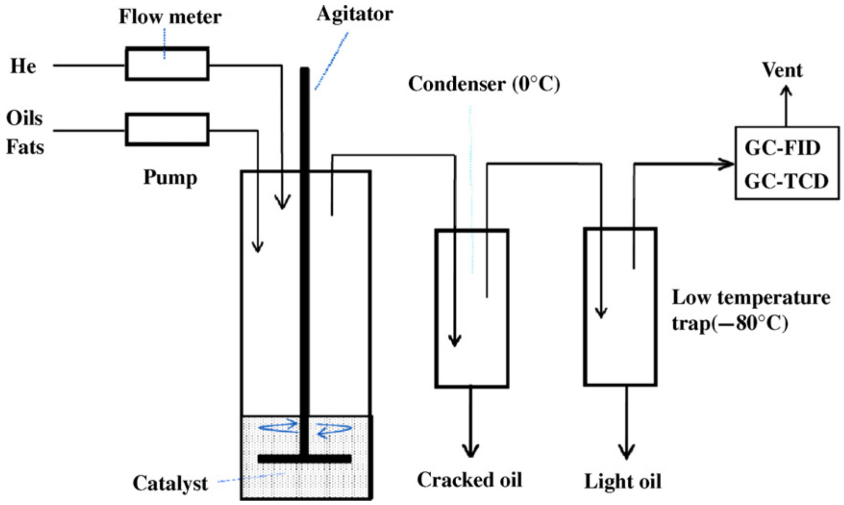

Fig. 1. Reaction apparatus for the catalytic cracking.

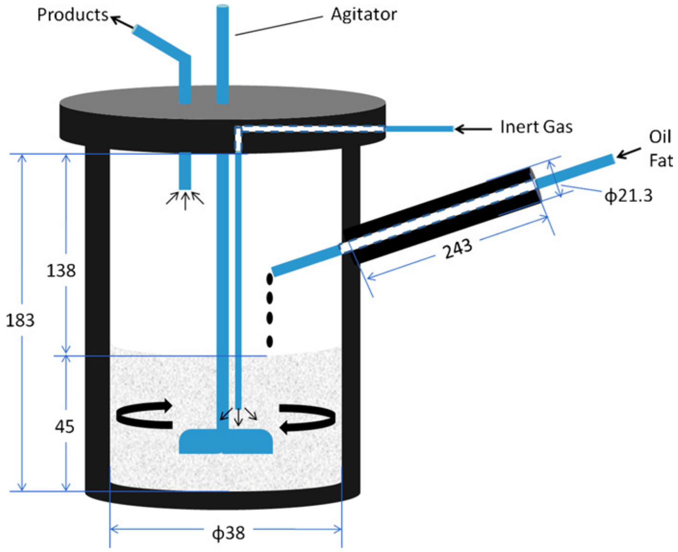

Fig. 2. Detail of agitated system reactor.

Product oils were analyzed by off-line capillary GC with or without hydrogenation. Total acid value and iodine value of the cracked oil were measured by potentiometric titration (ASTM D664 and ASTM D1959). The “acid value” is content of free acid and the “iodine value” is amount of unsaturated bond in product oils.

Contents of olefins and branched hydrocarbons were determined by the following method: (a) olefin contend: by the comparison of capillary GC chromatogram before and after the treatment of sample oil with 100% sulfonic acid (disappeared peak correspond to olefins); (b) branched hydrocarbons: sample oil was hydrogenated by H_2 with Pd/active carbon catalyst at 423 K and 2.0 MPa, which was followed by the GC analysis. The process has been known to hydrogenate all aliphatic olefins without skeletal conversion.

3. Results and discussion

3.1. *Cracking reaction of palm oil on solid catalysts*

Cracking reaction was conducted continuously, at longest, for 24 h during this period. Little change in the product pattern was observed but coke deposition on the catalyst. The coke could be removed by treating catalyst with air at around 723 K for 4 h.

