



Synthesis of biodiesel from castor oil: Silent *versus* sonicated methylation and energy studies



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ABSTRACT

In recent years, biodiesel is evolving to be one of the most employed biofuels for partial replacement of petrodiesel. The most widely used feedstocks for biodiesel production are vegetable oils. Among them, castor oil presents two interesting features as biodiesel raw material; on one hand, it does not compete with edible oils; on the other, the cultivar does not require high inputs. In this research, a comparison between conventional and ultrasound-assisted transesterification was carried out in terms of castor oil methyl ester (COME) yield and energy efficiency. Results show that sonicated transesterification leads to higher COME yields under lower methanol-to-oil molar ratio, lower amount of catalyst, shorter reaction time and lower amount of energy required. Ultrasound-assisted transesterification parameters were optimized resulting in the following optimum conditions: 20 kHz fixed frequency, 70% duty cycle, 40% sonication amplitude, 4.87 methanol-to-oil molar ratio, 1.4% w/w amount of catalyst and 3 sonication cycles (3 min 48 s) that provided 86.57% w/w COME yield. The energy required along each type of transesterification was measured leading to the conclusion that sonicated transesterification consumes a significant lower amount of energy than conventional one, thus achieving higher COME yield.

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1. Introduction

The most consumed energy sources during the major part of the twentieth century were petroleum-based fuels and coal. Provided that fossil resources are finite and their price follow an increasing trend along the years, new sources of energy compatible with our life style have been sought. Much of this energy consumption deals with road traffic that requires combustion engines in most occasions; thus, biodiesel (BD) is emerging as an alternative to diesel fuel and can be used either straight or mixed with conventional diesel fuel in different proportions showing some environmental benefits such as nontoxicity and biodegradability [1]. Chemically, BD is constituted by fatty acid methyl esters (FAME) from vegetable oils, animal fats, microbial oil and oils from microalgae. BD is synthesized through a well-known process called transesterification, in which one mole of triglycerides reacts with three moles of a short chain alcohol, yielding glycerol as by-product. The main objective of the search for new raw materials that do

not compete with human feeding is to avoid the potential increase of food costs derived from the use of edible oils to produce bioenergy. In fact, there are vegetable oils that are not suitable for human consumption and could suppose a viable alternative for BD production. An interesting plant in this field is castor (*Ricinus communis*), which grows wild in many tropical and sub-tropical countries without special care, because this plant tolerates very different climate conditions; temperatures between 20 and 26 °C and low humidity are the most appropriate conditions to achieve high yields [2]. For this reason, many countries, especially emerging ones, have increased castor oil production in a continuous way, the three largest producers being India, China and Brazil [2–4]. The main chemical feature of castor oil is the presence of a hydroxyl group on carbon-12 in the ricinoleic acid; this fatty acid (FA) constitutes between 87 and 95% of the FA composition of this oil. Transesterification of castor oil with ethanol, methanol and 2-propanol, including irradiation conditions have been carried out, providing promising results in terms of COME conversion (over 90% w/w) [5–8]. Despite castor oil BD is not endowed with especially good characteristics to be used as biofuel, owing to its high viscosity and density [9], it has been blended with diesel fuel for use in

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combustion engines [10]. In fact, the presence of ricinoleic acid in higher proportions prevents BD to meet international standards for BD quality. Moreover, blending diesel fuel with castor oil BD depicted higher emissions of hydrocarbons and carbon monoxide compared to conventional diesel fuel [11]. For these reasons, the mixture percentage has been limited to 10% [12]. The feasibility of the use of castor oil BD as automotive fuel is being studied in producing countries, like Brazil, where a standard has been proposed [13]. However, there are some properties of castor oil methyl ester as lubricity and high flash point, which make it attractive to be used in alcohol–diesel fuel blends. In fact, one of its drawbacks, as its high viscosity, could be seen as positive in these blends to compensate the low viscosity of primary alcohols [14,15].

