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Ultrasound-assisted biodiesel production from *Camelina sativa* oil

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HIGHLIGHTS

- *Camelina sativa* oil presents suitable chemical composition for biodiesel production.
- US leads to higher conversion, reduced reaction time and glyceride concentration.
- Stirring and heating cycles between sonication cycles improves FAME yield.
- US-aided transesterification consumes less energy for biodiesel synthesis.

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ABSTRACT

The main drawbacks of biodiesel production are high reaction temperatures, stirring and time. These could be alleviated by aiding transesterification with alternative energy sources, i.e. ultrasound (US). In this study, biodiesel was obtained from *Camelina sativa* oil, aided with an ultrasonic probe (20 kHz, 70% duty cycle, 50% amplitude). Design of experiments included the combination of sonication and agitation cycles, w/wo heating (50 °C). To gain knowledge about the implications of the proposed methodology, conventional transesterification was optimized, resulting in higher needs on catalyst concentration and reaction time, compared to the proposed reaction. Although FAME content met EN 14103 standard, FAME yields were lower than those provided by US-assisted transesterification. Energy consumption measurements showed that ultrasound assisted transesterification required lower energy, temperature, catalyst and reaction time.

1. Introduction

In recent years, the consumption of biodiesel (BD) has been increasing in the world and particularly in Europe. According to ASTM specifications, BD is defined as mono-alkyl esters of long chain fatty acids (FA) derived from vegetable oils or animal fats. The increase in BD production implies new challenges to the scientific community, including the use of raw materials respecting natural ecosystems and the constant search of benefits for the surrounding local population in terms of job generation. Probably, one of the most important challenges is to increase biofuel production using land unsuitable to grow food plants, so there will not be a competition between land for food and for energy (Pinzi et al., 2009). BD is produced through a chemical process called transesterification that involves the reaction between one mol of triglycerides and three moles of a short chain alcohol, being the most widely used methanol. The most common oils used in the production of BD are from vegetable origin. Rapeseed, soybean, palm, coconut, sunflower and other oils have been widely used as raw material for first-generation BD; this type of biofuels has already reached the stage of commercial production. On the other hand, there are oleaginous crops that do not compete with human food, like *Ricinus communis* (castor), *Pongamia pinnata*, *Jatropha curcas* and other non-edible oil-crops, which provide the so-called second-generation BD.

Nowadays, BD cannot compete with diesel fuel unless tax exemption is applied or a dramatic cost reduction is achieved through either the process or the raw materials. On one hand, low-input consumption oilseed crops are investigated to minimize the cost of raw material used for BD production. In this context, *Camelina sativa* is a non-food oilseed plant known as "gold of pleasure", depicting a high content of unsaturated FA (Moser and Vaughn, 2010). Although *C. sativa* oil is not commonly used for human feeding, it shows a very interesting chemical composition

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from the nutritional standpoint, being rich in tocopherols and vitamin E. In addition, over 50% of the FA are polyunsaturated, the main components being α-linolenic acid (ω-3 FA, about 35–45%) and linoleic acid (ω-6 FA, about 15–20%) (Putnam et al., 1993). In this sense, it is important to mention that saturation degree of oils is an important parameter related to BD properties; the higher the degree of unsaturation of the FA esters the lower the BD viscosity (Moser, 2009), which is a key feature to allow the use of BD as fuel in diesel engines. Moreover, it also provides good cold weather behavior, while affecting negatively cetane number and oxidation stability (Pinzi et al., 2009). This plant is member of the *Brassicaceae*, like rapeseed and can be grown in a variety of climate and soil conditions (Fröhlich and Rice, 2005). Moreover, it depicts several benefits from an agronomic point of view: (1) short growing season (85–100 days), (2) compatibility with another agricultural practices and (3) a wide climatic tolerance (cold, dry and semi-arid conditions) and well adaptation to the northern regions of North America, Europe and Asia (Moser, 2010). This versatility increases the interest of this oilseed plant as feedstock for BD production.