3.1.1. *(a) Products of the cracking reaction*

Table 1 shows the reaction results of a commercially available fresh palm oil at 703 K. Products were CO, CO_2, H_2O gaseous hydrocarbons (C_1–C_4), liquid hydrocarbons and residue. The amount of residue was determined as the weight difference between weight of the catalyst before and after use. Here, the oil is the condensed product in the 1st and 2nd trap. The unreacted triglyceride was not detected in the product, probably it did not come out of the reactor as well as the high boiling reaction products, because of their high boiling point. These materials are designated as “residue”. Table 2 shows the example of the composition of gaseous hydrocarbon.

It is clear from the data that silica gel or active carbon could catalyze and gives hydrocarbons with fairly high selectivity. However,

Table 1
Material balance of palm oil cracking.

Catalyst	Product yield [wt%]						AV[a] [mg KOH/g]	IV[b] [g I/100 g]
	Oil	Gaseous H.C	CO_2	CO	H_2O	Residue		
SiO_2	57.9	10.4	5.1	2.6	4.4	10.0	>4.10	85.2
MgO–SiO_2[c]	50.0	10.1	9.1	2.1	3.7	9.1	0.07	79.9
Carbon	60.3	13.4	6.7	2.3	3.2	6.4	>4.10	83.7
MgO–carbon	64.9	10.1	7.9	2.5	7.4	7.4	0.02	79.1
Spent FCC	48.3	11.7	1.7	1.6	2.6	19.9	>4.10	50.4
MgO[d]	65.9	5.1	9.7	2.2	4.2	5.6	2.68	80.4

Reaction condition: temperature 703 K, catalyst amount 50 ml, and feed late 13.5 g/h.

[a] Acid value (ASTM D 664).

[b] Iodine value (ASTM D 1959).

[c] 10 wt% MgO, 90 wt% SiO_2.

[d] 85 wt% MgO, 15 wt% SiO_2.

Table 2
Composition of gaseous hydrocarbon.

Products [wt%]	Catalyst				
	SiO_2	MgO–SiO_2	Carbon	MgO–carbon	Spent FCC
CH_4	7.7	7.7	7.7	9.2	9.0
C_2H_6	21.1	21.1	18.3	21.6	15.6
C_2H_4	8.0	8.0	4.6	5.6	4.9
C_3H_8	25.3	25.3	22.3	25.5	24.2
C_3H_6	30.2	30.2	42.7	31.9	24.6
n-C_4H_{10}	1.0	1.0	0.2	0.6	0.0
i-C_4H_{10}	0.0	0.0	0.0	0.3	18.1
1-QH_8	0.2	0.2	0.0	0.1	1.6
2-C_4H_8	6.5	6.5	4.3	5.3	0.0
n-C_5H_{12}	0.0	0.0	0.0	0.0	2.0

Reaction condition: temperature 703 K, catalyst amount 50 ml, and feed late 13.5 g/h (same reaction as shown in Table 1).

the spent FCC catalyst gave small amount of liquid and fairly large amount of residue. Products such as dry gas (which did not condense in 1st and 2nd traps), CO_2, CO, H_2O and coke, were formed with high yield.

Another remarkable phenomenon shown in Table 1 is that the supported MgO catalysts gave higher CO_2 yield and much lower acid values. This phenomenon suggests that MgO promote the decarboxylation of triglyceride or free fatty acid to make hydrocarbons and CO_2. The mechanism will be discussed later.

Table 2 shows the hydrocarbon composition for every catalyst. The points which should be noted are that the main products are olefins and paraffins (C_1–C_3) and that the gas composition is quite similar for each catalyst except spent FCC catalyst. Also, another point should be noted is that on the spent FCC catalyst isobutane (i-C_4H_{10}) was formed fairly large amount while its formation was negligible on other catalyst. This phenomenon suggests that the reaction on the spent FCC catalyst (solid acid) is the ionic type reaction while that on other catalyst is radical type reaction.

3.1.2. (b) Distribution of hydrocarbon

Figs. 3 and 4 show the product distribution based on the carbon base for the product of the reaction over SiO_2- and carbon-based catalyst, which showed excellent performances. The characteristic features of carbon number distribution are that they showed two peaks. One is the peak at C_3 (propylene). The second one positioned at C_{15}. The peak at C_3 should be caused by the dehydration of glycerine. The second peak which was located at C_{15} should come from the acid group of triglyceride. Other than C_{15} the product distributed on C_7–C_{20}. It is well known the acid group of palm oil is mainly composed of palmitic acid group of C_{16} (~45%) and oleic acid group C_{18} (~55%). If the acid group is kept in the product hydrocarbon, C_{15} and C_{17} peak should be the only 2 peaks. However, the carbon number of the product hydrocarbon distributed over wide range and no peak was detected at C_{17}. Although the reason was not clear, certain reactions of carbon–carbon dissociation occurred.

