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Fatty acids methyl esters from vegetable oil by means of ultrasonic energy

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Abstract

The transesterification of vegetable oil with short-chain alcohols, in the presence of base-catalyst, by means of low frequency ultrasound (28 and 40 kHz) in order to obtain biodiesel fuel was studied. By using ultrasounds the reaction time is much shorter (10–40 min) than for mechanical stirring. The quantity of required catalyst is 2 or 3 times lower. The molar ratio of alcohol/oil used is only 6:1. Normal chain alcohols react fast, while secondary and tertiary alcohols show some or no conversion after 60 min of reaction. Surprisingly, 40 kHz ultrasounds are much more effective in the reduction of the reaction time (10–20 min). Twenty eight kilohertz give slightly better yields (98–99%), but longer reaction time, while higher frequencies are not useful at all for the transesterification of fatty acids.

Keywords: Vegetable oil; Transesterification; Ultrasound; Base catalysis; Biodiesel

1. Introduction

The idea of using vegetable oil as a substitute for diesel fuel was demonstrated by the inventor of the diesel engine, Rudolph Diesel, around the year 1900, when vegetable oil was proposed as fuel for engines. 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. The oil use as diesel fuel was limited due to its high viscosity (near 10 times of the gas oil). In order to adapt the fuel to the existing engines the vegetable oils had to be modified.

Various derivatives such as microemulsions or blends of various vegetable oils with conventional fuel have been proposed as alternative fuels 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 substitute 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].

Transesterification is not a new process. The scientists Duffy and Patrick conducted it as early as 1853 [5]. Transesterification involves the reaction between an alcohol and a vegetable oil or animal fat that are mixtures of triglyceride (esters of glycerin with long chain fatty acids).

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 reaction takes place at the

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interface and it is a very slow process [6]. The reaction is catalyzed by alkali, acid or enzyme. Enzymes-catalyzed procedures, using lipase as catalyst, do not produce side reactions [7–9], but the lipases are very expensive for industrial scale production and a three-step process was required to achieve a 95% conversion [10]. Acid-catalyzed process is useful when a high amount of free acids are present in the vegetable oil [11,12], but the reaction time is very long (48–96 h), even at the boiling point of the alcohol, and a high molar ratio of alcohol was needed (20:1 wt/wt to the oil) [13].

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 [4,14] that produces tiny droplets, thus increasing the reaction area [14]. Today, mixing/heating is the process of choice used in industrial application in over 85 biodiesel plants worldwide [3].

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 [15].

We were interested in finding a more efficient alternative for biodiesel fabrication by the help of ultrasound. The aim of this study was to see the effects of low frequency ultrasonic irradiation on the transesterification of vegetable oil under base-catalysis conditions.

The results of the investigation of the transesterification of neat vegetable oil with short-chain alcohols (C1–C4) in the presence of ultrasound to give alkyl esters of fatty acids are given. Reaction conditions that affect the yield include the type and concentration of the catalyst, reaction time and ultrasound frequency.

2. Method

2.1. Reagents and materials

Sodium hydroxide (>96%) 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, tertiary-butanol), from Wako Chemicals had more than 99.5% purity and were used as received. The vegetable oil was of commercial edible grade and it had the following basic properties:

Acid value (i.e. the percentage of free fatty acids in the fat) = 1.247,
Iodine value (i.e. gram of iodine absorbed by 100 g of oil) = 70,
Saponification value (i.e. milligram of KOH required to neutralize the free fatty acids and to saponify the esters in 1 g of oil) = 195.

2.2. Procedures

The influence of low frequency ultrasound (28 and 40 kHz) versus traditional stirring on the bio-diesel production from neat vegetable oil, at room temperature, has been investigated. The reaction mixtures consisted in vegetable oil, alcohol and alkaline catalyst. The molar ratio of alcohol to oil was 6:1, and the quantity of catalyst was 0.5%, 1.0% and 1.5% (wt/wt) to the oil respectively. The hydroxide was dissolved into the alcohol prior to the addition of vegetable oil. The silent reactions were performed using a Matsushita Electric Ind., Model SCV35W stirrer at 1800 rot/min. The ultrasonic reactions were performed using Honda Electronics Ultrasonic Cleaners WS 1200-28 and WS 1200-40, with a total power of 1200 W, working power being set at 60%.

After the complete conversion of the vegetable oil, as determined by TLC analysis, the reaction was stopped and the reaction mixture was allowed to stand for phase separations: the ester mixture formed the upper layer and glycerin formed the lower layer. The residual catalyst and non-reacted alcohol were distributed between the two phases: some traces into the ester layer and a high amount in the glycerin layer (due to a high miscibility of the alcohol with glycerin). After the phases separation the traces of catalyst and alcohol were washed out with water from the esters mixture and the esters were dried over anhydrous calcium chloride. All experiments were performed in an Erlenmeyer type flask having 100 ml volume.

2.3. Sampling and analysis

Samples were taken at 10 min time intervals and analyzed by TLC (eluent chloroform/petroleum ether, 1:3 ratio) to check the conversion to biodiesel. TLC was chosen as a rapid analytical method and it gives quite accurate indication of oil and biodiesel content in the mixture After purification the biodiesel was analyzed using a Shimadzu GC-MS Model QP-2010, equipped with a DB-5 capillary column (0.53 mm × 30 m) J&W Scientific.

The chemical composition of the vegetable oil was determined on the basis of GC-MS analysis of the methyl esters. The mean molecular weight of the esters mixtures was calculated averaging the individual molecular weights of each constituent ester. For methyl esters the mean molecular weight was 293.65. The mean molecular weight of the oil was calculated averaging the individual molecular weights of each constituent triglyceride, according to the fatty esters analysis (Table 1). The average molecular weight of the oil was 878.23.