Fuel 125 (2014) 183–191

Contents lists available at ScienceDirect

Fuel

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

Influence of vegetable oil fatty acid composition on ultrasound-assisted synthesis of biodiesel

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HIGHLIGHTS

- The use of ultrasound reduces the transesterification reaction time.
- Lengths of chain and unsaturation degree have a special relevance on ultrasound assisted fatty acid conversion.
- RSM provides the optimal values of the reaction parameters to maximize FAME yield and minimize glyceride concentration.
- Unsaturated oils reach higher FAME yield than saturated ones, under US-assisted transesterification.

ARTICLE INFO

Article history:
Received 25 December 2013
Received in revised form 9 February 2014
Accepted 11 February 2014
Available online 22 February 2014

Keywords:
Transesterification
Auxiliary energy
Saturation degree
Length of chain
FAME

ABSTRACT

Ultrasound is considered as one of the most attractive energies to assist biodiesel transesterification. The objective is to reduce the reaction time while saving energy. In the present study, four oils showing a wide range of fatty acid composition have been transesterified using ultrasound as auxiliary energy. Samples included unsaturated fatty acids (rapeseed and soybean) oils and saturated fatty acids (coconut and palm) oils. Transesterification reactions were conducted in batch and an ultrasound probe working under a fixed frequency of 20 kHz was used to facilitate the overall process. According to the design of experiments, variable duty cycle and amplitude, besides different concentrations of basic catalyst (KOH) and methanol-to-oil molar ratio were studied. The optimal fatty acid methyl ester (FAME) values were 95.03% for rapeseed biodiesel, 94.66% for soybean biodiesel, 81.37% for coconut biodiesel and 93.08% for palm biodiesel. A response surface methodology (RSM) was applied to determine the reaction parameters with a significant impact on response variables. Results showed that the length of chain and in a lower extent unsaturation degree of fatty acids have a significant effect on ultrasound assisted transesterification. In this sense, oils with higher unsaturation degree and long hydrocarbon chains provide higher FAME yields and lower glyceride concentrations than those with saturated fatty acids and short hydrocarbon chains.

1. Introduction

The steady increase in fossil fuel prices and the dependence on oil from producing countries invite to search viable fuel alternatives to combustion engines. Biodiesel (BD) is a biofuel produced from vegetable oils or animal fats with some advantages over its counterpart from petroleum. It has lower toxicity, emits less greenhouse gases [1] and substantially lower noise pollution as compared to those emitted by diesel engines fueled with petroleum-derived fuel [2]. Triglycerides in BD raw materials are converted into fatty acid monoalkyl esters through a reaction called transesterification. This process has two main drawbacks: (1) slowness as it requires long time to achieve significant yields; (2) the need for continuous stirring and heating of the reaction mixture to ensure contact between the two immiscible reactants (methanol and oil). Although, petrodiesel is economically more competitive than BD, the production cost of the latter can be reduced by working more effectively while optimizing the synthesis process. For this reason, in recent years, to accelerate the reaction different alternative energies have been studied. In order to solve these problems, the transesterification assistance by microwave

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http://dx.doi.org/10.1016/j.fuel.2014.02.015
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Nomenclature

BD	biodiesel
CO	coconut oil
DG	diglycerides
DOE	design of experiments
DU	diunsaturated methyl esters
FAME	fatty acid methyl esters
FA	fatty acids
FID	flame ionization detector
GC	gas chromatography
HCV	high calorific value
ISO	international standard organization
LC	length of chain
MG	monoglycerides
MU	monounsaturated methyl esters
MUD	monounsaturation degree
PO	palm oil
PUD	polyunsaturation degree
RO	rapeseed oil
RSM	response surface methodology
SEC	size exclusion chromatography
SO	soybean oil
TG	triglycerides
THF	tetrahydrofuran
TU	triunsaturated methyl esters
TUD	total unsaturation degree
UNE-EN	Spanish norm-European norm
US	ultrasound
US cycles	ultrasonic cycles
cn	weight percentage of each methyl ester in the given fatty acid
$d_i(Y_i)$	desirability function
nCn	number of carbon atoms of each fatty acid
μ	kinematic viscosity
ρ	density

ovens [3], ultrasonic probes [4] or oscillatory flow reactors [5] have been proposed. Ultrasound (US) is one of the preferred energies in this field. The variability and versatility of US devices available in the market allow to carry out different designs of experiments.