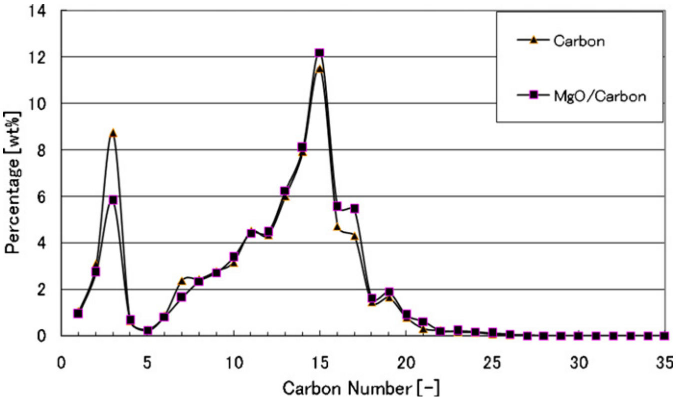

Fig. 3. Carbon number distribution of carbon based catalyst. Oil feed rate: 15 ml/h, catalyst: 50 ml, LHSV: 0.3 h^{-1}, temperature: 703 K, pressure: 0.1 MPa, carrier gas (He): 50 ml/min, –▲–: carbon, –■–: MgO/carbon.

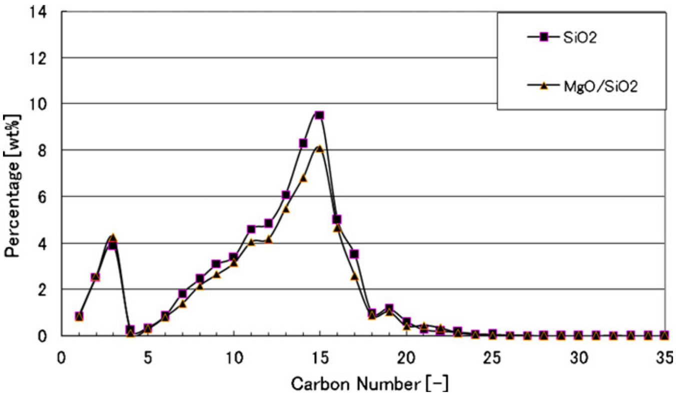

Fig. 4. Carbon number distribution of SiO_2 based catalyst. Oil feed rate: 15 ml/h, catalyst: 50 ml, LHSV: 0.3 h^{-1}, temperature: 703 K, pressure: 0.1 MPa, carrier gas (He): 50 ml/min, –■–: SiO_2, –▲–: MgO/SiO_2.

Table 1 also shows the acid value, which means the amount of free acid in the product. Showing that the acid value was quite low when the catalyst containing magnesium oxide. On the catalyst contained MgO, the production of CO_2 was rather high. These phenomena suggest that the decarboxylation of fatty acid to hydrocarbons was promoted by MgO, as indicated in Eq. (1).

$$RCOOH \xrightarrow[MgO]{} RH + CO_2 \qquad (1)$$

3.1.3. (c) Chemical structure of product hydrocarbons

Figs. 3 and 4 show the carbon number distribution with chemical structure. Chromatogram of capillary GC showed quite complicated one whose main peak was straight chain paraffins and straight chain olefins. The product contained little aromatics. Fig. 5 shows the n-paraffins and iso-paraffins C_{10}–C_{18} products, which was determined by the GC analysis of the hydrogenated product, telling that the product hydrocarbons are the mixture of straight chain and branched chain hydrocarbons. This structure should be the reason of the fluid point of the product at 258 K. The reason of the completely generation of branched hydrocarbons may come from the secondary reaction of olefins since the MgO–SiO_2 mixed oxide shows week acidity, which catalyze the skeletal isomerization of olefins.

