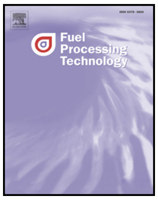
Fuel Processing Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel Processing Technology

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



In situ transesterification of *Cynara cardunculus* L. seed oil via direct ultrasonication for the production of biodiesel

A.A. Koutsouki [a], E. Tegou [b], S. Kontakos [c], M.G. Kontominas [a,d,*], P.J. Pomonis [a], G. Manos [e]

[a] *Department of Chemistry, University of Ioannina, Ioannina 45110, Greece*
[b] *General Chemical State Laboratory, Piraeus 18510, Greece*
[c] *Department of Social Administration and Political Science, Democritus University of Thrace, Komotini 69100, Greece*
[d] *Department of Chemistry, American University of Cairo, New Cairo 11835, Egypt*
[e] *Department of Crop Production, Technological Educational Institute of Epirus, Arta 47100, Greece*

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 20 January 2015
Accepted 21 January 2015
Available online xxxx

Keywords:
Biodiesel
Cynara cardunculus L.
In situ transesterification
Reactive extraction
Ultrasonication
Kinetics

ABSTRACT

Alkaline transesterification of *Cynara cardunculus* L. seed oil with methanol for biodiesel production is investigated. Both in situ transesterification and conventional transesterification were studied using ultrasonication (24 kHz, without external heating) and mechanical stirring (600 rpm, 60 °C). For in situ transesterification, the use of ultrasonication and mechanical stirring led to similar high % FAME content (96.0 and 93.0% respectively) after 20 min. However the % yield of the extracted methylesters using mechanical stirring was lower compared to ultrasonication (50.4 and 85.1% respectively). For in situ transesterification via ultrasonication the optimum conditions were: 9.5% NaOH w/w of oil and a 550:1 methanol to oil molar ratio. In conventional transesterification, using ultrasonication, a high % FAME content of methylesters (97.0%) was obtained after 20 min. Respective % FAME content for mechanical stirring was 95.8% after 1 h. In both cases of conventional transesterification 1% w/w of oil NaOH as catalyst and a 7:1 methanol to oil ratio were used. The kinetics used for methanolysis reaction using sonication or mechanical stirring involved the irreversible second order reaction followed by the reversible second order reaction close to equilibrium. *Cynara* biodiesel properties determined, comply with the specifications of the European Standard EN 14214.

1. Introduction

According to the reports of international agencies there will be an approximate 50% increase in the demand for energy by the year 2030. Moreover the resources of oil and gas are expected to be exhausted within the next 50 years, if their use continues at the present pace [1]. Consequently, the need for exploitation of alternative "greener" fuels has been increasing steadily. Biodiesel is an alternative fuel for diesel engines, derived from renewable resources such as vegetable oils and animal fats. It has the advantage of being biodegradable and able to reduce most exhaust emissions such as monoxide, unburnt hydrocarbons, and particulate matter [2,3]. The main disadvantage of biodiesel is its high price compared to conventional diesel.

Among various biodiesel production methods, transesterification is the most common. Transesterification converts triglycerides, by means of an alcohol, into fatty acid alkyl esters (biodiesel) and glycerol. In the conventional method, pre-extracted oil from seeds, by means of mechanical pressure or solvent extraction, is used as the raw material. However, the oil yield resulting from mechanical pressure is low while extraction requires large volumes of solvent primarily hexane. Hexane is classified as a hazardous pollutant and is responsible for atmospheric smog and global warming [4].

In situ transesterification or reactive extraction is a different method of production of alkyl-esters, directly from oil-bearing material. It was first studied by Harrington and D'arcy-Evans [5]. During in situ transesterification, methanol acts as an extracting solvent and at the same time as a reagent. Consequently, costs associated with oil extraction, cleanup and refining may be eliminated. Researchers working in this field agree that the main disadvantage of in situ transesterification is the extremely high volume of alcohol that is required compared to conventional transesterification, probably due to mass transfer difficulties [6].

All oil seeds eventually can be used for in situ transesterification. Research on this topic has been carried out using rape seeds, sesame seeds, cotton seeds, sunflower seeds, *Jatropha* seeds, rice seeds, castor seeds and soya seeds [7–17]. Selecting the ideal feedstock is essential given that raw material represents more than 75% of the overall biodiesel production cost [18].

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

* Corresponding author.
E-mail addresses: mkontomi@cc.uoi.gr, michail.kontominas@aucegypt.edu (M.G. Kontominas).

http://dx.doi.org/10.1016/j.fuproc.2015.01.024
0378-3820/© 2015 Published by Elsevier B.V.

Please cite this article as: A.A. Koutsouki, et al., In situ transesterification of *Cynara cardunculus* L. seed oil via direct ultrasonication for the production of biodiesel, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.01.024

Cynara cardunculus L. is a relative new energy crop originally found in the Mediterranean basin. It is an inedible crop and has high potential for energy production due to the fact that its lignocellulosic biomass can be used as solid fuel and its oil (25% w/w) for the production of biodiesel. Additionally, *Cynara* is a perennial crop and well adapted to harsh climate conditions making it a good candidate for the production of biodiesel [19].

The microstructure of plant tissue is complex, consisting of cells, intercellular spaces, capillaries and pores [20]. Reactive extraction can be affected by the morphology of the tissue being extracted and the location of the tissue components to be extracted [21]. Given that in situ transesterification of *C. cardunculus* L. has not been systematically studied [10], this work aims to investigate the factors that affect this process.

