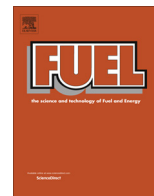




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An improvement to the transesterification process by the use of co-solvents to produce biodiesel

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HIGHLIGHTS

- The presence of co-solvents facilitates the reaction of transesterification.
- High yield and fast reaction could be obtained at relatively low temperature.
- The optimum conditions led to biodiesel with 98% ester content.
- Transesterification kinetics was described by a pseudo first order kinetic model.

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ABSTRACT

The use of several co-solvents such as acetone, diethyl ether (DEE), dibutyl ether (diBE), tert-butyl methyl ether (tBME), diisopropyl ether (diIPE) and tetrahydrofuran (THF) could produce important improvement to the transesterification process. The influence of catalyst concentration (KOH), methanol/oil molar ratio, methanol/co-solvent molar ratio, co-solvent type, catalyst type, agitation rate and reaction temperature was investigated. The process was mainly affected when DEE, tBME and THF were used, achieving biodiesel with high methyl ester content. The maximum methyl ester content was 97–98%, when 9:1 as methanol/oil molar ratio, 0.7 wt% KOH, 1:1 as co-solvent/methanol molar ratio, 700 rpm and 30 °C were used. In addition, fuel properties of the biodiesel were determined and its cetane number was estimated based on several correlations proposed in literature. The kinetics of the reaction was also analyzed by the determination of the rate constants. Arrhenius and Eyring Polanyi equations were used to find out the activation energy and the variations of the enthalpy and entropy of the system.

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1. Introduction

Globally, the awareness of energy issues and environmental problems associated with burning fossil fuels has encouraged many researchers to investigate the possibility of using alternative sources of energy instead of mineral oil and its derivatives. Among them, biodiesel seems very interesting and can replace diesel fuel in many different applications such as boilers and internal combustion engines without major modifications and just small decrease in performance. As is known, according to the directive 2003/30/EC, biodiesel is defined as “a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel” [1].

Blending of biodiesel with diesel fuel increases engine efficiency and contributes to rural development. In addition, biodiesel offers many advantages in environmental, technical, economic and social

aspects, with respect to diesel: it has renewable and biodegradable character; it is non-flammable and non-toxic; it does not contain sulphur and aromatics compounds; it has high cetane number, good lubricity, higher flash point and it reduces dependence on imported oil. On the other hand, biodiesel does not produce greenhouse effects, since only there is a small net contribution of carbon dioxide (CO₂) when the whole life-cycle is considered (including cultivation, production of oil and conversion to biodiesel) [2,3].

Biodiesel also shows higher density and viscosity than diesel, and could show freezing problems at low temperatures. These can be some of the disadvantages in biodiesel use, besides an increase in fuel consumption and nitrogen oxide emissions [4,5]. However, the use of pure biodiesel allows to reduce the total unburned hydrocarbons (–67%), CO emissions (–48%), CO₂ generation (–79%), particulate matter emissions (–47%), SO_x formation (–100%), polycyclic aromatic hydrocarbons (PAHs) generation (–80%) and nitrated PAHs formation (–90%) [6,7]

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Raw material cost is usually the most important factor in biodiesel final price. Edible and non-edible oils are used to produce this fuel. Also other products such as algae or biomass waste have been suggested as suitable raw materials [8]. In general, the synthesis of biodiesel is carried out by the transesterification reaction. This reaction generates fatty acid alkyl esters and glycerol and, in order to achieve an adequate rate, catalyst should be used [9]. Homogeneous (alkaline and acid) and heterogeneous catalysts can be utilized, although homogeneous alkaline catalysts (NaOH, CH₃ONa and KOH) are the most active. Nevertheless, this type of catalysts requires an expensive separation with high consumption of energy and large generation of wastewater. Moreover, the formation of soap by reaction between the catalyst and free fatty acids of the feedstock could be possible. So, many researchers have focused on how to decrease the severity of the reaction conditions [6,10].

In the transesterification reaction, methanol and oil phases are insoluble. Hence the mass transfer between both phases affects to the reaction rate initially. A rise in reaction temperature can improve the solubility, although this process implies higher energy consumption and just an increase of 2–3 wt% of the solubility with temperature increases of 10 °C [11]. Therefore, additional ways to enhance the system solubility, such as the use of co-solvents, have been researched [12–18]. Co-solvents can increase the mutual solubility of methanol and vegetable oil at lower reaction temperatures, increase the reaction rate and they are usually easy to be recovered and reused.

