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In situ and conventional transesterification of rapeseeds for biodiesel production: The effect of direct sonication

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ABSTRACT

Rapeseeds were used for the production of biodiesel *via* alkaline transesterification. The effect of direct sonication (24 kHz) during *in situ* and conventional transesterification was studied without the use of external heating and was compared to that of mechanical stirring (600 rpm, 60 °C). In the *in situ* transesterification the use of ultrasonication and mechanical stirring led to a similar high % FAME content (97.2 ± 0.4 and 95.7% ± 0.8 respectively) after 120 min. However the % yield of the extracted methyl esters using mechanical stirring was considerably lower compared to ultrasonication (37.0 and 80.6% respectively) when same conditions were applied (7.5% NaOH w/w of oil, 400:1 methanol to oil molar ratio). The kinetics study of the rapeseed oil methanolysis process *via* direct sonication and mechanical stirring showed that the reaction rate constant is not affected by the method of stirring under specific conditions. Properties of rapeseed biodiesel determined agree with the specifications of the European Standard EN 14214.

1. Introduction

Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats (Georgogianni et al., 2008a). These oils and fats cannot be used directly in a diesel engine because they have very high viscosities (10–17 times greater than conventional diesel) and low volatility (Demirbas, 2007). Various methods can be applied in order to reduce the viscosity of biodiesel such as transesterification, blending with diesel, microemulsification and pyrolysis. Among these, transesterification is the most common because of its simplicity and high yields in alkyl esters produced. Transesterification converts triglycerides, by means of an alcohol, into fatty acid alkyl esters (biodiesel) and glycerol. In the conventional method, pre extracted oil from oil seeds is used as raw material. The main extraction methods include: mechanical extraction, solvent extraction and enzymatic extraction which are characterized by low oil yield, use of organic solvents and high costs respectively (Haas et al., 2004; Atabani et al., 2012).

It has been demonstrated that extraction and transesterification can be performed simultaneously using methanol which acts as an extracting solvent and at the same time as a reagent (Harrington and D'Arcy-Evans, 1985). This combined route is termed "*in situ* transesterification" or "reactive extraction". The advantages are that costs associated with oil extraction, cleanup and refining may be eliminated. In addition, in order for the overall cost of the procedure to be further reduced, the remaining oil-free seed meal can be used in different applications, such poultry feed (Haas et al., 2013). However, the major disadvantage is the extremely high volume of alcohol required compared to conventional transesterification, probably due to mass transfer limitations (Koutsouki et al., 2015). However, studies have shown that the pre-treatment of the feedstock can reduce the required amount of methanol during *in situ* transesterification. More specifically, Haas and Wagner (2011) reported that the combination of flaking, extrusion and drying of soybeans before *in situ* transesterification achieved a minimum nearly threefold reduction in the methanol requirement compared with that for soybeans that had been only flaked and

Abbreviations: TG, triglycerides; DG, diglycerides; MG, monoglycerides; GL, Glycerol; ME, methyl esters; MeOH, methanol; FAME, fatty acid methyl esters.

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dried. Also, the removal of moisture of the seeds prior to *in situ* transesterification can reduce the required amount of the reagents. In particular, Haas and Scott (2007), achieved a 60% reduction in methanol and a 56% reduction in NaOH use by drying the substrate compared to the transesterification of full-moisture flakes.

Research on *in situ* transesterification has been carried out using rapeseeds, sesame seeds, cotton seeds, sunflower seeds, Jatropha seeds, rice seeds, castor seeds, soya seeds and cynara seeds (Kildiran et al., 1996; Haas et al., 2004; Siatis et al., 2006; Georgogianni et al., 2008a,b; Shiu et al., 2010; Kasim and Harvey, 2011; Hincapie et al., 2011; Zakaria and Harvey, 2012; Abo El-Enin et al., 2013; Kartika et al., 2013; Qian et al., 2013; Koutsouki et al., 2015). In addition, the need of minimizing the use of high quality lipids for biodiesel production, has led to the development of methods to use low quality fatty raw materials, such as waste greases, soapstock, or by-products from corn fermentation and animal rendering industry (Haas et al., 2007). Given the fact that each seed has different tissue morphology, reactive extraction could give different results for different feedstock (Atabani et al., 2012).

Rapeseed (*Brassica napus*) is listed as the third most important oil producing crop in Greece. Along with sunflower it has the highest efficiency in biodiesel production (liters of biodiesel produced/hectare of rapeseed cultivation) (Yu et al., 2013). Moreover, the seed contains 40% oil while the meal contains 38–43% protein which can be used as animal feed (Qian et al., 2013). This can reduce rapeseed oil cost compared to other energy crops.

