

Original Paper

Development of Direct Production Process of Diesel Fuel from Vegetable Oils

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A new direct production process was developed for making high quality diesel fuel from oils and fats. In this process, which was operated under atmospheric pressure by using neither methanol nor hydrogen, no glycerin was produced. The product of the present process was composed of small amount gas (CO₂, light hydrocarbons and minor amount of CO) and liquid hydrocarbons (C₁₀-C₂₀). The liquid product was composed of olefins and paraffins with straight and branched chain structure.

Key Words

Catalytic cracking, Decarboxylation, Hydrocarbon production, Low acid value, Low iodine value

1. Introduction

Conversion of vegetable oil or animal fat to diesel fuel is one of the promising technologies to make renewable fuels, especially the petroleum alternatives for transportation fuel. The most popular technology for this purpose is the transesterification of triglycerides by methanol to methyl esters of fatty acids and glycerine¹⁾. It has been largely industrialized to make biodiesel. Other processes are catalytic, non-catalytic cracking or hydrocracking to hydrocarbons and water^{2,3)}.

The former one is operated at 310-360 K with excess methanol and alkali compounds such as NaOH, KOH, NaOCH₃, or alkaline earth oxide. This process is operated under atmospheric pressure and the reaction proceeds almost quantitatively. The product is separated into two phases. One is methyl ester (target product) and the other is the glycerin which contains 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^{2,4,5)}. This process is operated in the hydrocarbon solvent and gives straight chain paraffins composed of the same chemical structure to that of the triglyceride. The product shows high cetane number (40-50). It consumes hydrogen and makes water as by-product.

The last one is the cracking reaction at high tempera-

ture as 673-773 K. The non catalytic reaction of triglyceride proceeds via the free radical mechanism and gives liquid product which is rich in naphtha and carbon oxides³⁾. Liquid product contains hydrocarbons and oxygen-containing compounds and tarry matter. The reactions involved are assumed to be quite complicated. The catalytic cracking are conducted at around 723 K over solid acid catalyst such as USY, REY, HZSM-5, MCM-41 and SBA-5⁶⁻¹¹⁾. Main products are the gasoline-range hydrocarbons which contain paraffins (mainly branched), olefins and aromatic hydrocarbons. Other byproducts are water and CO₂. These reactions are not suitable for making middle distillate hydrocarbon.

The present study is concerned with a new catalytic cracking of a variety of triglyceride, which aims at the selective production of diesel fuel composed of hydrocarbon, with the by-production of CO₂. The diesel fuel has been predicted to increase in their consumption as the transportation fuel and has been produced from petroleum. The target reaction is expected as in Fig. 1. Where, it requires solid catalysts, but no additional feed.

When the products are ideally produced from the equa-

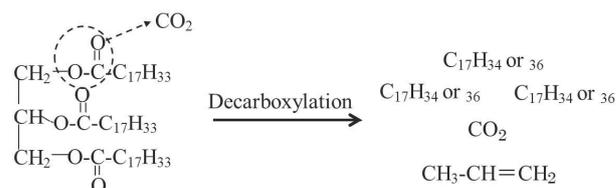


Fig. 1 The target reaction scheme

tions, the yields of liquid hydrocarbons, CO₂ and dry hydrocarbon gas are 79 wt%, 16 wt% and 5 wt%, respectively.

2. Experimental

2.1 Reaction apparatus and procedure

Catalysts were prepared by impregnating a commercially available silica gel (Fujisilicia, Q-10, 313 m²/g) and active carbon (wood made 1,100 m²/g) with magnesium oxide from aqueous solution of magnesium nitrate, drying at 393 K and calcining under N₂ atmosphere at 823 K. MgO loading was 10 % by weight.

Catalytic reactions were conducted in flow reaction systems, at around 703 K under atmospheric pressure, by using an agitated reactor as shown in Fig. 2. The used catalyst was granule with the average diameter of 1.2 mm. The reactor used was an autoclave type one (ϕ 38 mm \times 180 mmL) which was heated electrically from outside. Into the agitated catalyst bed (50 ml, about 25 g) feed oil was introduced continuously (15 mL/h) for 5 h with carrier gas (He: 50 mL/min). The apparent LHSV was 0.3 h⁻¹.

