

DEVELOPMENT OF DIRECT PRODUCTION PROCESS FOR BIO-DIESEL FUEL

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It was developed a new direct production process for making the high quality diesel fuel from fat. In this process, where it is operated under atmospheric pressure using neither methanol nor hydrogen and no glycerin is produced. The product of the present process is composed of gaseous product small amount of (CO, CO₂ and light hydrocarbons) and liquid hydrocarbons (C₁₀ - C₂₀, olefins and paraffins with straight and branched chain structure).

Keywords: catalytic cracking, decarboxylation, hydrocarbon production, low acidity and iodine value

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 technologies for this purpose is the transesterification of triglycerides by methanol to methyl esters of fatty acids and glycerine [1]. They are largely industrialized to make biodiesel. Another one is hydrocracking, catalytic or non-catalytic cracking to hydrocarbons and water [2][3].

The former one is operated at 310-360K with excess methanol and alkali compounds such as NaOH, KOH, NaOCH₃, or alkaline earth oxide. This process can be operated under atmospheric pressure and the reaction proceed almost quantitatively. The product is separated into two phases. One is methyl ester (target product) and another is the glycerine 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 giving the product with high cetane number (80-90). It consume hydrogen and makes water as by product.

The last one is the cracking reactions at high temperature as 673-773K. The non catalytic reaction of triglyceride proceeds via the free radical mechanism and gives a liquid product which is rich in naphtha and gases which contain gaseous hydrocarbons, CO and CO₂ [3]. 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 723K over solid acid catalyst such as USY, REY, HZSM-5, MCM-41 and SBA-5 [6][7][8][9][10][11]. The main product is the gasoline-range hydrocarbons which contain paraffins (mainly branched), olefins and aromatic hydrocarbons. Other byproducts are water and CO₂. These reaction are not suitable for making middle distillate hydrocarbon.

The present study report a new catalytic cracking of a variety of triglyceride which aimed at the selective production of diesel fuel and CO₂. It has been well known

that bio-diesel fuel, which is made from vegetable oils, is one of the most promising answer for protecting the increase in the green house gases. Because, the diesel fuel has been predicted to increase in their consumption as the transportation fuel and has been produced from petroleum.

Table 1. Comparison of existing and present process

	Raw materials	Product	By-product	Reaction type	Condition	Catalyst
FAME	Oils, Methanol	Fatty acid methyl ester (FAME)	glycerin	Ester exchange	Low temperature, Normal pressure	Alkali catalyst (NaOH, KOH, CH ₃ ONa etc.)
BHD	Oils, H ₂	Paraffin	H ₂ O, CO ₂	Hydro cracking	High temperature, High pressure	Hydrogenate catalyst
This Study	Oils and Fats	Hydro-carbon	CO ₂ , Hydro-carbon gas	Catalytic cracking	400~430°C, atmospheric pressure	Spent industrial catalyst, Ceramic catalyst

EXPERIMENTAL

Reaction stoichiometry has been assumed as in Fig.1. Where, it requires solid catalysts, either ceramic or others.

When the products are ideally produced from the equations, the yields of liquid hydrocarbons, CO₂ and dry gas are 79wt%, 16wt% and 5wt%, respectively.

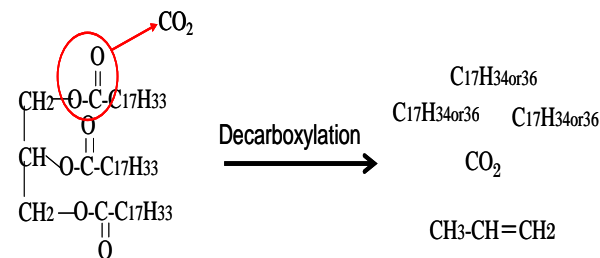
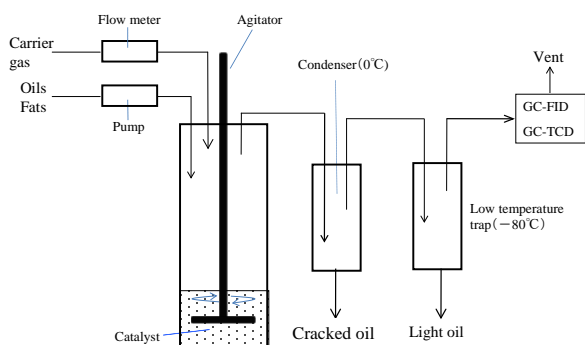


