Fuel 104 (2013) 614–619

Contents lists available at SciVerse ScienceDirect

Fuel

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

Microwave assisted transesterification of waste frying oil and concentrate methyl ester content of biodiesel by molecular distillation

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HIGHLIGHTS

- Waste cooking oil was utilized for biofuel production.
- Biodiesel was obtained from waste cooking oil by transesterification reaction.
- Transesterification reaction time was reduced using microwave heating system.
- Methyl ester content of biodiesel was enriched by molecular distillation.
- Optimum distillation conditions were determined using 4 × 3 factorial design.

ARTICLE INFO

Article history:
Received 23 December 2011
Received in revised form 6 June 2012
Accepted 20 June 2012
Available online 13 July 2012

Keywords:
Waste cooking oil
Microwave synthesis unit
Transesterification
Molecular distillation
Factorial design

ABSTRACT

In this study, microwave assisted transesterification of waste frying oil was carried out in the presence of sodium methoxide ($NaOCH_3$). Parametric studies were performed to investigate suitable reaction conditions such as catalyst amount (0.5–0.75–1.0–1.5 wt.%), reaction time (3–5–7–9 min), temperature (55–60–65 °C), and oil:methanol ratio (1:4–1:5–1:6). Methyl ester content of biodiesel was determined as 90.04–98.85%.

Methyl ester content of biodiesel was increased from 90.04% to 97.74% by molecular distillation at 170–200 °C, 10 mbar and 0.12–0.24 mL/min feed flow rate. Optimum distillation conditions were determined as 0.18 mL/min feed flow rate and 170 °C evaporator temperature by using 4 × 3 factorial design.

1. Introduction

Renewable fuels have come to play an important role in meeting the world's energy requirements. There is a need to find out an alternative fuel to fulfill the energy demand. The use of vegetable oils' derivatives as alternative fuels has increased due to the diminishing oil reserves and the environmental consequences of exhaust gases from petroleum-fueled engines. Biodiesel (fatty acid methyl ester, FAME) is an alternative fuel, produced by transesterification of oil [1–3]. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and, consequently, to the greenhouse effect [4,5].

Transesterification reaction consists of transforming triglycerides into fatty acid alkyl esters in the presence of an alcohol, such as methanol or ethanol, and a catalyst, with glycerol as co-product [2]. Reaction can be catalyzed by alkali, acids or enzymes. Alkali catalysts are the most widely used as they accelerate the process and the reaction conditions are more moderate [1].

The overall biodiesel cost comprises raw material (production and processing), catalyst, biodiesel processing (energy, consumables and labor), transportation (raw materials and final products) and local and national taxes. To date, most biodiesel plants are using refined vegetable oils as their main feedstock. Therefore,

Abbreviations: Adj MS, adjusted mean square; Adj SS, adjusted sum of square; ANOVA, analysis of variance; BF_3, boron trifluoride; DF, degree of freedom; DG, diglyceride; FAME, fatty acid methyl ester; FFA, free fatty acid; GC, gas chromatography; MG, monoglyceride; MSTFA, *N*-methyl-*N*-trimethysilyltrifluoroacetamide; $NaOCH_3$, sodium methoxide; *R*-Sq, *R* squared; *R*-Sq (adj), adjusted *R* squared; *S*, standard deviation; Seq SS, sequential sum of squares; TG, triglyceride; WCO, waste cooking oil.

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http://dx.doi.org/10.1016/j.fuel.2012.06.084

the cost of refined vegetable oils contributed nearly 80% of the overall biodiesel production cost [6]. The use of waste cooking oil instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be about half price of virgin oil [7]. The production of biodiesel from WCO is one of the better ways to utilize it efficiently and economically, besides, meeting partly the global energy demand [8].

In various literatures, it has been reported that WCO contains large amount of free fatty acids (FFAs) along with moisture which are required to be removed to prevent soap formation as FFA of WCO are sensitive to alkali catalyst [9]. The high FFA content (>1% w/w) causes soap formation and low yield of biodiesel product [10].

There are several reports on transesterification of waste cooking oil (WCO) using different reactor and heating system [1,11,12]. An alternative heating system "microwave irradiation" has been used in transesterification reactions of WCO in recent years [13–15].

Molecular distillation is generally accepted as the most suitable method for separating and purifying both thermo-sensitive and high-molecular-weight compounds. This is possible because the low operating pressure and the small distance between the condenser and the evaporator which is of the order of the mean free path of evaporating molecules. The operating pressures are in the order of 0.0001–0.001 mmHg [16,17]. This process has advantages over other techniques that use solvents as the separating agent, avoiding problems with toxicity [18,19].