2.2 Product analysis

The product which came out of the reactor was cooled with 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). Total acid value and iodine value of the cracked oil were measured by potentiometric titration (ASTM D664 and ASTM D1959). Carbon number distribution of the product was determined with a capillary GC (column: CBP1). The chemical structure of the product (straight- and branched-structure) was determined by the capillary GC after it was hydrogenated under pressured hydrogen in the presence of Pd/Carbon catalyst.

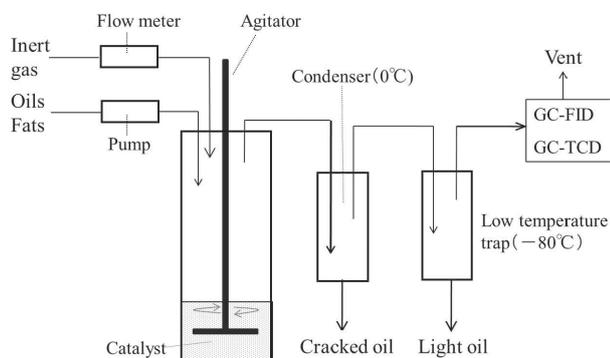


Fig. 2 Reaction apparatus for cracking oils

3. Results and discussion

3.1 Reaction of a variety of vegetable oils

3.1.1 Products

In the present system triglyceride didn't come out of the reactor because the boiling point of the feed is higher than 703 K. Fig. 3 shows the reaction results of a variety of vegetable oil over MgO-SiO₂ catalyst and MgO-carbon catalyst. Raw product was slightly colored oil, whose main component was hydrocarbons (>99 wt%), gaseous product which contain C₁-C₄ hydrocarbon and carbon oxides. More than 90 % of carbon oxides were CO₂. Residue was higher boiling products or coke which didn't come out of the reaction vessel (about 10 wt%). As shown in Fig. 3 each raw material gave similar hydrocarbon yield (70-75 wt%). Another characteristic feature of the product was that the carbon number of the hydrocarbons distributed widely C₅-C₂₅ even though the carbon number of acidic group of the triglyceride was limited to C₁₂-C₁₈¹²⁾¹³⁾. This phenomenon will be discussed later. Table 1 shows the distribution of gaseous hydrocarbons produced by the catalytic cracking of palm oil. It is clear from the data that the main gaseous product was C₃H₈ and C₃H₆. It is suggested that the C₃ hydrocarbon comes from glycerin group of the feed. Fig. 4 shows the carbon oxides yield and acid value. It shows that supported MgO promotes the formation of CO₂ and reduce the acid value, suggesting the promotion of decarboxy reaction by MgO.

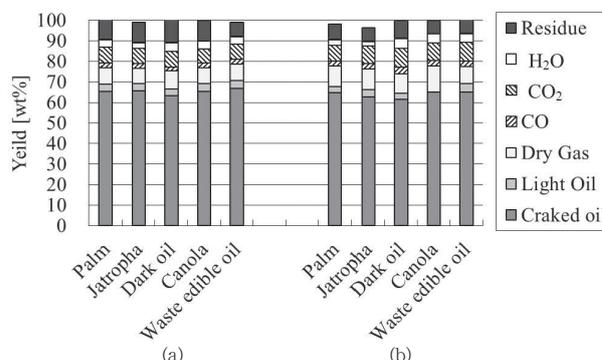


Fig. 3 Material balance of various vegetable oils (a)MgO-SiO₂, (b)MgO-Carbon

Table 1 Distribution of gaseous hydrocarbon

Products [wt%]	Palm oil	
	SiO ₂	MgO-SiO ₂
CH ₄	7.7	12.0
C ₂ H ₆	21.1	25.4
C ₂ H ₄	8.0	9.1
C ₃ H ₈	25.3	27.0
C ₃ H ₆	30.2	26.4
n-C ₄ H ₁₀	1.0	0.2
i-C ₄ H ₁₀	0.0	0.0
C ₄ H ₈	6.7	0.0