Fig.1: Stoichiometry of catalytic cracking reaction

Reaction apparatus and produce

Catalysts were prepared by impregnating a commercially available silica gel (Fujisilicia, Q-10, 313m²/g) and active carbon (wood made 1,100m²/g) with magnesium oxide from aqueous solution of magnesium nitrate, drying at 393K and the calcinating it under N₂ atmosphere at 823K. MgO loading was 10% by weight. Reactions were conducted in the flow reaction systems, at around 703K under atmospheric pressure, with an agitated reactor as shown in Fig.1. The used catalyst was a powder with the average diameter of 1.2mm. Into the agitated catalyst (50ml) bed feed oil was introduced (15ml/hr). The product which came out of the reactor was cooled with 2-stage condenser which was kept at 273K and 193K, respectively. The uncondensed gaseous products were exhausted after being analyzed with on-line GC (TCD and FID). Total acid value and iodine value in cracked oil were measured by potentiometric titration (ASTM D664 and ASTM D1959).



RESULTS AND DISCUSSION

Fig.2 : Experimental apparatus of catalytic cracking system

1. Reaction of a variety of vegetable oils

Products

The Present system triglyceride didn't come out of the reactor because the boiling point of the feed is higher than 703K. 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 and 99% was hydrocarbons (liquid hydrocarbon and propylene rich gaseous hydrocarbon). Also, more than 90% of carbon oxides was CO₂. Residue is higher boiling products or coke which didn't come out of the reaction vessel (about 10wt%). As shown in the Fig.3 each raw material gave similar product yield (70-75wt%).

The carbon number distribution of the product oil shown in Fig.4 and Fig.5, 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 and the main component was C₁₅ and C₁₇ hydrocarbons, which was dependent on fatty acid of included raw materials. And carbon number distribution didn't give difference between MgO-SiO₂ and MgO-carbon. It means this reaction is scarcely affected for the distribution by the product hydrocarbon from carrier material of catalyst.

Fig.6 shows acid value and CO, CO₂ yield of cracked oils. MgO-carbon catalyst's products were lower acid value than MgO-SiO₂. Especially, palm oil acid value was about 0.1KOHmg/g, which is much lower than the critical

value for B-5 and neat standard (Japanese standard; 0.5). And catalytic cracking system gave similar acid value from vegetable oil and dark oil (high free fatty acid content). This result suggests that are converted to hydrocarbons via the decarboxylation reaction of free fatty acid.

Table.2 shows pour point of raw material and the cracked products. Catalytic cracking system gave the product with low pour point products. Especially, the pour point of the cracked oil of waste edible oil was about 258K, which is lower than Japanese standard (268K) and petroleum gas oil. It suggests catalytic cracking products include branched hydrocarbons.

