Fuel 168 (2016) 22–26

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Ultrasonic-assisted production of biodiesel from *Pistacia atlantica Desf.* oil ☆

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HIGHLIGHTS

- Atlas pistache could be a potential substitute to petro diesel.
- The best models for both the yield and energy consumption were full quadric models.
- The yield and energy under optimum condition was equal to 96.6% and 32 kJ.

ARTICLE INFO

Article history:
Received 7 January 2015
Received in revised form 13 November 2015
Accepted 17 November 2015
Available online 30 November 2015

Keywords:
Biodiesel
Atlas pistache oil
Renewable energy
Ultrasonic

ABSTRACT

The objective of this research was to study the feasibility of biodiesel production from *Pistacia atlantica* (Atlas pistache) oil using ultrasonic system. Results showed that the best models for both the yield and energy consumption were full quadric models with suitable coefficients of determination (0.98, 0.99) and least mean squared errors (MSE) (0.351, 17.14). With increasing the amplitude and pulse, the methyl ester content increased. When reaction time and molar ratio increased to range of 5–7 min and 5–6, respectively, methyl ester content increased; while when these parameters increased out of range, yield decreased. The major properties of Atlas pistache methyl ester met the requirements of EN 14214 biodiesel standard and consequently, Atlas pistache can be a potential substitute to petro diesel.

1. Introduction

Biodiesel is a promising renewable substitute source of fuel which is produced from tree born oils, vegetable based oils, fats of animals and even waste cooking oil. It is identified as one of the key solutions for the alarming global twin problems of petrodiesel depletion and environmental degradation [1]. Although biodiesel was discovered at the beginning of 20th century by Rudolf Diesel, but extensive research on this fuel began at the tail end of the 20th century, when demand increased for petrodiesel [2]. Biodiesel is comprised of fatty acid alkyl esters and is generally produced from the transesterification of triglycerides in vegetable oils or animal fats. In this reaction, the stoichiometric molar ratio of alcohol to triglycerides is 3:1 [3]. Amongst alcohols, methanol is the most common used alcohol because of being more reactive and least expensive one [4]. In the transesterification reaction, an alkaline, acid or enzyme catalyst is often used to promote the reaction rate and product yield. Alkaline catalysts such as sodium hydroxide and potassium hydroxide have been found more effective [5]. Different operational and process conditions such as reaction time and temperature, molar ratio of alcohol to oil and catalyst concentration are among the important factors affecting biodiesel production [6].

Since this reaction can occur in the interfacial region among the liquids and also because of the fact that fats and alcohols are not totally miscible [7], transesterification is a relatively slow process. As a result, vigorous mixing is required to increase the surface contact between the two immiscible phases and, thus, to produce an emulsion. In the base-catalyzed procedure, some soap is formed and it acts as a phase-transfer catalyst, thus helping the mixing of the reactants [3,7].

☆ This work was supported by the Shahrekord University – Iran.
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http://dx.doi.org/10.1016/j.fuel.2015.11.063
0016-2361/

It has been observed that the transesterification reaction time can be significantly reduced by irradiating the reactants with ultrasonic sound waves at room temperature [8]. Ultrasonic waves are sound waves that are above normal human hearing range (i.e., above 18–20 kHz) [9]. The effect of ultrasonic waves on liquids has been explained in detail by Suslick. Ultrasound frequencies range from 20 kHz to l0 MHz, with associated acoustic wavelengths in liquids of roughly 0.15–100 mm. These wavelengths are not on the scale of molecular dimensions [10]. Instead, the chemical effects of ultrasound derive from several nonlinear acoustic phenomena, of which cavitation is the most important one. Acoustic cavitation is the formation, growth, and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound. When sound passes through a liquid, it consists of expansion (negative pressure) waves and compression (positive pressure) waves. These cause bubbles (which are filled with both solvent and solute vapor and with previously dissolved gases) to grow and recompress. Under proper conditions, acoustic cavitation can lead to implosive compression in such cavities. Such implosive bubble collapse produces intense local heating, high pressures, and very short lifetimes [3,11].

One of the sources for biodiesel production is *Pistacia atlantica* which is often grown in mountains. Its kernel contains 55% oil which makes it as a valuable renewable resource for biodiesel production. Different varieties of this fruit are grown in Kordestan, Kermanshah, Kerman, Fars, Lorestan, Kohkiluyeh & Boyer Ahmad, Sistan & Baluchestan, and Khuzestan provinces of Iran. From each tree, about 500–1000 g oil is obtained which can be more in rainy years and suitable conditions.