The main handicap in the transesterification reaction is the need of a deep contact between two very different chemical species, namely triglycerides, of non-polar nature and short chain polar nature alcohols. The conventional transesterification method involves continuous heating and stirring and long reaction times to reach satisfactory BD yields. This is the main reason why several alternative methods for BD production, demanding lower reaction time and reagent amount, have been studied in recent years. To overcome the problem of mass transfer between two immiscible phases, two approaches have been explored. On one hand, it can be achieved by making the phase transfer more intensive (mixing, sonication). The importance of mixing has been reported by many researchers [16,17]. On the other hand, waiving the resistance at the interphase is proposed. Transesterification using alcohol (methanol and ethanol) under supercritical conditions and co-solvents are clear examples [18–20]. Among these possibilities, ultrasound (U/S) is considered one of the most attractive alternative sources of auxiliary energy to enhance BD synthesis [21,22]. From a physical standpoint, ultrasonic energy results from acoustic waves at a frequency higher than the upper limit of the human hearing range [23] capable of generating high local temperatures and pressures through the vibratory motion of the molecules in the propagation medium [24]. As a result of these vibrations, turbulences are originated and the number of effective collisions between reactive molecules increases accordingly; thus, the reaction is accelerated taking place a phenomenon known as cavitation [25]. There are different available ultrasonic devices that allow holding chemical reactions satisfactorily. In the last decade, publications on U/S-assisted BD synthesis through ultrasonic baths, ultrasonic probes or horns and sonochemical reactors have been reported [25–32]. One of the most widely used devices is the ultrasonic probe that allows direct sonication of the reaction medium and tuning of some physical characteristics of U/S like frequency, duty cycle and amplitude. According to previous studies [28,33], frequency, duty cycle and amplitude of U/S determine the amount of energy introduced into reaction mixture and have a potential influence on subsequent BD yield. Moreover, kinetic studies on sonicated transesterification (ST) highlights the benefits of the intense micro-mixing that produce the use of ultrasound [34,35].

The present study attempts to conduct the U/S-assisted synthesis of BD using a non-edible feedstock (castor oil) and to compare results with those from conventional transesterification. One of the major drawbacks during the production of castor oil BD is the separation of COME from glycerol. The presence of OH-group in the ricinoleic acid forms hydrogen bonds with glycerol and water in the reaction mixture. Owing to low BD production and the various aforementioned experimental handicaps of castor oil transesterification, it was decided to assist the reaction with U/S as an alternative energy. In addition, new BD samples were centrifuged in order to shorten the phases-separation step. So far, sonicated castor oil transesterification has been held in ultrasonic baths, under indirect sonication [36,37]. In this paper, an U/S probe allows direct sonication, taking advantage of the applied energy. The main

objectives of this work are to reduce reaction time to produce COME and to compare sonicated and conventional transesterification in terms of energy consumption.

2. Materials and methods

2.1. Raw material and reagents

Castor oil was supplied by Guinama (Valencia, Spain). For BD production, CH₃OH and KOH were supplied by Panreac Química (Barcelona, Spain). For BD quality analysis, 1,2,4-butanetriol, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), 1,2,3-tricaproyl glycerol (tricaprine), n-heptane, pyridine and methyl heptadecanoate were provided by Sigma–Aldrich (Steinheim, Germany). 2-propanol, toluene, an ethanolic solution of phenolphthalein (10 g/L), benzoic acid, PA-ACS glacial acetic acid, PA-ACS water, soluble starch, potassium iodide, 0.1 N sodium thiosulfate and trichloromethane, were provided by Panreac Química. For FA determination, hexane was supplied by JT Baker (Pennsylvania, USA) and sodium methoxide by Sigma–Aldrich.

2.2. Instruments

An ultrasonic probe was selected to operate under a fixed frequency of 20 kHz, with a varying range of both duty cycle and amplitude. The maximum power was 450 W. The probe was inserted in a constant temperature water bath. This device was purchased from Branson Ultrasonic Corporation (Danbury, Connecticut, USA). On the other hand, traditional transesterification was carried out with the help of an Ovan MBG05E heater-stirrer, which provides a maximum power of 500 W, purchased from Espier Group (Barcelona, Spain).

Two different power quality analyzers were selected. One of them was a Fluke 435 energy analyzer that operates at a maximum value of 1000 V. The other one was Fluke 43B analyzer operating at a maximum voltage of 1250 V. Both instruments were supplied by Fluke (Everett, Washington, USA).

2.3. Energy consumption studies

To gain knowledge about the implications of the use of U/S vs. the traditional reaction, energy consumption was measured when either the ultrasonic probe or the heater-stirrer device was used. For this reason, both instruments were connected to the three phase power quality analyzer Fluke 435. The Fluke 43B power quality analyzer provided voltage (229.1 V) and frequency (50 Hz) of the electrical current outlet data.

To establish a comparison from the point of view of energy cost between each produced biofuel (sonicated and conventional), it is necessary to define a parameter that reflects the produced fuel mass (g) as a function of the energy required for its synthesis. Thus, fuel Specific Consumption (SC) in g/Wh corresponds to the amount of produced biofuel mass divided by the amount of energy required for its production (Eq. (1)).

$$SC = \frac{\text{Biodiesel mass (g)}}{\text{Energy consumption (Wh)}} \quad (1)$$

Another interesting parameter that reflects the energy efficiency of a specific fuel is the ratio between the amount of energy per mass unit (J/g) generated by its combustion provided by the fuel LCV divided by the amount of energy per mass (J/g) unit required for its synthesis (Eq. (2)).

$$EUI = \frac{\text{Low calorific value } \left(\frac{\text{J}}{\text{g}}\right)}{\text{Amount of energy per mass unit required for its synthesis } \left(\frac{\text{J}}{\text{g}}\right)} \quad (2)$$

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