Fig. 5 shows the total carbon number distribution on MgO–SiO_2 catalyst with olefin and paraffin separation. The figure shows that each product contain olefins with 20–40 wt%. The content increased with the increase in the carbon number and the total olefin content in the product was 47% by weight. This facet also, supports the low fluid points of the product.

3.2. Reaction of a variety of vegetable oils

Fig. 6 shows the reaction results of a variety of vegetable oil over MgO–SiO_2 catalyst, showing that vegetable oils tested were reacted almost completely to give hydrocarbon oil, propylene rich gas and CO_2. About 10 wt% of high boiling material (its composition was not clear) remained in the reactor with catalyst (designate as residue). The carbon number distribution of the product oil was similar for each samples such as used cooking oil (origin of fresh cooking oil was the mixture of canola oil, soy bean oil and palm oil) or even the "dirk oil" whose main component was free fatty acid gave the similar results spite of the different structure of triglyceride. Product

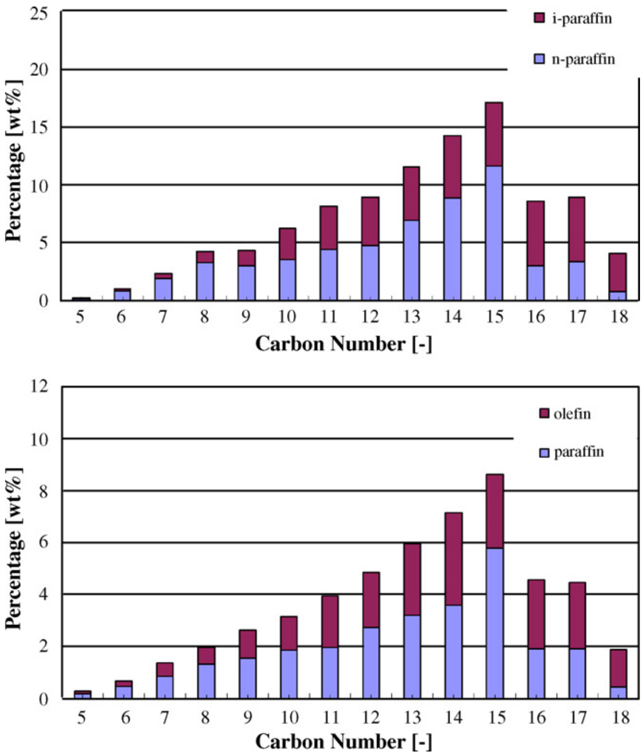

Fig. 5. Chemical structure of product hydrocarbons (the same oil with Fig. 3). Oil feed rate: 15 ml/h, catalyst: 50 ml, LHSV: 0.3 h^{-1}, temperature: 703 K, pressure: 0.1 MPa, carrier gas (He): 50 ml/min, 🟦 : *i*-paraffin, 🟪 : *n*-paraffin, 🟦 : paraffin, 🟪 : olefin.

hydrocarbon was rather similar and the main component was C_{15} hydrocarbons. These results also suggest the possible intermediate is free acid. Also, the cracking of C–C bond proceed simultaneously or successively with decarboxylation or decarbonylation.

3.3. *Discussion on the reaction path way and role of MgO*

Fig. 7 shows the probable reaction pathway of the decarboxy-cracking of triglycerides. It should be noted that the product contained water. Since the feed material contained little moisture, the water in the product should be attributed to the dehydration of the reactant. Since the reaction is the complete mixed type (CSTR), water vapor always exist in the reactor the water which has been generated by the dehydration of glycerin can be utilized for the hydrolysis of triglyceride. Also, the fact that free fatty acid (dark oil) gave the similar product pattern suggests that one of the main unit reaction involved was the decarboxylation of free acid.

Based on these concepts, the most plausible reaction pass way of the hydrocarbon production can be summarized as in Fig. 6.