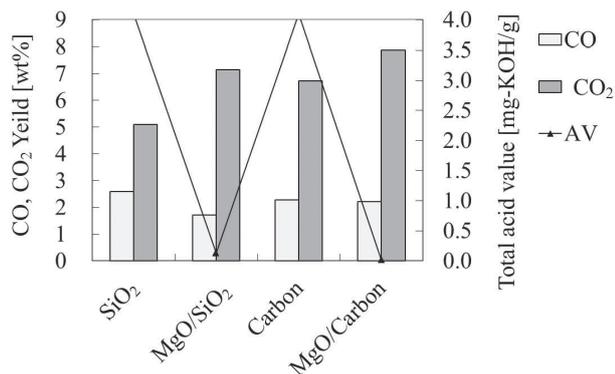


Fig. 4 Acid value and carbon oxide yield of palm oil cracking

The carbon number distribution of the product oil shown in Fig. 5 and Fig. 6, which was similar for each samples such as waste edible oil (origin of fresh cooking oil was the mixture of canola oil, soy bean oil and palm oil) or even the “dark oil” whose main component was free fatty acid gave the similar results. Product hydrocarbon was rather similar to each other and the main component was

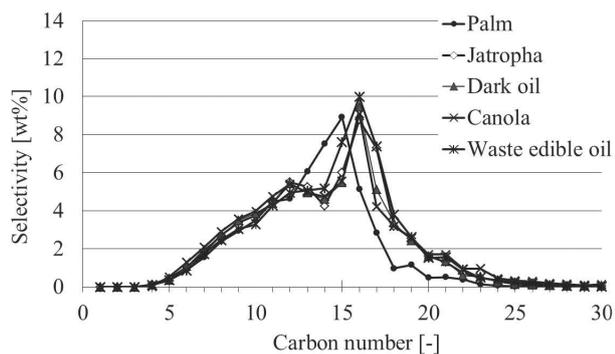


Fig. 5 Carbon number distribution of cracked oil using MgO-SiO₂ catalyst

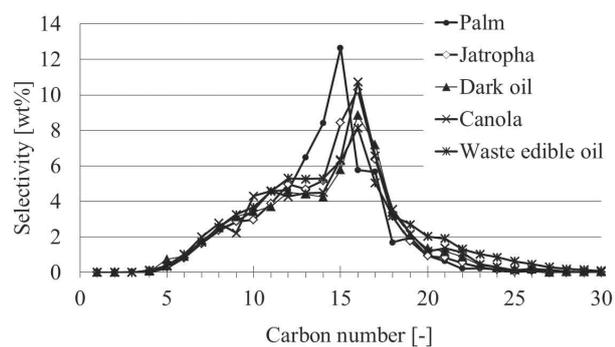


Fig. 6 Carbon number distribution of cracked oil using MgO-Carbon catalyst

C₁₅ and C₁₇ hydrocarbons, which was dependent on fatty acid group of raw materials. Carbon number distribution didn't show large difference between MgO-SiO₂ and MgO-carbon. It means that this reaction is scarcely affected for the distribution by carrier material of the catalyst.

Fig. 7 shows acid value of cracked oil and the yield of CO, CO₂. Products on the MgO-carbon exhibited lower acid value than that on the MgO-SiO₂. Especially, the acid value of palm oil product, about 0.1 mg-KOH/g, which is much lower than the critical value for B-5 (5 vol% FAME in gas oil) and neat standard (Japanese standard; 0.5).

This catalytic cracking system gave similar acid values of product for vegetable oil and dark oil (mostly composed of free fatty acid). This result suggests that hydrocarbons are produced via the decarboxylation reaction of free fatty acid. Fig. 8 shows the carbon number distribution of cracked palm oil. It is clear that the supported MgO has little effect on the molecular weight of the product.

Table 2 shows the pour point of raw material and the cracked products. Catalytic cracking system gave the prod-

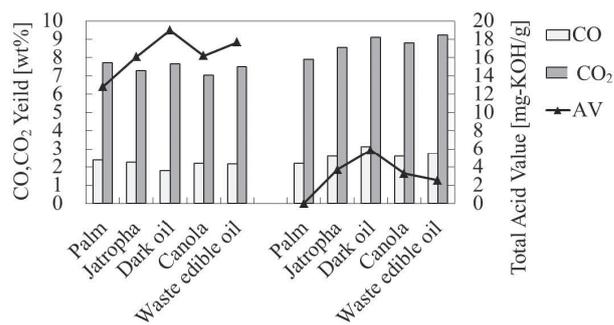


Fig. 7 Acid value of cracked oil

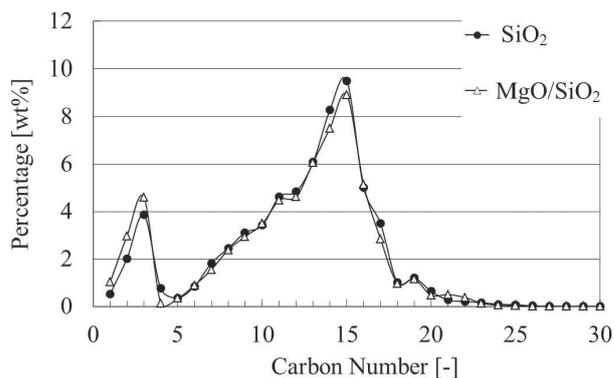


Fig. 8 Carbon number distribution of the production hydrocarbon from palm oil cracking

