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Biodiesel synthesis from saturated and unsaturated oils assisted by the combination of ultrasound, agitation and heating

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HIGHLIGHTS

- Ultrasound has become an attractive alternative energy for biodiesel production.
- Combinations between cycles of sonication and cycles of stirring were carried out.
- Desirability function shows the optimal values for each reaction parameter.
- Unsaturated oils achieved conversions over UNE EN 14013 standard.
- Heating at reaction temperature within sonication cycles shows a positive influence over FAME yield and properties.

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ABSTRACT

Ultrasound-assisted synthesis of biodiesel is a well known process that has been widely used in recent years. A reduction of the processing time and the amount of required catalyst as well as the possibility to work at room temperature have been achieved in most cases. Normally, the use of ultrasound replaces the conventional agitation and heating required to establish close contact between the two immiscible phases involved in this reaction (triglycerides and methanol). However, it may be not sufficient depending on the type of oil. In the present study, transesterification of oils with very different fatty acids composition has been conducted by combination of sonication and agitation cycles either at room temperature or at 50 °C. Application of ultrasound was carried out with an ultrasonic probe at 20 kHz frequency, 70% duty cycle and 50% amplitude. The experimental designs were planned by using the response surface methodology intended to find optimal values allowing a significant saving in the amount of catalyst and total reaction time required. Thus, oils with high content of unsaturated fatty acids (e.g. rapeseed and soybean oils) were found to reach biodiesel yields higher than the minimum value provided by the standard EN 14103 in shorter reaction times (below 15 min) compared to traditional transesterification. On the contrary, oils with high content of saturated fatty acids (e.g. coconut and palm oils) did not reach the required yield of 96.5% w/w. Finally, it may be concluded there is a positive influence of stirring and heating at reaction temperature between consecutive ultrasonic cycles on FAME yield and properties.

1. Introduction

The foreseeable future exhaustion of oil resources in the word and the high present price of oil barrels make advisable to seek for alternatives to obtain fuels for internal combustion engines. One of these alternatives is biodiesel (BD) that, from the chemical point of view, is constituted by fatty acid monoalkyl esters from vegetable oils, animal fats or microbial oil. The reaction for BD production is transesterification, in which one mol of triglycerides reacts with three moles of alcohol resulting in three moles of fatty acid monoalkyl esters and one mol of glycerol. The advantages of BD as compared to petrodiesel are that the former is a renewable source of energy [1], emits less greenhouse gases [2] and may recycle an environmentally challenging residue such as waste oil. The main factor that contributes to the final price of BD is the raw material [3], the price of which is variable and depends on the type of oil used and the fluctuations of the market, a factor that

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is not easy to control. The reaction parameters that can be optimized to reduce the final cost of BD are the time of the transesterification reaction, that may involve hours [4], the contact between the immiscible phases involved in the reaction (that requires continuous stirring), the amount of reagents and the reaction temperature [5]. The efficiency of mass transfer between the two immiscible phases (non polar triglycerides and polar methanol) provides the time required to achieve appropriate yield of the transesterification reaction, thus making of paramount importance a high contact surface between the two phases. While stirring has been traditionally used to increase contact between the involved phases, ultrasonic devices are presently replacing the former by virtue of the cavitation phenomenon [6]. Cavitation is created by power US that generates pressure waves in the reaction medium promoting an increase of local temperature and pressure [7–9] which facilitates the reaction kinetics [10,11] (thus reducing reaction time). Transesterification reaction can be chemically catalyzed by bases [12–14], acids [15–17] or biochemically catalyzed by enzymes [18–20]. The amount of catalyst also requires optimization to reduce its presence to a minimum. In this sense, application of power US is also beneficial as it favors the formation of free radicals in polar media, thus decreasing the need for catalysts. The improvements in BD production due to US application have promoted research in this field to consolidate this energy as a viable alternative for BD production. There are various ultrasonic devices available in the market that can be used with this aim: ultrasonic baths [13,21], ultrasonic probes [22–24] and ultrasonic reactors [25,26]. Ultrasonic baths are devices designed for cleaning laboratory glassware or degassing solutions, which have several limitations when used for other purposes (namely, they do not allow direct sonication in the reaction medium, so the amount of energy per unit area that reaches the reaction system is limited). In contrast, ultrasonic probes and ultrasonic reactors allow direct sonication and tune of some physical characteristics of US (duty cycle and amplitude). Thereby, multiple experimental designs has been carried out by combining characteristic parameters of the transesterification reaction (molar ratio, amount of catalyst, reaction time, temperature and stirring speed) and physical characteristics of US [27]. Thus, the main objectives to be achieved with the use of US for BD production are: (1) shortening of the reaction time, (2) decreasing of the amount of catalyst and (3) saving energy by reducing heating and stirring. However, as the US probe has limitations of maximum temperature, sonication duration is limited. This fact may provide incomplete transesterification reactions, thus providing excessive amount of unreacted glycerides. This problem needs to be fixed to extend the use of US-assisted transesterification. Although batch processes have been widely studied, BD production has gradually been moved towards continuous process to simulate industrial conditions, thus optimizing both energy and reaction times [6,28,29]. On the other hand, both design of experiments (DOE) and data processing are key elements for the development of successful novel technology. Proper design can reduce the number of experiments and amount of reagents. The response surface methodology (RSM) consists of the application of a group of mathematical and statistical techniques used for the development of an appropriate functional relationship between the response of interest and a number of associated control or input variables [30]. Previous research in this field corroborates this application [14] including studies about US-assisted transesterification [31,32]. In sum, previous studies have shown that sonication is not enough to meet FAME yields considering international standards for BD quality that establish a minimum of 96.5% w/w [33]. Thus, the main goals of the present research were to evaluate the effect of ultrasound on BD production and the differences, if any, between BD achieved via sonication-assisted transesterification and sonication plus agitation and heating-assisted transesterification, to help the reaction to complete. Moreover, in this work, the effect of the raw material chemical composition in ultrasound plus agitation plus heating-assisted transesterification is studied. Considering RSM, the input parameters are those involved in the reaction (amount of catalyst and reaction time), while the response variables are the concentration expressed as percentage weight-in-weight (of oil) of fatty acid methyl esters (FAME), monoglycerides (MG), diglycerides (DG) and tryglicerides (TG). Four raw materials (rapeseed, soybean, coconut and palm oils) were selected because they cover a wide range of fatty acid composition.

