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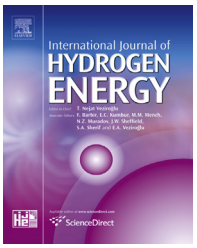

Short Communication

Large-scale biodiesel production from Moroccan used frying oil

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ABSTRACT

Biodiesel was synthesized by transesterification in the presence of NaOH as the catalyst. The project was developed with the goal of optimizing the biodiesel production starting from locally used frying oil. The process was implemented for a 400 L/batch production in rural areas, to be used on farms and to provide fuel for machinery and electricity generating.

It was important to develop a robust and simple procedures and to use the minimum amounts of chemicals (e.g. NaOH). The reaction was performed employing an optimized methanol/oil molar ratio of 6:1 and a reaction temperature equal to 90°C. A yield of 93.8% was achieved with low cost raw materials. The GC-MS, ^{1}H NMR, ^{13}C NMR, FT-IR and TGA/DTG analyses of the final product confirmed that in the chosen experimental conditions the biodiesel did not contain traces of glycerol. Its characteristics were found to be as good as those of the biodiesel obeying the European standards.

Introduction

The increasing incertitude on the world energy production and supply, the environmental problems emerging from the use of fossil fuels and the fluctuating prices of crude oil are the major reasons that urged the search for alternative durable fuels. The proved reserves of oil and natural gas may not answer the growing demands of energy in the next future. In this context of search for new energy sources and the worry about the global warming, biodiesel is a serious substitute of petroleum at least in the transportation sector [1,2]. Biodiesel also offers many advantages such as its biodegradability, low toxicity and a more favorable emission profile with the possibility of using it directly in diesel engines without any modification. In addition, large number of raw materials can be used in its production (such as fresh or used edible oils, algae and animal fats) [3–5]. Biodiesel can be mixed with fossil fuels or used as is in diesel engines without any transformation [6]. From an environmental point of view, biodiesel represents a worthy approach to the problem of greenhouse gas emission and a mean to introduce sustainable development in rural areas by

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using it in water pumping, heating, cooking and electricity generating [7].

Biodiesel is a mixture of long-chains mono-alkyl esters resulting from the reaction of lipids with a short-chain alcohol [8]. The most commonly used alcohols are methanol and ethanol. The glycerin is the main by-product of biodiesel production. At the industrial level, methanol is the most used alcohol due to its low price [9,10]. However, production of biodiesel via edible oils was strongly criticized by some non-governmental organizations (NGOs) stigmatizing the idea of converting food in fuels while millions of persons suffer from starvation. Selection of raw material for biodiesel production is the key factor to reduce the cost of manufacturing.

The total annual growth of oil consumption in Morocco is around 2.6 percent. By 2025 it is expected to climb to 50 percent. Therefore, to cover its energy needs Morocco will be confronted with huge challenges, ranging from the production to the processing of different oils [11]. Waste frying oils are daily generated in large quantities. Their use in biodiesel production instead of edible oils will result in the lowering of energy cost and in a better preservation of the environment [3–6].

Biodiesel is synthesized by transesterification. This pseudo-homogeneous reaction is catalyzed by bases (mainly by NaOH or KOH) [12–14]. This is the most widely used process at industrial level. Other catalytic methods such as acid, enzymatic, heterogeneous or supercritical synthesis are currently under investigation [14–17].

The main objective of this work is essentially the optimization of a large-scale biodiesel production (400 L/batch) by transesterification of waste frying oil with methanol. Particular attention will be focused on the minimization the catalyst amount. The purity and the features of the products will also be investigated. The results of the biodiesel characterization (by NMR, FT-IR, TGA/DTG) will be looked at and confronted with the European standards. The aim of this comparison is to introduce less expensive techniques that are available even in isolated regions.

Materials and methods

Materials

The used frying oil was supplied by 'Kilimanjaro Environment', the Moroccan leader company in collecting waste oils which also will be soon producing biodiesel. Before its use, the oil was pre-treated by centrifugation then filtered and dehydrated at 115°C. For comparison purposes, vegetable oil of commercial grade was used. Chemicals such as Potassium hydroxide (85%), sodium hydroxide (98.5%), chlorhydric, sulphuric and phosphoric acids, hexane, ethanol, diethyl ether were supplied by Panreac. Methanol was supplied by 'Kilimanjaro Environment'.

Methods

Fuel properties

The physical and the chemical properties such as viscosity, density, acid value of the reactants and the produced biodiesel were determined according to the ASTM standards [12]. The obtained values were compared with the European standards of biodiesel [18].

Characterization

Fatty acids composition in the methyl esters was determined by gas chromatographic mass spectrometric (GC-MS) system. The analyses were performed using a Perkin Elmer Clarus 680 GC System, fitted with a capillary column, VB-5 (Methylpolysiloxane à 5% phenyl, 30 m, 0.25 mm i.d. 0.25 μm film thickness). Ultra-high purity helium (99.99%) was used as the carrier gas at a constant flow of 0.2 mL/min. The injection, transfer line and ion source temperatures were set at 220, 200 and 200°C, respectively. The ionizing energy was 70 eV. Electron multiplier (EM) voltage was obtained from auto tune. All the data were recorded by collecting the full-scan mass spectra within the scan range 20–600 *m*/z. The injected sample volume was 0.1 μl with a split ratio of 50:1. The oven temperature program was: 140°C held for 5 min, 4°C/min (heating rate), 250°C held for 5 min. The unknown compounds were identified by comparing the spectra obtained with mass spectrum libraries.

The nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were recorded at 298 K with a BRUKER AVANCE 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as the solvent and the internal standard, respectively. ^{1}H NMR spectra were recorded with pulse duration of 2 μs, a recycle delay of 1.0 s and 8 scans. The ^{13}C NMR (75 MHz) spectra were obtained with a pulse duration of 2 μs, a recycle delay of 1.89 s and 160 scans.

Infrared spectra were collected by using a VERTEX 70 spectrometer equipped with ATR MIRACLE DIAMANT technique. The device has a spectral range of 4000–600 cm^{-1}. The data were recorded by co-adding 16 scans at a resolution of 4 cm^{-1}.

TGA/DTG analyses were carried out using a Labsys™ Evo (1F) Setaram apparatus. The sample (10 mg) was introduced in the oven in a platinum crucible under helium atmosphere and a flow of 60 mL/min. The heating rate was chosen equal to 10°C min^{-1} and the scanned temperature range from 25 to 800°C.

Biodiesel production: transesterification

The biodiesel production was carried out in a set of reactors and tanks displayed in Fig. 1. The whole installation is available at Kilimanjaro Environment Company based in Casablanca, Morocco. The biofuel synthesis was performed as it follows: a solution of NaOH in methanol was prepared in the tank A (400 L) using different pumps. This mixture was added under stirring to the oil preheated at 60°C in the reactor R (600 L). Then the temperature of the recovered mixture was increased up to 90°C and kept at this value for 90 min. The methyl esters phase was first separated from the glycerin by decantation in the tank D (600 L). The recuperated biodiesel was stored in the tank B (600-L), then purified as previously described [12]. Special attention was paid to the recovery of methanol. The volume of methanol used in the operating conditions was around 80 L but 30–35% of it were recovered.

The biodiesel yield was calculated using Eq. (1) [12]:

$$\%\text{Yield} = \frac{\text{weight of product (g)}}{\text{weight of oil (g)}} \times 100 \quad (1)$$

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