Table 2 Pour point of various fuel

	Palm oil				Waste edible oil		Gas oil (Petroleum)
	Raw material	FAME	BHD	Catalytic cracking	Raw material	Catalytic cracking	
Pour point [K]	298	293	293	260	265	258	268

uct with low pour point products. Especially, the pour point of the cracked oil of waste edible oil was about 258 K, which is lower than Japanese standard of petroleum gas oil (268 K). It suggests that the products of this system contain branched hydrocarbons.

3.1.2 Chemical structure of Product hydrocarbons from palm oil

Chromatograph of capillary GC shows quite complicated one and shows mixture of olefins and paraffins. Olefin content was about 30 mol% with little aromatics. Fig. 9 shows the ratio of straight chain paraffins and branched chain paraffins in C₆-C₁₈ 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. The reason of the generation of branched hydrocarbons may come from the secondary skeletal isomerization of olefins. The isomerization reaction can be attributed to the acidic character of the SiO₂-MgO surface complex, which should be formed by the reaction of SiO₂ and MgO at high temperature¹⁴. This structure should be the reason of the low pour point of the product as low as 258 K.

Product hydrocarbons are the mixture of paraffin and olefin as described in 3.1.1 and Table 1. Although the stoichiometry of reaction in Fig. 1 indicates that glycerin is converted to C₃H_n, the products are the mixture olefins or paraffins. This phenomenon should be attributed to the transfer hydrogenation by hydrogen atoms generated during coke (residue) formation which is the popular phenomenon observed in the cracking reactions at high temperature¹⁵.

3.2 Applicability of the process to a variety resource

Other than vegetable oils, lard, beef tallow, rice bran could be successfully applied for producing hydrocarbon oil with this process. Animal fat has been known to be dif-

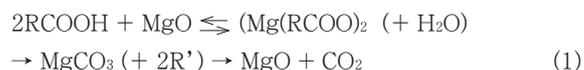
ficult to apply FAME method, because it produces high pour point product.

Animal fats (lard and beef tallow) gave high oil yield about 70 wt%, which was same level to vegetable oils. Also, rice bran gave hydrocarbons, directly. Hydrocarbon products, which are shown in Fig.10, distributed from C₆-C₂₀, and its peak point was C₁₇ hydrocarbon, probably derived from C₁₈ fatty acid, included in raw materials.

As a result, it can be said that this catalytic cracking system can be applied for various oils, fats and even oil containing materials.

3.3 Discussion on the catalysis of MgO-supported catalyst and reaction path way

As mentioned in the experimental section, only MgO peak was detected in the catalyst before and after the reaction. Also, products on the MgO-SiO₂ showed low acid value and fairly rich in branched hydrocarbons. These phenomena suggest that the MgO-SiO₂ catalyst has both acid site (SiO₂-MgO surface mixed oxide) and bulk MgO. SiO₂-MgO mixed oxide has been known to show weak acidity which catalyzes the structural isomerization of olefins. MgO has been known to react with carboxylic acid to make Mg salt of acids (at low temperature and carbonate at higher than 473 K). MgCO₃ is converted to MgO and CO₂ at higher temperature than 673 K. Therefore, the decarboxylation on MgO-SiO₂ catalyst can be shown as follows:



The wide distribution of carbon number of the product hydrocarbon is hard to be attributed to the simple secondary reactions of olefins, since this catalyst is not active to crack olefins. One possibility is as follows : Two carboxylic acid molecules are dehydro-condensed to make higher ketones¹⁶. Then the ketone is decomposed to smaller ketone and hydrocarbon.

