Development of Catalytic Process for Bio-Diesel Production

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Abstract: It was developed a new direct production process for making the high quality diesel fuel from fat. In this process, where it was operated neither under atmospheric pressure with solid catalyst, neither methanol nor hydrogen used and no glycerin is produced. The product of the present process was composed of gaseous product (CO, CO_2 and light hydrocarbons) and liquid hydrocarbons (C_{10} - $C_{20,}$ olefins and paraffins). Acid value and Iodine value of the neat product was much lower than the critical value for B-5 Japanese standard. Also, the melting point of the raw product was lower than Japanese standard.

Keywords: catalytic cracking, no methanol and no glycerin, low acidity and iodine value

1. Introduction

Fatty acid Triglyceride (FAT) has been considered to be one of the most promising raw materials for bio fuel manufacturing. For making bio fuel FAT can be converted to either (1) methyl ester of fatty acid by the trans esterification with methanol (FAME) or (2) hydrocarbons by the hydrogenolysis with gaseous hydrogen. The trans esterification are usually catalyzed by alkali- or alkaline earth hydroxide to make FAME and glycerin. The hydrogenolysis of FAT is catalyzed by a conventional hydrotreating catalyst under pressurized conditions to make paraffinic hydrocarbons is another method to utilized it. The present study is related to the new solid catalysts and the catalytic process of FAT to make middle aliphatic hydrocarbons and CO_2(Table 1).

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	60-80℃, Atmospheric pressure	Alkali catalyst (NaOH, KOH, CH_3ONa etc.)
BHD	Oils,H_2	Paraffin	H_2O, Propane	Hydro cracking	High temperature, High pressure	Hydrogenate catalyst
This Study	Oils and Fats	Hydro-carbon	CO_2, Hydro-carbon gas	Catalytic cracking	400～430℃, Atmospheric pressure	Spent industrial catalyst, Ceramic catalyst

2. Experimental

The catalysts developed are the solid one containing magnesium compound. They are used under atmospheric pressure. The catalysts can be used either in the fix bed or in the agitated bed at around 400℃.

Reaction apparatus are shown in Figure 1. Into the reaction vessel liquid feed material is introduced continuously and is heated reaction temperature (400-430℃) under atmospheric pressure, where the decomposition proceed to make hydrocarbons and CO_x. The products are gases under reaction conditions to come out of the reaction zone automatically, and condense liquid products suitable for diesel fuel from the stand point of boiling range (hydrocarbons, water and by-product). Gaseous products come out of the system through the gas washer.

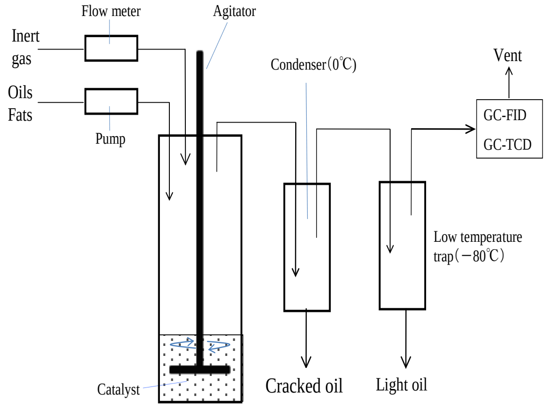

Figure 1. Agitated bed system

Products were hydrocarbon mixture whose carbon number distribute C_8 - C_{20} depending on the raw material of FAT. CO_2 is also another main product, but glycerin was not formed. When the product is ideally produced from the equations, the yields of liquid hydrocarbons, CO_2 and dry gas are 79wt%, 16wt% and 5wt%, respectively.

3. Results and Discussion

Some of the results on a couple of feed are shown in Table 2. Raw product was slightly colored and 99% was hydrocarbons. Also, more than 90% of carbon oxides were CO_2. Residue was higher boiling products or coke which didn't come out of the reaction vessel. As shown in the table each raw material gave similar product yield (70-75wt%).

Acid value and Iodine value of the neat product from palm is was 0.1 and 80, respectively. This value is much lower than the critical value for B-5 (Japanese standard; 0.5 and 120, respectively). And melting point of the raw product was about -15℃, which is also lower than Japanese standard (-5℃).

Other than palm oil, waste edible oil, Jatoropha oil, lard, beef fat, rice bran and dark oil have been successfully applied for producing diesel oil with this process.