2. Experimental procedures, materials and methods

2.1. Raw materials

Raw materials for BD production were rapeseed oil provided by IFAPA (Instituto de Formación Agraria y Pesquera, Córdoba, Spain), soybean oil purchased from Guinama (Alboraya, Valencia, Spain), coconut oil from Acofarma (Terrassa, Barcelona, Spain), and palm oil from Químics Dalmau (Barcelona, Spain).

2.2. Methodology, reagents, apparatus and instruments

2.2.1. Ultrasonic probe and heater–stirrer device

All sonications were performed by a Branson digital ultrasonic sonifier −20 kHz and 450 W – (Danbury, Connecticut, USA) working in a thermostated water bath. The device allows setting the amplitude of power supply output voltage in the range from 10% to 100% of nominal converter amplitude. Duty cycle may be either intermittent (pulse duration adjustable from 0.1 s to 59.9 s) or continuous processing time. The horn frequency varies from 19.850 to 20.050 kHz. An Ovan heater–stirrer model MBG05E (500 W) supplied by Espier Group (Barcelona, Spain) was used to hold the conventional transesterification.

2.2.2. Devices employed for energy studies

Power measurements and subsequent energy measures were carried out by two different types of analyzers. The first one was a Fluke 435 three phase power quality analyzer operating at a maximum input voltage of 1000 V rms, a nominal voltage range of 50–500 V internally divided in three ranges (500 V, 250 V and 125 V), a maximum peak voltage of 6 kV, a nominal input current of 0.1–3000 A rms and a nominal frequency range of 40–70 Hz. The second one was a Fluke 43B power quality analyzer operating at a maximum input voltage of 1250 V rms, a nominal voltage range of 50–500 V internally divided in three ranges (500 V, 250 V and 125 V), a maximum peak voltage of 6 kV, a nominal input current of 0.5–40 A rms and a nominal frequency range of 40–70 Hz; both supplied by Fluke (Everett, Washington, USA).

2.2.3. Reagents and analyses performed to characterize vegetable oils and biodiesel samples

For BD production, methanol and potassium hydroxide were acquired from Panreac (Barcelona, Spain). Density and kinematic viscosity were monitored according to EN ISO 3675 and EN ISO 3104 protocols, respectively. Flash point was determined by Seta Flash series 3 plus from Instrumentación Analítica S.A. (Madrid, Spain) following the standard EN ISO 2719. High calorific value (HCV) was measured using a calorimeter bomb model IKA C200 (Ponteranica, Italy). Analyses were carried out following the ASTM D240 standard. Acid value was determined according to EN ISO 660; the reagents used were 2-propanol, toluene, phenolphthalein solution in ethanol (10 g/L), benzoic acid and potassium hydroxide, all supplied by Panreac. Peroxide value was determined according