The objective of this research was to study of the feasibility of biodiesel production from Atlas pistache oil using ultrasonic.

2. Materials and methods

2.1. Materials

In order to supply the required oil for biodiesel production, the oil should be prepared before the reaction. Hence, the purified oil was methylated using Metcalfe et al. method [12], and the prepared sample was injected into Gas Chromatograph to determine fatty acids profile and molecular weight of the used oil [3].

KOH (grade 99%) and methanol (grade 99.9%) were supplied from Merck Chemical Industries, Germany. The materials were used without further purification. Also, the standards required to be considered in gas chromatography (i.e. the methyl ester of fatty acids C18:2, C18:1, C18:C17, C16:1, C16:0) and n-Heptanes were supplied from Sigma Aldrich company.

2.2. Equipment

A new ultrasonic set-up was used to carry out the research experiments. An ultrasonic processor (Hielscher Model UP400S, USA.) was utilized to perform the transesterification reaction. The equipment consisted of processor, sonotrode, and PC controller (Hielscher Model, UPC400T, USA). The processor operated at 400 W and 24 kHz frequency. The amplitude and the pulse for the reaction were adjustable from 20% to 100%. The titanium sonotrode (H22D) with a diameter of 22 mm and a length of 100 mm was used to transmit the ultrasound wave into the liquid [13].

2.3. Methods

2.3.1. Oil extraction

Oil was extracted from Atlas pistache mature seeds using hexane. For this purpose, the ground dried Atlas pistache seeds (40 g) were placed into a cellulose paper cone and extracted with 400 ml hexane using a soxhlet extraction apparatus for 8 h. The solvent was removed via a rotary vacuum distillation at 40–50 °C flushing with nitrogen to blanket the oil during storage. The residue was weighed and stored at −20 °C until it was analyzed. Oil weight was determined from 40 g of the seed powder to calculate the lipid content. The result was expressed as the lipid percentage in the seed powder dry matter. The physical and chemical properties of Atlas pistache oil are shown in Table 1.

2.3.2. Analysis of fatty acids composition

The oil was converted to methyl ester using the Metcalfe method [12,14]. Then, the extracted fatty acid methyl esters (FAMEs) dissolved in CHCl3 and analyzed by a gas chromatograph.

A Perkin–Elmer Clarus 580 gas chromatograph (GC) operating under conditions of the EN 14103 standard was used in this study. The GC equipped with a split–splitless mode injection system, flame-ionization detector, and TR-CN 100 High polar (30 m × 0.32 mm, 0.25 μm) column was used for FAME analysis. The gas chromatographic conditions were injection port temperature (250 °C), initial oven temperature (210 °C), heating rate (5 °C/min), final temperature (230 °C), detector port temperature (250 °C), hydrogen gas flow rate (45 mL/min), air flow rate (450 mL/min). The injection volume was 1 μL.

The titration method [15] was utilized to determine free fatty acids. Also, in order to determine the water content in the oil, the distillation method was used (ASTM, D4006-7). It should be noted the free fatty acid (FFA) content of oil using the titration method was 0.9%.

2.3.3. Saponification number

The SN was determined according to the AOAC Official Method 920.160 [16].

2.3.4. Kinematic viscosity

The SVM 300 (Anton Paar, Austria) was used for measuring kinematic viscosity. The kinematic viscosity was determined according the ASTM D-445.

2.3.5. Transesterification

A mixture of methanol and potassium hydroxide was agitated using a magnetic stirrer for 5 min to form the methoxide and water. Then, Atlas pistache oil was mixed with the previously prepared potassium methoxide in a conical flask. Afterward, the mixture was transferred to the reaction chamber to be subjected to ultrasound waves. The amplitude and time of the reaction were adjusted by a PC controller.

Table 1
Fatty acid profile and properties of used Atlas pistache oil.

Properties	Unit	Amount
Density at 15 °C	g cm^{-3}	0.912
Kinematic viscosity at 40 °C	cSt	42.3
Saponification Number	mg K/g oil	101.15
Iodine value	g I_2/100 g oil	100.59
Water content	mg g^{-1}	0.16
Myristic (C14:0)	wt.%	0.21
Palmitic (C16:0)	wt.%	13.63
Palmitoleic (C16:1)	wt.%	1.72
Stearic (C18:0)	wt.%	3.1
Oleic (C18:1)[a]	wt.%	47.52
Linoleic (C18:2)[a]	wt.%	32.33
Linolenic (C18:3)[a]	wt.%	1.09
Other fatty acids	wt.%	0.4

[a] Carbon atoms number: double bond number.