In order to improve the performance of transesterification and thus reduce biodiesel production cost it is important to develop new production methods and novel reactor types. Ultrasonic irradiation has been studied as a new and more efficient mixing tool for biodiesel production, as higher yields and shorter reaction times can be achieved using a lower amount of catalyst and energy compared to conventional methods (Veljković et al., 2012). Various mechanisms may be activated by ultrasound energy promoting various effects. The mechanisms involved are not always known, however most investigators accept that the formation and collapse of micro bubbles are responsible for most of the significant chemical effects observed (Kumar et al., 2010a,b). Ultrasonic irradiation has been used to promote transesterification for biodiesel production using conventional catalyst (such as KOH, NaOH), heterogeneous catalysts (SrO, Na/SiO_2) and enzymes (Kumar et al., 2010a,b, 2012, 2011; Salamatinia et al., 2012; Gharat and Rathod, 2013). It has also been reported that biodiesel produced *via* ultrasonic irradiation shows better characteristics according to the available standards, better clarity, less FFA and residual amount of catalyst remaining in the fuel (Salamatinia et al., 2012).

In the present work direct sonication was used for the production of biodiesel from rapeseeds *via in situ* and conventional transesterification using NaOH as catalyst. The method of direct sonication was studied during transesterification without the use of an external heat source and was compared to that using mechanical stirring. To the best of our knowledge no studies has been carried out on the use of *in situ* transesterification of rapeseeds for the production of biodiesel using direct sonication. This constitutes the novelty of the present study. Furthermore the effect of process parameters such as methanol to oil molar ratio and catalyst concentration was investigated during *in situ* transesterification *via* direct sonication. Because of its wide industrial potential use, the reaction kinetics of methanolysis, being fundamental to reactor design, were also included in the present study. More specifically, a kinetic model was applied for the simulation of the triglyceride (TG) conversion and fatty acid methyl esters (FAME) formation using both direct sonication and mechanical stirring. Lastly, rapeseed biodiesel was characterized by determining its physical and chemical properties.

2. Methods

2.1. Materials and reagents

Methanol, hexane, and sodium hydroxide [purity > 96, 96 and 99% respectively] from Merck were used. Rapeseeds and unrefined rapeseed oil were provided by the Department of Plant Production of the Technological Educational Institute of Epirus in Arta, Greece.

2.2. Equipment

In this study an ultrasonic processor (Model UP 400S, Dr. Hielscher GmbH) was used. The sonicator power output was 400 W at a fixed frequency of 24 kHz with the following horn dimensions: 300 mm × 210 × 145 mm (length × width × height). The diameter of the tip was 7 mm (maximum ultrasonic intensity 300 W cm^{-2}). The horn was made of titanium alloy with 10 levels of amplitude.

2.3. Procedures

2.3.1. *Conventional oil transesterification* via *mechanical stirring (600 rpm)*

Unrefined rapeseed oil (80 g, 0.1 mol), methanol (30 ml, 0.7 mol) and NaOH (1.0 wt.% of the oil) were refluxed in a 250 ml two necked round bottom glass flask equipped with a water condenser. The flask was immersed in a thermostated bath filled with glycerol, the temperature of which was controlled by a proportional integral derivative (PID) temperature controller. The mixture was stirred *via* a mechanical stirrer (600 rpm) and the internal vessel temperature (measured *via* a temperature probe) was 60 ± 2 °C. At various time intervals (2, 4, 6, 12, 20, 40, 60 min) reaction mixture samples of 1 ml were removed from the reaction mixture, neutralized, washed with water and dried.

The reaction was stopped after one hour and the two phases of the mixture were separated using a separatory funnel. After removal of glycerol phase the ester phase was acidified to pH: 2–3, using 4% w/v methanolic solution of citric acid and washed with warm distilled water to adjust pH to 7. It has been shown that the washing water temperature influences the rate of mass transfer of glycerol from the biodiesel into water achieving better purification. A higher washing temperature gives a higher diffusivity of glycerol from biodiesel to the water phase increasing the mass transfer coefficient (Atadashi et al., 2010). Methyl ester phase was dried using Na_2SO_4. The isolated methyl esters were analyzed by gas chromatography.

2.3.2. In situ *transesterification* via *mechanical stirring (600 rpm)*

In order to determine the optimum conditions for the *in situ* transesterification of rapeseed *via* ultrasonication a series of experiments were carried using different concentrations of methanol and NaOH. An additional series of experiments were carried out to compare ultrasonication to mechanical stirring. Different methanol (550, 400 and 300/1 methanol to oil molar ratio), catalyst (7.5 and 9.5% NaOH) concentrations and reaction times (2 and 4 h) were used to optimize extraction of methyl esters.

Rapeseeds were dried overnight in an oven (120 °C) and comminuted using pestle and mortar. Sieves were used in order to separate ground seeds into different sizes. 20 g of 0.3–1.0 mm ground seeds were transferred to the previously described reactor. Methanol (170:1–550:1 molar ratio to oil) and NaOH (3.5–7.5% w/w of oil in the seed) were added and the mixture was heated to reaction temperature (60 ± 2 °C). After 2 h the reaction was stopped and the mixture was filtered. Methyl esters were isolated as described above.