SONOLYTICAL PRODUCTION OF BIO-DIESEL FUEL FROM NON-EDIBLE VEGETABLE OIL

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ABSTRACT

Transesterification of non-edible vegetable oil such as Jatropha Crucus and Siringa oil to produce bio-diesel fuel(BDF) can be accelerated by ultrasonic irradiation at 40kHz even with small amounts of basic catalyst (0.5%) compared with conventional mechanical stirring. Esterification of free fatty acids with acidic catalyst also could be accelerated by ultrasonic irradiation. 90% yield could be achieved in 1 hour by sonolysis, on the other hand only 80% yield could be achieved after 5 hours by conventional mechanical stirring in the esterification of free fatty acids such as stearic, palmitic and oleic acids. Fast reaction took place with primary alcohols even with long chain such as hexanol and octanol, however no reaction could be observed with secondary or tertiary alcohols with shorter chain such as isopropanol and ter-butanol. Exhaust gas from bus fueled with BDF produced contained small amounts of hydrocarbon, CO, SO2, particulates matter and poly aromatic hydrocarbons.

INTRODUCTION

Vegetable oils have good heating power and provide exhaust gas with almost no sulfur and aromatic polycyclic compounds. Due to the fact that vegetable oils are produced from plants, their burning leads to a complete recyclable CO_2. Various derivatives have been proposed as an alternative fuel for diesel engines [1, 2]. The esters of vegetable oils or animal fats appear to be the most promising alternative. Today, methyl or ethyl esters of fatty acids are used as alternative to petroleum-based diesel fuels under the name of "biodiesel" [3].

Bio-diesel fuels have many advantages over petroleum diesel fuel: produce less smoke and particles, have higher cetane number, produce lower carbon monoxide and hydrocarbon emissions, are renewable, biodegradable and non-toxic. When ethyl esters are used as fuel the advantage of totally recyclable CO_2 cycle is obtained since ethyl alcohol could be of vegetal origin [4].

To complete the reaction stoichiometrically a 3:1 molar ratio of alcohol to triglyceride is necessary. Due to the fact that the transesterification is an equilibrium reaction, an excess of alcohol is used to displace the reaction towards esters formation. Fats and alcohols are not totally miscible, so their In

the base-catalyzed procedure, some soap is formed and it acts as phase transfer catalyst, thus helping the mixing of the reactants. Base-catalyzed process is strongly affected by the mixing of the reactants and/or by efficient heating [4、5] that produces tiny droplets, thus increasing the reaction area [5]. Today, mixing/heating, is the process of choice used in industrial application in over 85 biodiesel plants worldwide.

Low frequency ultrasonic irradiation is a useful tool for emulsification of immiscible liquids. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impinge one liquid to another.

METHOD

Reagents and materials

Sodium hydroxide (95%) and potassium hydroxide (85%) were purchased from Wako Chemicals and used after milling, to facilitate the dissolution in alcohol. The alcohols employed in the reactions (methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-butanol, *tertio*-butanol), from Wako Chemicals had more than 99.5% purity and were used as received.

Fatty acids (Oleic acid, palmitic acid, stearic acid) and catalysts (H_2SO_4, CH_3COOH) were purchased from Wako Chemicals.

Procedure

A biodiesel fuel from free fatty acids with ethanol was investigated in the presence of various types of homogeneous acid catalyst. The test temperatures were 10, 20, 30, 40, 50 and 60 °C. The reaction mixtures consisted of oleic acid with ethanol and acid catalyst (H_2SO_4, CH_3COOH). The molar ratio of ethanol to oleic acid was 1:1, 2:1, 3:1, 4:1, 6:1, and 10:1 and the quantity of the homogeneous catalysts were 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10%wt to the weight of oleic acid. All the experiments were conducted for 10 hour under the ultrasonic irradiation condition and stirring conditions.

The stirring experiments were performed using a Matsushita Electric Ind., (SCV 35W stirrer at 1800 rot/min). The ultrasonic experiments were carried out using a Honda Electronics Ultrasonic Cleaner (WS 1200-40, 40 kHz with a maximum power of 1200W). The working power was set at 60% of the maximum power, which corresponds to 700W for 10L solution by calorimetry. After sonication, 3 ml of reaction mixture was taken and neutralized immediately by a sodium hydroxide solution to stop the further reaction.

Analysis

The samples were analyzed for ethyl ester, and glycerol by using a High Performance Liquid Chromatography (HPLC) (Shimadzu, SCL-10Asp), which consisted of an ODS column (STR ODS-II, 25cm in length x 4.6mm in inner diameter, Shinwa Ch. Ind. Co.) and refractive index detector (Shimadzu, RID-10A) the temperature of column oven was kept at 40°C and flow rate of carrier solvent of acetone/acetonitrile (70/30) was 0.4 ml/min. The sample injection volume was 50μl and the peak identification was made by comparing the retention time between the sample and standard compound.

RESULT AND DISCUSSION

As shown in Fig.1, ultrasound irradiation accelerates the BDF production from free fatty acid. Fig.2 shows the relationships between conversion of fatty acids (oleic, palmitic and stearic acids) and irradiation time at 60°C, molar ratio 3/1and 5 %wt H_2SO_4 under ultrasonic irradiation condition, where the result obtained under the stirring condition was drawn in this figure for comparison. The irradiation time dependence of the ester conversion was almost the same irrespective of a kind of free fatty acid.