Several research has been done using molecular distillation unit such as isolation of bio-oil, removing of heavy residues from Brazilian crude oil, separation of diacylglycerols from enzymatically hydrolyzed soybean oil, purification of 1,2-diacylglycerols from vegetable oils, recovery of tocopherol from deodorizer distillate of rapeseed oil, enrichment of decanoic acid in cuphea fatty acids, separation of free fatty acid in rapeseed soapstock and separation of impurity of biodiesel [20–27].

Aim of this study is to obtain biodiesel from waste cooking oil using microwave heating system. Further objectives have been to examine the efficiency of molecular distillation for removing impurities of biodiesel (having low methyl ester content) such as glycerol and glycerides to enrich FAME content and to evaluate optimum distillation conditions such as temperature and feed flow rate.

2. Material and methods

2.1. Materials

Waste cooking oil (sunflower oil) was supplied from Refectory of Anadolu University, Eskisehir–Turkey. Methanol, sodium methoxide, pyridine and MSTFA (*N*-methyl-*N*-trimethysilyltrifluoroacetamide) were supplied from Aldrich. Standards of fatty acid methyl esters were purchased from Accu Standards.

2.2. Equipment

Transesterification reactions were carried out using Start S model microwave synthesis unit, supplied from Milestone Company-Italy. The system (Fig. 1a) was equipped with a reflux condenser, a magnetic stirrer bar and a non-contact infrared continuous feedback temperature system which allows continuous stirring and constant temperature control.

Distillation was performed using laboratory scale molecular distillation unit (UIC KDL-1) to concentrate methyl ester content of biodiesel. Main part of the system has a vertical, double jacketed cylinder (evaporator) with an internal condenser and a rotating roller wiper basket with an external drive (Fig. 1b). Maximum evaporator temperature and evaporation surface area of the distillation unit are 300 °C and 1.8 dm^2, respectively. The vacuum is provided by a mechanical pump and a diffusion pump.

Fatty acid composition of WCO and methyl ester content of biodiesel samples were determined by Agilent 6890 N gas chromatography apparatus equipped with flame ionization detector.

2.3. Experimental procedure

2.3.1. Transesterification reaction

Transesterification reactions were carried out in the presence of sodium methoxide (0.5%, 0.75%, 1.0%, 1.5% by weight of oil) at various reaction temperatures (55, 60, and 65 °C) using oil:methanol molar ratio of 1:4, 1:5, 1:6. The catalyst was dissolved in methanol and the resulting solution was added to the oil. This reaction mixture was then irradiated by microwave field under reflux. After 3–9 min (depending on the experiment) the reaction was captured by immersing the mixture in an ice bath then centrifuged at 4000 rpm for 10 min and the top methyl ester phase was separated from glycerol phase. Upper layer was washed with deionized water in order to remove impurities.

Reaction conditions are given in Table 1.

2.4. Analytical methods

2.4.1. Determination of physicochemical properties of waste cooking oil

Relative fatty acid composition of WCO was determined as the methyl esters of fatty acid by gas chromatography analysis using Agilent 6890 N gas chromatography apparatus with HP-Innowax column (60 mL × 0.25 mm ID × 0.25 μm film thickness) after converting fatty acids into methyl ester forms using 14% BF_3 in methanol [28]. A necessary procedure associated with this analysis is lipid derivatization. This process changes the volatility of lipid components, and improves peak shape and thus provides better separation [29]. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. Temperature program was started at 60 °C, heated at 4 °C/min to 220 °C and heated to 240 °C at 1 °C/min, staying at this temperature for 10 min [30].

Relative density, viscosity, saponification number, acid value, peroxide value and iodine value of WCO were determined according to standard methods [28,31].

2.4.2. Determination of ester content of biodiesel

Biodiesel purity is defined as the methyl ester content of biodiesel. The methyl esters were firstly derivatized by *N*-methyl-*N*-trimethysilyltrifluoroacetamide (MSTFA) at 25 °C, for 15 min which is known as silylation. Silylation is the most common method used to derivate organic compounds containing active hydrogen atoms (e.g. —OH,=NH, —NH_2, —SH and —COOH), which results in products with reduced polarity, enhanced volatility and increased thermal and catalytic stability necessary for optimal sensitivity and resolution of various components in mixtures by GC analyses. Therefore the methyl esters obtained from the transesterification of WCO were reacted with MSTFA at 25 °C, for 15 min. After silylation, the methyl esters, MG, DG, TG and ester content were identified using gas chromatography (Agilent 6890 N) equipped with DB-5HT column (15 m × 0.32 mm ID × 0.10 μm film thickness) and flame ionization detector. Temperature program was started at 50 °C, heated at 15 °C/min to 180 °C and heated to 230 °C at 7 °C/min, then heated at 10 °C/min to 370 °C, staying at this temperature for 20 min [30,32].

2.4.3. Fuel properties of biodiesel

Physical properties of biodiesel such as relative density, viscosity, flash point, heating value and ester content were determined using standard test methods according to EN 14214.