Conversion of Vegetable Oil to Biodiesel Using Ultrasonic Irradiation

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The influence of low frequency ultrasounds (28 and 40 kHz) versus mechanical stirring on the transesterification reaction of neat vegetable oil with methanol under base-catalysis was studied and the results are presented. It was found that the optimized variables of 6:1 methanol/oil (mol/mol), 0.5% NaOH (wt/wt), and 40 kHz ultrasonic irradiation at 25 °C for 20 min gave a maximum isolated ester yield of 98%.

In past years, biodiesel, defined as the methyl esters of fatty acids, has developed as an alternative to fossil fuels. The strongest motivational factor is the concern about global pollution. The use of biodiesel has many environmental benefits: less greenhouse effect, less air pollution, less water and soil pollution, and less health risks. Today over 85 biodiesel production plants are working worldwide.[1]

Biodiesel is produced by the transesterification of vegetable oils and fats with short chain alcohols (methanol or ethanol). Since vegetable oils are produced from agricultural resources, biodiesel is a renewable and biodegradable form of energy. Transesterification is the chemical transformation of one ester into another; vegetable oils (mixtures of glycerol esters of fatty acids) are transformed into alkyl esters that compose biodiesel. This process takes place in the presence of acidic, basic or enzymatic catalysis.

Each method has its advantages and disadvantages. The acid-catalyzed process is suitable if the oil has a high free fatty acids content. The reaction is slow and a high molar ratio of alcohol to oil is required (up to 30:1).[2] Canakci et al.[3] studied biodiesel production using sulfuric acid as the catalyst. When the reaction time was increased from 48 to 96 h, the ester conversion increased from 87.8% to 95.1%. In another study of the acid catalyzed transesterification, Crabbe[4] found that the optimized parameters for a 99.7% conversion were 40:1 mol/mol ratio of alcohol to oil, 5% H_2SO_4, 95 °C, and 9 h.

The advantage in using enzymes is a clean process without any by-products. The most significant barrier is the high price of the lipase. Immobilized lipase is more effective than free lipase due to the increased number of active sites.[5] In a three-step process, Shimada[6] obtained a 98.4% conversion of the oil to biodiesel.

The alkali-catalyzed procedure is the most convenient requiring only a 6:1 molar ratio of alcohol to oil and a low quantity of catalyst (usually NaOH or KOH). At present it is the process of choice in almost all biodiesel production plants around the world. The main disadvantage of using the alkali catalyst is the side reaction-formation of soap that consumes the catalysts thus decreasing the biodiesel yield, especially when the oil has a high content of free fatty acids.[7,8]

Because of the fact that the oil and alcohol are immiscible, the mixing intensity is also an important parameter that must be considered. Alcantara et al.[9] studied the effect of stirring speed and found that at 300 rpm, the oil conversion was only 12% after 8 h, while at 600 rpm, the reaction was complete within 2 h. They concluded that the efficient mixing of the reagents is essential for a high conversion in a short time.

In the last two decades, sonochemistry, the chemical reaction during ultrasound irradiation, has developed as an expanding research area. The ultrasonic field is known to produce chemical and physical effects that arise from the collapse of cavitation bubbles. Low frequency sonication can be used to produce emulsions from immiscible liquids. The collapse of cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge one liquid to another.[10] This effect could be employed for biodiesel preparation.

The aim of this study was to investigate the methanolysis of neat vegetable oil in the presence of low frequency ultrasounds. The results of the transesterification reaction during ultrasonic irradiation versus mechanical stirring under base-catalysis are presented.

Sodium hydroxide (95%) and methanol (>99.5%) were purchased from Wako Chemicals and used as received. The vegetable oil was of commercial edible grade.

The sonications were carried out using Honda Electronics Ultrasonic Cleaners WS 1200-28 and WS 1200-40 (28 and 40 kHz frequencies, and 400 W). The mechanical stirrer was a Matsushita Electric Ind., Model SCV35W, with an adjustable speed up to 4500 rpm.