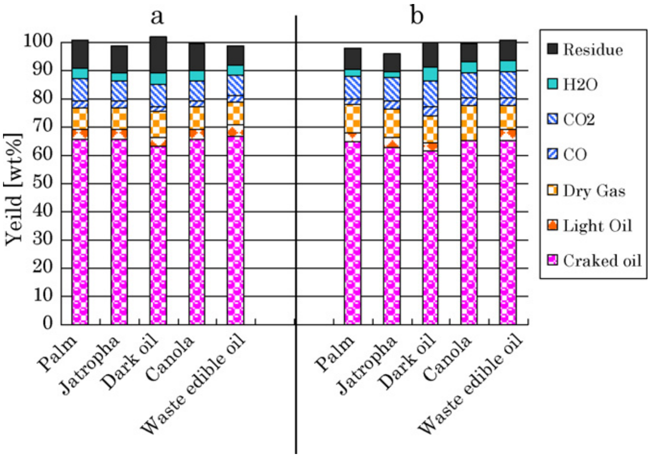

Fig. 6. Material balance of various vegetable oils. (a) MgO–SiO_2 catalyst, (b) MgO-active carbon catalyst. Oil feed rate: 15 ml/h, catalyst: 50 ml, LHSV: 0.3 h^{-1}, temperature: 703 K, pressure: 0.1 MPa, carrier gas (He): 50 ml/min, ■: residue, 🟦 : H_2O, ▨ :CO_2, ◩ : CO, 🟧 : dry gas, ◪ : light oil, 🟪 : cracked oil.

The major route of the cracking reaction are thought to be (1) the hydrolysis of triglyceride to glycerine and free acid, (2) the dehydration of glycerine to gaseous hydrocarbons and water, (3) decarboxylation of free acid to hydrocarbons and CO_2 and (4) decarbonylation and (5) the secondly reactions of hydrocarbons. In the reaction step (3), MgO promotes the decarboxylation to make CO_2 and hydrocarbon.

The reaction why MgO promote the decarboxylation can be explained as follows: MgO can make $MgCO_3$ by the reaction of carboxylic acid.

$$MgO + RCOOH \rightarrow MgCO_3 + RH \tag{2}$$

If CaO is used instead of MgO the produce $CaCO_3$ is so stable under reaction condition that high temperature (>973 K) is necessary to decompose to CaO [22]. However, $MgCO_3$ is easy to decompose to CO_2 and MgO under reaction conditions (from equilibrium calculation)

$$MgCO_3 \rightarrow MgO + CO_2 \tag{3}$$

Really, the XRD analysis of used catalyst showed only MgO peak. Therefore, MgO can work as catalyst for decarboxylation.

Reaction intermediates has not been clarified yet. The characteristic pattern of the product composition MgO–SiO_2 or MgO–carbon is quite different from those catalyzed by spent FCC catalyst that and rather large amount of C_2 hydrocarbons with little or no *i*-C_4H_{10} suggest that the triglyceride decomposition proceed via free radicals. Free radical mechanism can also explain the wide range of product distribution.

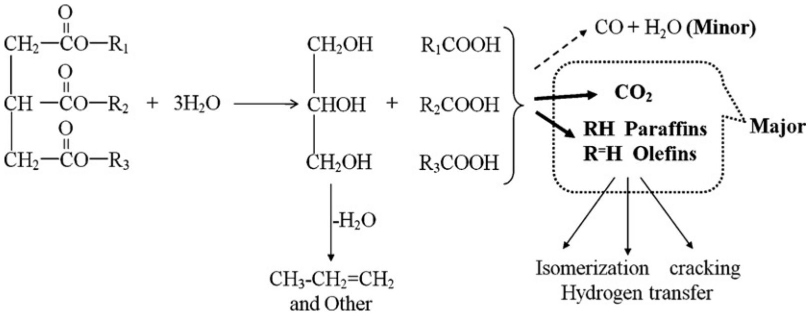

Fig. 7. Reaction network of catalytic cracking using MgO supported catalyst.

4. Conclusion

It was found the MgO–supported catalyst promoted the decarboxy-cracking of palm oil and other triglyceride to make middle-distillate range hydrocarbons, which was the mixture of olefins and paraffins with straight chain and branched chain structure, which were assumed to be derived from the dehydration of glycerine and the decarboxylation of ester or the free acid which is followed by the C–C bond dissociation. The supported MgO promoted the formation of CO_2 and the suppression of free acid formation.

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