Reducing the reaction time and decreasing the energy requirements could also lead to reduced BD production cost. To overcome the first problem, the mass transfer between two immiscible phases must be improved. Oils with a high percentage of triglycerides (of non-polar nature) are mixed with short-chain alcohol (preferably methanol than ethanol) of polar nature. In conventional transesterification, the adequate mass transfer is achieved by heating and stirring vigorously the reaction mixture, to stimulate a quick contact between reagents (Stamenkovic et al., 2007). Moreover, the reaction temperature needs to be relatively high, slightly below methanol boiling point (65 °C). In this way, high BD conversions are achieved after almost one-hour reaction time with the consumption of high amount of energy for heating and stirring, thus increasing the production cost of BD. As a result, in recent years, several alternative energy sources able to provide low reaction time at room temperature and reduced amount of catalyst-consumption transesterification for BD production have been proposed. Among these auxiliary energies, ultrasound (US) (Veljkovic et al., 2012) and microwaves (Hernando et al., 2007; Kumar et al., 2011) allow significant reductions in reaction time and temperature. Another alternative to conventional transesterification consists on the use of oscillatory flow reactors (Harvey et al., 2003) and supercritical and subcritical methanol (Patil et al., 2010). Among these possibilities, the energy source that allows a suitable adaptation to large scale production is provided by US. US waves are acoustic frequencies above the range of human hearing (Leonelli and Mason, 2010) and have been applied in diverse fields as medicine, industry, environment protection, chemistry and molecular biology (Mason, 2007). Regarding chemistry, US has been used to improve the kinetics of chemical reactions, because US irradiation cause the formation of free radicals and various other extremely reactive species (Luque De Castro and Priego Capote, 2007). The key to accelerate chemical reactions is a phenomenon known as cavitation that is the origin of sonochemical effects. Cavitation is the implosion of the bubbles that are generated when molecules of the propagation medium begin to vibrate (Rocha et al., 2014; Suslick, 1989). As a result, high local temperatures are reached in a few seconds after US application (Flint and Suslick, 1991). In the last decade, the transesterification reaction has been carried out using ultrasonic baths (Stavarache et al., 2003), ultrasonic probes (Lee et al., 2011) and ultrasonic reactors (Le et al., 2010; Thanh et al., 2010). The first studies were carried out in ultrasonic baths at fixed frequencies; these devices had little versatility and do not allow direct sonication of the reaction mixture. This problem was later fixed by the use of ultrasonic probes, providing the option of tuning some of the physical characteristics of US (frequency, duty cycle and amplitude) thus allowing more sophisticated design of experiments (DOE). Eventually, a significant enhancement of the reaction was achieved with the use of ultrasonic reactors, as small-scale industrial working conditions could be reproduced in the laboratory.

The main goal of this work is to study the feasibility of US-assisted transesterification, in combination with agitation cycles (with or without heating at 50 °C) to produce BD from *C. sativa* oil. The sonochemical parameters involved in the US-assisted transesterification were firstly optimized to maximize the reaction yield. BD from conventional transesterification was produced and the reaction products were further compared with those provided by the ultrasonic process. Finally, the demand of energy by the different BD synthesis processes was measured and compared.

2. Methods

2.1. C. sativa oils

BD production was carried out from samples of *C. sativa* oil obtained by two different extraction methods, namely mechanical pressing (A) and chemical extraction with hexane (B), both given by Institute of Heavy Organic Synthesis "Blachownia" (Kędzierzyn-Koźle, Poland).

2.2. Reagents

2.2.1. Reagents used for transesterifications

For transesterification reactions, the reagents used were methanol (MeOH) and potassium hydroxide (KOH) from Panreac Química (Barcelona, Spain).

2.2.2. Reagents used for properties analysis

For FAME determination, methyl heptadecanoate was used as internal standard, purchased from Sigma–Aldrich (Steinheim, Germany); for mono-, di- and triglyceride content (MG, DG and TG, respectively) and glycerol determination, the reagents used were methanol, pyridine and n-heptane, the last two ones supplied by JT Baker (Center Valley, Pennsylvania, USA), while 1,2,4-butanetriol, 1,2,3- tricaproil glycerol (tricaprine), N-Methyl-N-(trimethylsilyl) and trifluoroacetamide (MSTFA) were supplied by Sigma–Aldrich. Hexane and sodium methylate, from Panreac, were employed for FA determination.

For the determination of the acid value, 2-propanol, toluene, phenolphthalein, ethanol, benzoic acid and potassium hydroxide were used as reagents; similarly, for peroxide value, glacial acetic acid, water PA-ACS, starch, potassium iodide, sodium thiosulfate and trichloromethane were used, all acquired from Panreac Química and JT Baker.

2.3. Devices used in transesterification processes

2.3.1. Sonicated transesterifications

The application of US was carried out by a digital ultrasonic horn (Branson 450) made up of a titanium alloy with a tuner that allows working with a variable amplitude and duty cycle. The device also includes a thermostated water bath in order to dissipate the heat produced by US application. Both the horn and the water bath are included into a soundproof chamber. The frequency of the horn is set at 20 kHz, the maximum power reached being 450 W. It was supplied by Branson Ultrasonic Corporation (Danbury, Connecticut, USA).