The vegetable oils are mixtures of the triglycerides of fatty acids. The transesterification reaction is a three-step consecutive equilibrium reaction. The overall reaction is:

$$\text{Triglyceride} + 3\text{ROH} = 3\ \text{Methyl Esters} + \text{Glycerin}$$

A 3:1 stoichiometric molar ratio of alcohol to oil is required. In practice, a larger quantity of alcohol is necessary to drive the reaction to completion. In industrial processes, a molar ratio of 6:1 is usually employed.[11,12] The glycerin formed as a by-product has a large number of applications in various industrial processes, therefore, the overall biodiesel production is a low waste process.

The reaction mixture consisted of 30 g neat vegetable oil, 9 ml methanol (6:1 molar ratio methanol to oil) and sodium hydroxide-0.5%, 1.0% and 1.5% (wt/wt) ratio to vegetable oil. The oil average molecular mass was calculated based on the fatty acids methyl esters composition using a GC-MS Shimadzu Model QP-2010. The test reactions were stirred at room temperature (25 °C) and 1800 rpm. The sonications were performed under the same conditions (25 °C) in the ultrasonic fields of 28 and 40 kHz respectively. Samples were taken at 10 minute intervals and analyzed by TLC to check the conversion of the vegetable oil to biodiesel. We considered that a complete conversion occurred when no traces of oil were found in the test

Table 1. The yields of isolated methyl esters

Method	0.5% (wt/wt) NaOH		1.0% (wt/wt) NaOH		1.5% (wt/wt) NaOH	
	Time/min	Yield/%	Time/min	Yield/%	Time/min	Yield/%
Stirring	60	80	10	91	10	35
28 kHz Ultrasound	40	98	10	95	10	75
40 kHz Ultrasound	20	98	10	91	10	68

samples. After the complete conversion, the reaction mixtures were allowed to stand for at least 8 h for phase separation. The esters mixture formed the upper layer and the glycerin, the lower layer. The residual catalyst and unreacted methanol were distributed between the two phases. After the separation of the phases, the excess methanol and residual catalyst were washed out of the ester with water and the esters were dried over anhydrous calcium chloride.

The concentration of the catalyst is an important parameter of the transesterification reaction. The concentration of the catalyst had a strong influence on the yield of the isolated methyl esters. As one can see in Table 1, the addition of a large amount of catalyst did not lead to an increase in the biodiesel yield. Some of the sodium hydroxide reacted with the oil, leading to the formation of soap, thus the separation of esters became difficult. The higher catalyst concentration increased the solubility of the methyl esters in the glycerol phase due to the fact that the formed soap acted as a phase transfer catalyst. As a result, a significant amount of methyl esters remained in the glycerol after phase separation thus even further decreasing the yield of the isolated product.

The reaction performed under 40 kHz ultrasonic irradiation was complete after 20 min, while under 28 kHz, it was complete after 40 min while in the presence of mechanical stirring, the total reaction time was 60 min. Theoretically, there are no important differences in the formation and collapse of cavitation bubbles at 28 and 40 kHz. However, the transesterification yield under ultrasonic irradiation at 40 kHz was slightly higher. At the present time, we do not completely understand these results. When the catalyst concentration was increased to 1.5% (wt/wt), the reactions performed in the presence of NaOH lead to the formation of a high amount of soap, thus decreasing the biodiesel yields. We found that the optimal parameters for the biodiesel production under 40 kHz frequency ultrasonic irradiation are 0.5% NaOH (wt/wt), 6:1 molar ratio of methanol to oil, and a time to complete reaction of 20 min.

Low frequency ultrasonic irradiation proves to be a valuable tool for the preparation of biodiesel fuel. The advantages like short reaction time, room temperature, low quantity of catalyst and low quantity of methanol make this procedure a valuable technique, economically viable, which can be even used for the industrial scale preparation of biodiesel fuel.

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