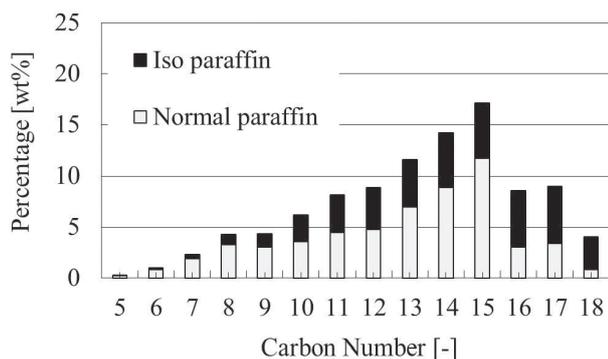
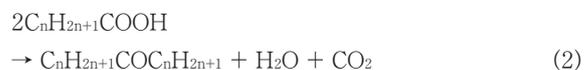


Fig. 9 Chemical structure of palm oil product

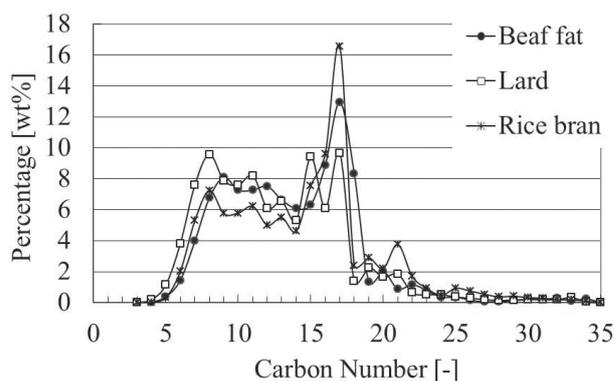
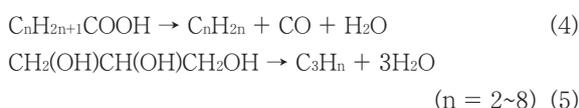


Fig. 10 Carbon number distribution of various materials



Really, small amount ketones with high carbon number ($C_nH_{2n+1}COC_nH_{2n+1}$) and other ketone were detected in the product.

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 reactant. Also, the fact that free fatty acid (dark oil) gave the similar product pattern suggests that one of the main unit reaction involved is the decarboxylation of free acid to CO and water. Also, the dehydration of glycerin, which is formed by the hydrolysis of tri-glyceride, is the source of water.



Based on these concepts, the most plausible reaction pathway of the hydrocarbon productions can be summarized as in Fig. 11. The major route of the cracking reaction are thought to be (1) the hydrolysis of triglyceride (catalytic or non-catalytic) to glycerin and free acid, (2) the dehydration of glycerine to gaseous hydrocarbons and water, (3) the decarboxylation of free acid to hydrocarbons, CO₂ and H₂O and (4) the secondly reactions of hydrocarbons. In the decarboxylation step, MgO is thought to catalyze the decarboxylation to make CO₂ and hydrocarbons. Another main reaction may be the (5) dehydro, decarboxy condensation of carboxylic acid to higher ketone and its cracking to lower hydrocarbons.

3.4 Diesel engine test of cracked oil of waste edible oil

The product was directly used for the operation of a conventional test diesel engine. The results showed that the performance was comparable in term of calorific value and concentration of exhaust gas (NO_x and CO) with that

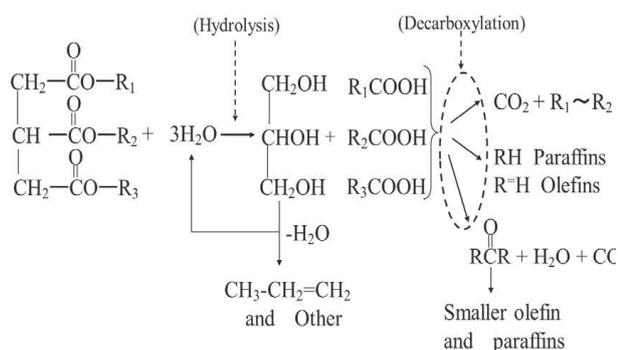


Fig. 11 Reaction mechanisms of catalytic cracking using MgO supported catalyst

of the commercial gas oil. Also, net thermal efficiency was even better than it.

4. Conclusion

Catalytic cracking of vegetable oil or animal fat over SiO₂- or carbon- supported MgO gave CO₂ and liquid hydrocarbons with high yield. Liquid hydrocarbons were the mixture of paraffins and olefins which distributed mainly from C₁₀-C₂₀. Acid value of the product was lower than that of Japanese standard for bio-diesel fuel. The product was proved to be an excellent diesel fuel by the engine test.

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