The use of a mixture of methanol and tetrahydrofuran led to a reaction rate 15 times higher than the reaction rate with methanol at low temperature [13]. Tetrahydrofuran was also used to obtain biodiesel from *Jatropha curcas* seed oil; then, 40 °C was the optimal reaction temperature [14]. Acetone as co-solvent was suitable to produce biodiesel at room temperature by using 4.5:1 as acetone/methanol molar ratio, 1 wt% KOH and less than 30 min as reaction time [15]. Acetone was also used to obtain 98% conversion at 40 °C, with 20 wt% acetone, 5:1 M ratio of methanol/oil, 1 wt% KOH and 30 min as reaction time [16]. The transesterification of cotton seed oil into biodiesel was carried out using diethyl ether, dichlorobenzene or acetone as co-solvent. The optimal reaction temperature was 55 °C for 10 min with 0.75 wt% KOH as catalyst concentration [17]. The ethers are usually good as co-solvent because contain the balance of polar and nonpolar entities required to lower the interfacial surface tension between methanol and vegetable oil [18]. In some cases, the use of a co-solvent allowed the production of biodiesel from grain based feedstock, waste cooking oils and animal fats; although co-solvents must be completely removed from glycerol and biodiesel phase, because of its possible hazard and toxicity [19].

In most of previous works, only one compound was evaluated as co-solvent. For this reason the aim of this work is the study of several co-solvents in the transesterification of rapeseed oil, using methanol as alcohol. A wide overview has been obtained in this work since five compounds were used as co-solvent and whole reaction conditions have been assayed. Catalyst type and concentration, reaction temperature, methanol/oil molar ratio, co-solvent type, co-solvent/methanol molar ratio and agitation rate were studied. In addition, a kinetic and thermodynamic analysis was carried out and fuel properties were determined.

2. Materials and methods

2.1. Materials

Rapeseed oil was provided by Research Center “La Orden-Valdesequera” (Badajoz-Spain) Section of Non-Food Crops. It was

characterized and its fatty acid profile and properties are shown in Table 1. Potassium hydroxide, 85% (KOH) (pellets GR for analysis), was supplied by Merck. Lithium hydroxide 1-hydrate, 99% (LiOH·H₂O), barium hydroxide 8-hydrate, 97% (Ba(OH)₂·8H₂O), aluminium chloride anhydrous, 98% (AlCl₃), zinc chloride, 97% (ZnCl₂) and boron trifluoride, 14% in methanol (CH₃BF₃O), were purchased from Panreac. p-toluenesulfonic acid monohydrate, 98.5% (p-TsOH·H₂O), was supplied by Sigma-Aldrich. Methanol (96%) and all used co-solvents were also purchased from Panreac. The boiling points of the co-solvents were: Acetone (55 °C), DEE (34–35 °C), tBME (55–56 °C), diIPE (68–69 °C), diBE (142–143 °C) and THF (65–67 °C)

2.2. Reaction procedure

According to the experimental installation used in previous works [20–22], the reactions were carried out in a 1000 mL spherical reactor, provided with a thermostat, mechanical stirring, sampling outlet and condensation systems. The same amount of oil was used for all experiments (250 g). Firstly, the oil was placed into the reactor and it was heated up to the reaction temperature. A solution of the established catalyst concentration in methanol was prepared. The desired amount of co-solvent was added to the previous mixture, and the resulting liquid solution was added to the reactor. At spaced intervals, samples were taken out from the reaction mixture and its methyl ester content was determined. Samples and final reaction mixture were placed in separatory funnels to separate the glycerol. Next, the methyl ester phase was heated to remove methanol and co-solvent. Biodiesel was also washed with deionizer water to remove the remaining catalyst. The remaining water was removed by heating at 110 °C.

The studied variables and their intervals of variability were the following: temperature (20, 27, 30, 35 and 40 °C), agitation rate (500, 700, 900 and 1100 rpm), methanol/oil molar ratio (6:1, 9:1 and 12:1), catalyst type (KOH, Ba(OH)₂, LiOH, p-TsOH, ZnCl₂, AlCl₃ and BF₃), concentration of KOH (0.5, 0.7 and 1.0 wt%), co-solvent type (DEE, tBME, diIPE, diBE, THF and acetone) and methanol/co-solvent molar ratio (1:0.5, 1:1, 1:1.5 and 1:2). Reaction time (120 min), oil type (rapeseed) and alcohol type (methanol) were fixed as common parameters in all experiments.

2.3. Methods of analysis

Methyl ester content was determined by means of gas chromatography. A chromatograph Varian 3900 with FID detector and a silica capillary column of 30-m of length, 0.32 mm of ID and 0.25 μm of film thickness, were employed to carry out the analysis. Helium was used as carrier gas. The injector temperature was 270 °C and the detector temperature, 300 °C. The oven was maintained at 200 °C for 21 min, then, it was elevated to 220 °C at 20 °C min⁻¹ and maintained for 10 min. Internal standard

Table 1
Rapeseed oil fatty acid profile and properties.

<i>Fatty acid profile</i>	
C16:0 palmitic	3.5%
C18:0 stearic	0.9%
C18:1 oleic	64.4%
C18:2 linoleic	22.3%
C18:3 linolenic	8.2%
Density _{15°C}	906.8 kg m ⁻³
Viscosity _{40°C}	32.0 cSt
Iodine value	112.2 g ₁₀₀ g ⁻¹
Acid value	2.29 mg _{KOH} g ⁻¹

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