As stated above, the main obstacle to large-scale commercialization of biodiesel production is its high cost. Consequently, recent research has focused on developing new methods in order to reduce this production cost. Along this line, novel reactor types have been developed that can improve the performance of transesterification. Recent research in Sonochemistry suggests ultrasonic irradiation as a new and more efficient mixing tool for the production of biodiesel, as higher yields and shorter times can be achieved using less catalyst and energy compared to conventional methods [22].

In the present study *C. cardunculus* L. was used to produce biodiesel using direct sonication via conventional transesterification and in situ transesterification. Specifically, thermal effects of sonication during transesterification were studied without using an external heat source. Moreover the effect of the following reaction parameters was studied: a) different methanol to oil molar ratios, b) different catalyst concentrations and c) ultrasonic irradiation versus mechanical stirring. In addition, basic reaction kinetics were applied to experimental data to determine the order of kinetics of conventional transesterification process using both ultrasonication and mechanical stirring. Last but not least, physical and chemical properties of *Cynara* biodiesel were determined and compared to those specified by the European Standard EN 14214 for biodiesel and conventional diesel.

2. Experimental

2.1. Reagent and materials

Sodium hydroxide (>99%), methanol (>96%) and hexane (>96%) from Merck were used. *C. cardunculus* L. seeds and unrefined oil from *Cynara* were provided by the Department of Crop Production of the Technological Educational Institute of Epirus in Arta, Greece.

C. cardunculus L. moisture and oil content were determined to be 9.1 and 21.0% respectively. The seeds were used after drying and their moisture content after drying was 1.7%. Fatty acid composition of *C. cardunculus* L. oil was determined to be: 11.6% Palmitic acid (16:0), 3.4% Stearic acid (18:0), 31.0% Oleic acid (18:1) and 53.8% Linoleic acid (18:2). The acid value of oil was determined to be 1.2%. Based on this FFA value, alkaline transesterification was correctly chosen for experimental biodiesel production.

2.2. Equipment

An ultrasonic processor (Model UP 400S from Dr. Hielscher GmbH) was used in this study. 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 tip diameter 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)

NaOH (1.0 wt.% of the oil) was dissolved in methanol (7/1 methanol to oil molar ratio) and mixed with 80 g pre-extracted unrefined *Cynara* oil. The mixture was refluxed in a 250 ml two necked round bottom flask equipped with a water condenser. The flask was immersed in a thermostated oil bath, with temperature control being achieved using a proportional integral derivative (PID) temperature controller. The temperature was set at 60 ± 2 °C and the mixture was stirred via a mechanical stirrer (600 rpm). Mixing started at $t = 0$ min. Reaction mixture samples of 1 ml were removed from the flask at various time intervals, neutralized, washed with water and dried. The ester phase was analyzed by gas chromatography.

After 1 h the reaction was stopped. The mixture was placed in a separatory funnel for phase separation. The glycerol was removed and the ester phase was acidified with 4% w/v methanolic solution of citric acid and washed with warm distilled water to adjust pH to 7. Esters were dried using Na_2SO_4 followed by evaporation or residual moisture and methanol using model R 110 Buchi rotary evaporator (R110, Freiburg, Germany) at 90 °C under vacuum (vacuum pump, model D-79112 KNF Neuberger, Freiburg, Germany). The isolated methylesters were analyzed by gas chromatography.

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

Entire *Cynara* seeds (20 g) were dried overnight, comminuted using pestle and mortar and transferred to the previously described flask. NaOH (9.5% w/w of oil in the seed) was dissolved in methanol (650:1 molar ratio to oil) and the solution was mixed with the seeds. The mixture was heated to reaction temperature under mechanical stirring as described above. After completion of the reaction the mixture was filtered and purified as described above.

2.3.3. Conventional oil transesterification via direct ultrasonication (24 kHz)

NaOH (1.0 wt.% of the oil) was dissolved in methanol (7/1 methanol to oil molar ratio) and mixed with 80 g pre-extracted unrefined *Cynara* oil. The mixture was placed in a 250 ml Erlenmeyer flask equipped with an ultrasonic transducer and a digital temperature probe to record changes in temperature. The probe sonicator was placed at 1 cm depth from the surface of the solution. The amplitude of the ultrasonic processor was set at 80% and the cycle at 0.7. Mixing started at $t = 0$ min. When the reaction was completed, the product was purified as described above.

2.3.4. In situ transesterification via direct ultrasonication (24 kHz)

Entire *Cynara* seeds (20 g) were treated as in Section 2.3.2. NaOH (3.5–14% w/w of oil in the seed) was dissolved in methanol (450:1–650:1 molar ratio to oil) and the solution was mixed with the seeds. The mixture was placed in a 250 ml Erlenmeyer flask equipped with the above ultrasonic transducer and a digital temperature probe. The probe sonicator was placed at 1 cm depth from the surface of the solution. The amplitude of the ultrasonic processor was set at 80% and the cycle at 0.7. Mixing started at $t = 0$ min. When the reaction was completed the product was purified as described above.

2.4. Sampling and analysis

The amount and composition of methylesters in biodiesel were determined as follows: 100 mg of sample and 1 ml of methyl heptadecanoate solution (10 mg/ml), used as an internal standard, were placed in a 10 ml vial diluted with 9 ml hexane. One microliter of the solution was injected in an Agilent 6820 Series Gas Chromatograph System equipped with a split/splitless injection system, a flame ionization detector (FID), and a

Please cite this article as: A.A. Koutsouki, et al., In situ transesterification of *Cynara cardunculus* L. seed oil via direct ultrasonication for the production of biodiesel, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.01.024