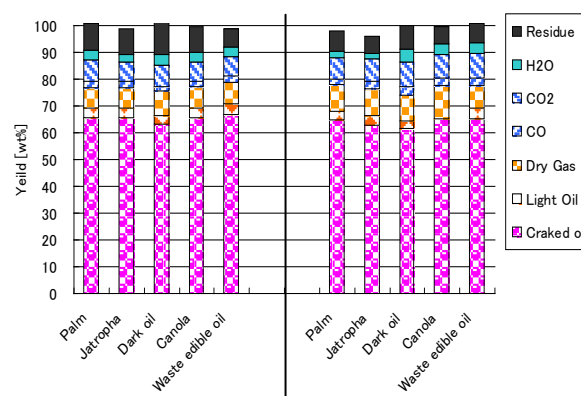


Fig.3: Material balance of various vegetable oils

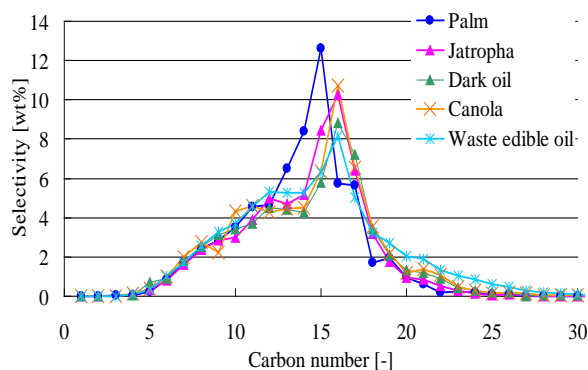


Fig4.: Carbon number distribution of cracked oil using MgO-SiO₂ catalyst

(a) MgO-SiO₂ catalyst, (b) MgO-Active carbon catalyst

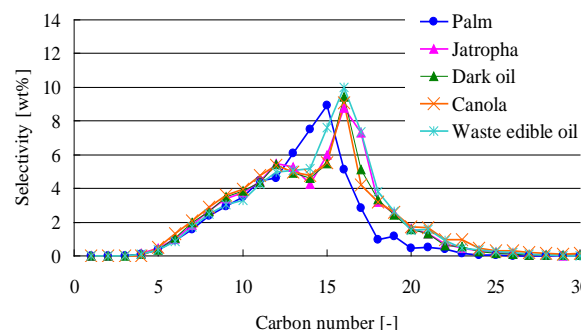


Fig.5 : Carbon number distribution of cracked oil using MgO-Carbon catalyst

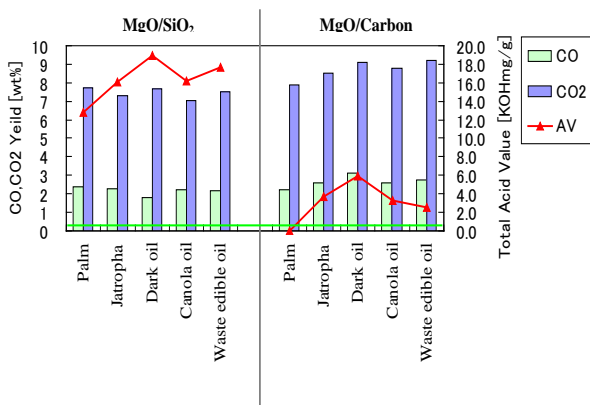


Fig.6 : Acid value of cracked oil

Table2 : Pour point of various diesel products

	Palm oil				Waste edible oil		Gas oil (Petroleum)
	Raw material	FAME	BHD	Catalytic cracking	Raw material	Catalytic cracking	
Pour point [°C]	25	20	20	-12.5	-7.5	-17.5	-7

Chemical structure of Product hydrocarbons of palm oil

Chromatograph of capillary GC shows quite complicated one whose peak material was straight chain paraffins and straight chain olefins. Olefin content was about 30mol% with little aromatics. Fig.7 shows the n-paraffins and iso-paraffins in C₁₀-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 reaction of olefins. This structure should be the reason of the fluid point of the product at 258K.