The hydrocarbon product distributed from C_8 to C_{20}. Whose peak point was C_{15} or C_{17}. This carbon number distribution was very close to that of gas oil (C_{12}-C_{20})(Figure 2). Peak point of carbon distribution depended on the fatty acid part in triglyceride. And this fatty acid is depended on production location and seasons. For example, palm oil contain mainly palmitic acid (C_{16}^{-}), and Jatoropha oil contain mainly oleic acid and linoleic acid ($C_{18}^{=}$).

Figure 3 shows effects of various catalysts and spent FCC catalyst. Sea sand gave fairy high oil yield, but produced large amount residues, which was like asphalt. SiO_2, carbon and Al_2O_3 based catalyst gave high oil yield and low residue yield. Spent FCC catalysts gave oils yield lower than other catalysts. It produced lower hydrocarbons and large amount of coke. In case of the MgO-containing catalyst, CO_2 yield was higher than MgO free catalyst, and the acid value was much lower than it. And this phenomenon suggests that the, decarboxylation was activated by MgO. As the result, SiO_2, Carbon and Al_2O_3 containing MgO catalysts were effective in this process.

4. Conclution

New Bio-diesel producing process by the direct catalytic cracking of fat gave high yield of liquid products from a various raw materials (vegetable oils and animal fats) without any co-feed and by-product. Product oil was found to be suitable for diesel fuel, which was mainly composes of C_{10}-C_{20} hydrocarbon and acid value and iodine value were lower than Japanese standard.

Table 2. Reaction results of various vegetable oils

	Waste edible oil	Palm	Jatoropha
Cracked Oil (wt%)	76.1	74.3	67.5
Dry Gas (wt%)	5.1	7.9	7.2
CO, CO_2 (wt%)	6.9	5.2	7.5
Residue (wt%)	11.3	9.3	11.9
H_2O (wt%)	2.8	3.0	0.7
Acidity Value (KOHmg/g)	-	0.1	-
Iodine Value (Ig/g)	-	80	-

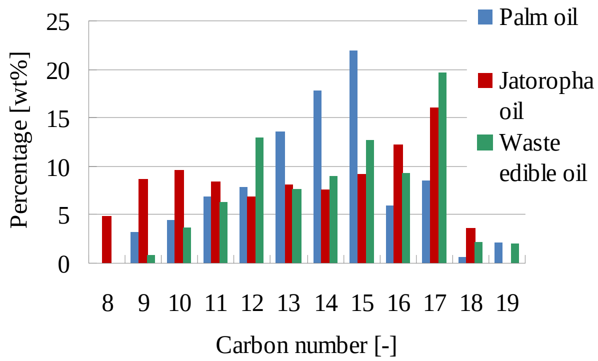

Figure 2. Carbon number distribution of cracked oil from vegetable oils

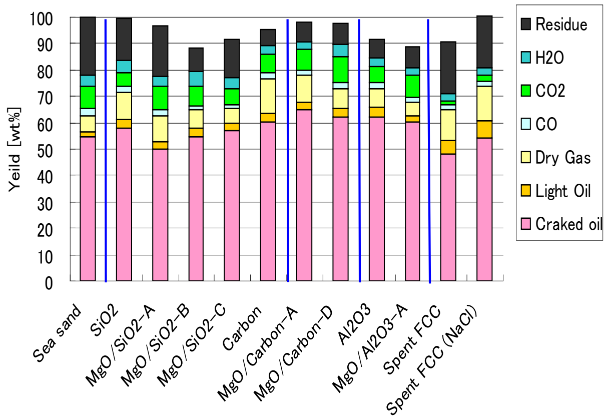

Figure 3. Material balance of palm oil

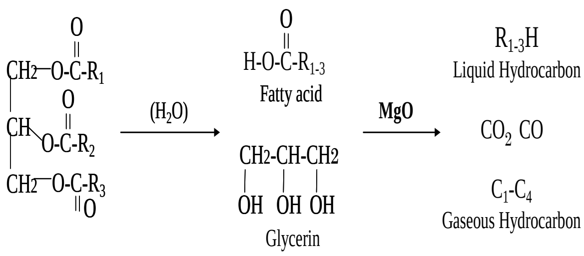

Figure4. Reaction mechanisms of catalytic cracking