US consists on acoustic waves propagating in a material medium [6]. The sonication of the reaction leads the molecules to vibrate and collide with each other, resulting in a temperature increase of the reaction medium and the surrounding environment. This phenomenon, known as cavitation, increases the reaction speed, thus making possible to reduce the amount of catalyst [7]. US can reduce the reaction time required for transesterification from hours to minutes [8]. Sonication creates an emulsion in the reaction medium that increases the contact surface between the two immiscible phases. In this way, the speed of mass transfer between phases is significantly faster; the principal consequence of this phenomenon is that agitation and heating can either be suppressed or take place within a shorter period of time.

Several studies describe the synthesis of ultrasound-assisted BD [9–11]. In most cases, BD production has been assisted by simple devices such as ultrasonic baths, designed for cleaning and degasing, that do not allow direct sonication of the reaction medium and have an irreproducible behavior [12–14]. Ultrasonic probes and ultrasonic reactors allow direct sonication to the reaction medium, and the evaluation of the effect of the physical characteristics of US (i.e. duty cycle and amplitude) on the reaction yield. The earliest uses of ultrasonic probes to assist BD production allowed conversion yields above 96.5%, by working in batch [15–17]. The subsequent use of ultrasonic reactors made possible to work either in batch or continuous modes. These devices, similar to those used at industrial scale, are of special interest for potential scaling at industrial size. The main problem of US-assisted transesterification is that, in most cases, BD does not meet the standards of quality [9,18]. To achieve a content of fatty acid methyl esters (FAME) and glycerides that fulfill the UNE EN 14214 standard, optimization of transesterification parameters is mandatory. For doing that, statistical methods, which allow the simultaneous optimization of inter-related variables, should be used. A useful tool for process optimization consists on Response Surface Methodology (RSM), which allows reducing the number of experiments and, consequently, the final cost. Also, the use of RSM shows the interactions between reaction parameters and evaluates the significance of them on the response variables, as well as the range within which the reaction parameters exert a significant impact on response variables [19,20].

Regarding the raw material, there is a great variety of oils and fats that can be used to produce BD. Oils from oleaginous plants are widely used with this aim. Provided that fatty acid composition influences biodiesel optimization, properties and engine performance [2,21], the main objectives of the present study were (a) to optimize the US-assisted synthesis of biodiesel from different raw materials (selected oils were from rapeseed, soybean, coconut and palm) showing a wide range of fatty acid composition; and (b) to study the influence of the chemical composition of the oil fatty acids (FA) on the US-assisted transesterification. To study the effect of several factors (amount of catalyst and US cycles) on the FAME yield and glycerides production, a preliminary screening using a factorial design and a surface response was carried out.

2. Materials and methods

2.1. Vegetable oils

Soybean oil was purchased from Guinama (Alboraya, Valencia, Spain), coconut oil from Acofarma (Terrassa, Barcelona, Spain), palm oil from Químics Dalmau (Barcelona, Spain) and rapeseed oil was provided by IFAPA (Instituto de Formación Agraria y Pesquera, Córdoba, Spain).

2.2. Methodology, reagents and apparatus

2.2.1. US device

US was applied by means of a Branson 450 digital sonifier (20 kHz and 400 W) including a cylindrical titanium alloy probe (12.70 mm diameter) and a thermostated water bath. The device adjusts 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.

2.2.2. Analyses performed to characterize vegetable oil samples

Physical tests consisting of density and kinematic viscosity were performed according to UNE EN ISO 3675 and UNE EN ISO