From various experiment, it is determined the optimum condition for the transesterification of fatty acids as follows,

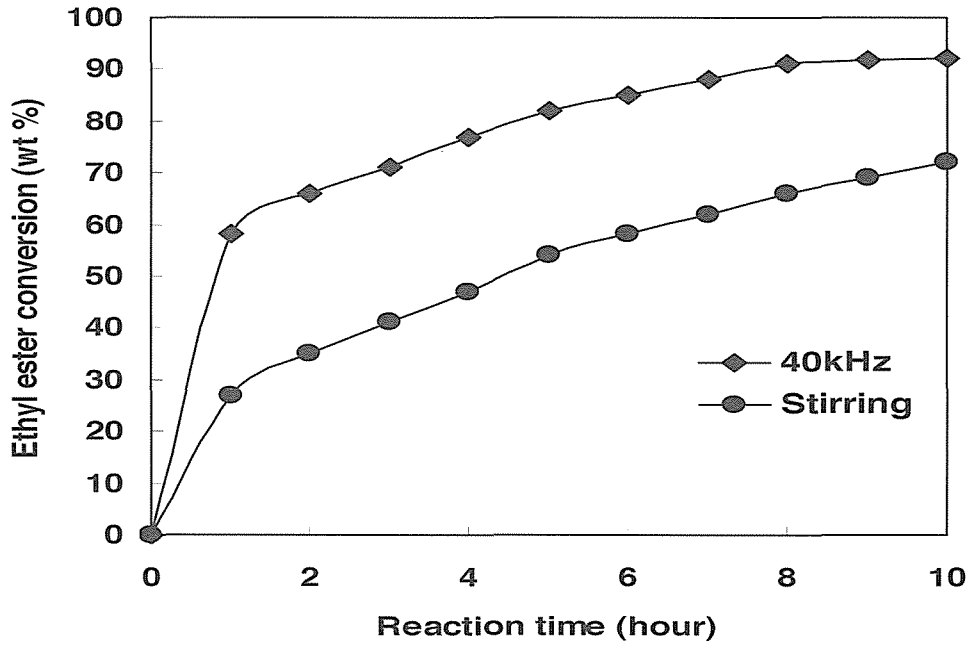
(1) molar ratio = 3/1,

(2) catalyst concentration = 5%wt H_2SO_4

(3) test temperature = 60 °C (within the test temperature conducted)

(4) H_2SO_4 catalyst is much more effective than CH_3COOH (which shows no conversion)

However, the optimal condition is recognized to be much superior to that obtained for triolein with regard to catalyst concentration and test temperature, even for molar ration (considering 3/1 for one carboxyl and 6/1 for three carboxyls).



20°C, molar ratio 3/1and 5 %wt H_2SO_4

Fig.1 Acceleration of sonolysis to BDF production from fatty acid

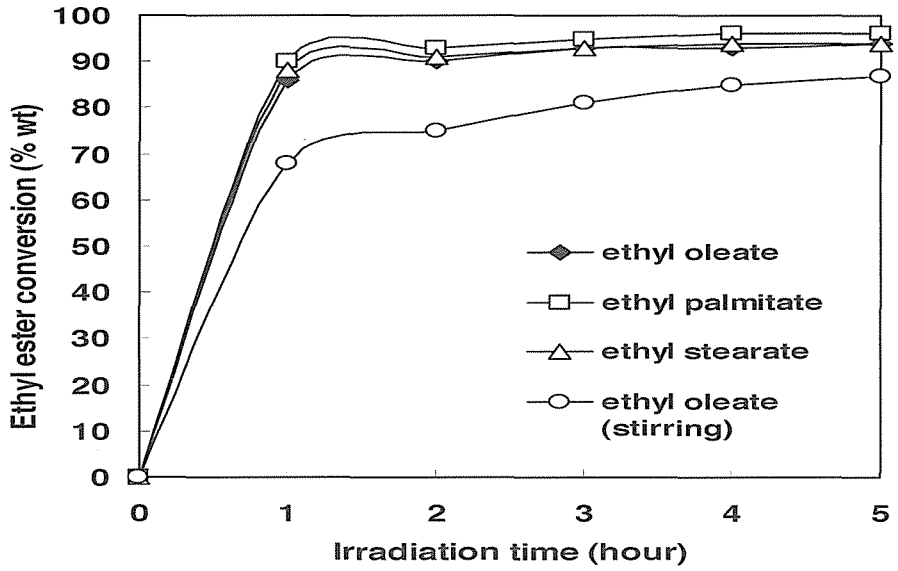


Fig.2 BDF production from oleic, stearic and palmitic acid

CONCLUSION

Ultrasonic irradiation condition is efficient, time saving and economically functional for transesterification of fatty acid with ethanol to produce biodiesel fuel. The optimum condition for the production of ethyl ester under the ultrasonic irradiation condition was as follows: molar ratio of ethanol to oleic acid 3:1 with H_2SO_4 concentration of 5%wt and irradiation time 2 hour at 60°C. The increasing in the irradiation time, as well as molar ratio contributes to high conversion and quality of esters. The transesterification of fatty acid with ethanol under ultrasonic irradiation provides a possibility for producing cheap alternative fuels, which could reduce pollution and protect the environment.

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