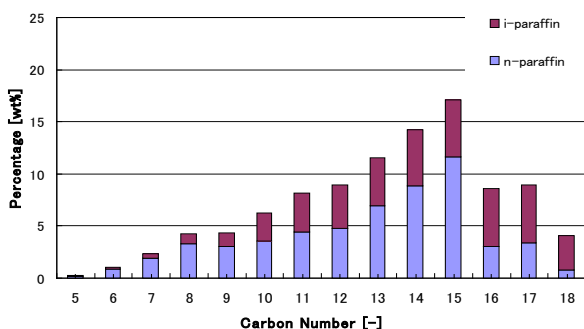


Fig.7 : Chemical structure of palm oil product

2. Applicability for a variety resource

Other than vegetable oils, lard, beef tallow, rice bran have been successfully applied for producing diesel oil with this process. Animal fat is difficult to using FAME method, because it's produce high pour point product.

Animal fats (lard and beef tallow) gave high oils yield about 70wt%, which is same level to vegetable oils. Also, rice bran gave hydrocarbon directly. The hydrocarbon product distributed from C₈-C₂₀ its peak point was C₁₇ hydrocarbon, probably derived from C₁₈ fatty acid, which was included in raw materials. Carbon number distribution is very close to that

of gas oil (C₁₂-C₂₀) (Fig.8).

As a result, catalytic cracking system can be applied for various oils and fats. And, it is suggested that present system, can lead to the direct extracting method (can skip extraction process of oils) of oil containing.

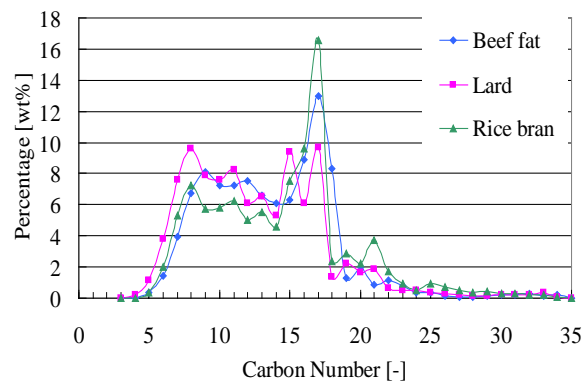


Fig.8 : Carbon number distribution of various materials

3. 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 its performance was comparable or even better than that of the commercial gas oil.

4. Comparison with other bio-diesel process

In table 1 are shown the comparison of 3 processes. From the data in the table1 and experimental data, the merit of this process is as follows:

1. No additional raw material.
2. No by product other than CO₂ and dry hydrocarbon gas.
3. Simple process under mild conditions.
4. Applicability for a wide variety of fat resources.
5. Possibility of the direct application of the product to diesel engine.

5. Discussion on the reaction path way

Fig.9 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. 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.

Based on these concepts, the most plausible reaction pass way of the hydrocarbon production can be summarized as in Fig.9. 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 CO₂ and (4) the secondly reactions of hydrocarbons. In the reaction step(3), MgO catalyzed the decarboxylation to make CO₂ and hydrocarbons.

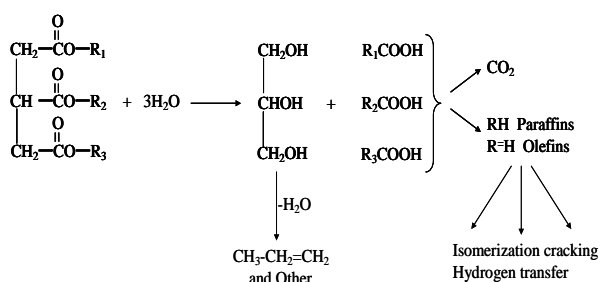


Fig.9 : Reaction mechanisms of catalytic cracking using MgO supported catalyst

CONCLUSION

New Bio-diesel producing process by the catalytic cracking system gave high yield of liquid products from a various raw materials (vegetable oils and animal fats). Liquid products were hydrocarbons which distributed from C10-C20 are suitable as the diesel fuel. Acid value and iodine value being lower than Japanese standard.

ACKNOWLEDGEMENT

This work was supported partly by The JST (Japan Science and Technology Agency) fund.

The authors appreciate professor Sadami Yoshiyama (The University of Kitakyushu) for the diesel engine test of the product.

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