Renewable Energy 145 (2020) 99–105

Contents lists available at ScienceDirect

Renewable Energy

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

Production of biodiesel from waste shark liver oil for biofuel applications

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ARTICLE INFO

Article history:
Received 25 November 2018
Received in revised form
18 April 2019
Accepted 1 June 2019
Available online 5 June 2019

Keywords:
Biodiesel
Waste shark liver oil
Transesterification
Design of experiments
Homogeneous acid and base catalysis

ABSTRACT

Biodiesel is a renewable alternative to "petro-diesel". There is an established conventional production technology based on refined vegetable oils. However, this is always more expensive than petroleum-based diesel, mainly due to the feedstock cost, and the biodiesel market is based on subsidies. Use of a cheap non-edible feedstock, such as waste shark liver oil (WSLO), would reduce the biodiesel production cost and make the process more economically viable.

In this study, production of fatty acid methyl ester (FAME) from WSLO using both acid (H_2SO_4) and base (NaOH) catalysts were investigated using a Design of Experiments approach (response surface methodology). Due to the high levels of FFA (free fatty acids) homogeneous alkali-catalysed transesterification of WSLO was less effective than the acid-catalysed process, resulting in WSLO to FAME conversion of 12% after 60 min, with maximum FAME conversion of about 40% after 15 min. Acid-catalysed WSLO transesterification achieved 99% FAME conversion at 10.3 M ratio of methanol to WSLO, 6.5 h reaction time, 60 °C temperature, and 5.9 wt % of H_2SO_4 catalyst.

1. Introduction

Biodiesel, derived from vegetable oils or animal fats, is a renewable replacement for petro-diesel in compression ignition engines [1]. Its quality is dictated by ASTM D6751 [2] in the USA & Canada, and EN 14214 in the European union [3]. The main component is fatty acid methyl esters (FAMEs) of long-chain fatty acids [4]. As a clean-burning alternative to diesel fuel, biodiesel has various environmental benefits, including biodegradability, very low toxicity, and reduction in emissions of CO_2 and lower particulate matter and sulphur [5]. Due to the environmental benefits of biodiesel combustion, various government policies have mandated the blending of biodiesel with petro-diesel, resulting in a growth in biodiesel production and consumption [6].

Biodiesel is commonly produced via triglyceride (usually vegetable oil) transesterification and/or free fatty acid (FFAs) esterification reactions in the presence of alcohols [7]. Many types of alcohol can be used for this application, including propanol, butanol, ethanol and methanol., Methanol is most commonly used due to its low price and availability [8]. The rate of reaction is determined by a number of factors, namely: catalyst type and concentration, alcohol/oil molar ratio, reaction time, temperature, moisture content of the oil and the mixing rate [9]. In conventional biodiesel production process, refined vegetable oils and homogeneous base catalysis are frequently used.

The alkali-catalysed transesterification process requires low levels of FFA (<2.5%) to avoid soap formation and catalyst deactivation [10], as shown in Equation (1). The oil and alcohol feedstocks are also required to be substantially anhydrous with total water content less than 0.06 wt%, as water may favour the saponification reaction [11]. Water also promotes ester (FAME) hydrolysis to form FFAs as shown in Equation (2), leading to catalyst deactivation and saponification reactions.

$$RCOOH + NaOH \rightarrow RCOO^{-}Na^{+} + H_2O \quad (1)$$

$$RCOOCH_3 + H_2O \xrightarrow{\text{Base Catalyst}} RCOOH + CH_3OH \quad (2)$$

The ester saponification subsequently reduces the FAME conversion and renders the separation of ester and glycerol difficult [12–14]. Soap formation decreases FAME conversion, necessitates the use of more catalyst and alcohol, decreases catalyst efficiency, prevents product separation and consume more energy [15].

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https://doi.org/10.1016/j.renene.2019.06.002
0960-1481/

Therefore, alkali catalysis is not suitable for biodiesel production from feedstock containing high FFA and water contents. Acid-catalysed transesterification can tolerate high levels of FFAs in the feedstock. The most commonly used acid catalyst for biodiesel production is H_2SO_4, due to its higher activity, low price and availability [12,16]. Major disadvantages of acid catalysts are lower reaction rates, longer reaction times, higher reaction temperature conditions, and higher investment costs for higher grade materials to withstand the corrosive effect of the acids in the equipment.

Notwithstanding the advances in biodiesel production technology, the cost of biodiesel remains substantially higher than that of petro-diesel. Hence, a major challenge to biodiesel consumption is high production cost [17]. This is mainly due to the high cost of feedstocks, which accounts for 70–95% of the total biodiesel production cost [18]. This has caused increasing research interest in the use of cheap, non-edible feedstocks, such as waste oils to improve the production cost and make the process economically viable.

Previous studies have shown that for refined vegetable oil transesterification at 6:1 methanol to oil molar ratio at 1 h reaction time and 5250 kg/h oil throughput, about 2390 MJ/h (5.83 MJ/kg) of energy is required for methanol recovery and 7448 MJ/h for downstream biodiesel purification [19]. Therefore, energy requirements for methanol recovery and biodiesel purification in the conventional biodiesel process correspond to 23.3% and 72.6% of the total energy costs (10256 MJ/h), respectively. The methanol recovery and biodiesel purification costs account for over 95% of the total energy consumption in the conventional biodiesel technology, whiles heating costs for the reaction vessel, pumping and glycerol purification consume less than 5% of the total energy required [19]. Hence, the estimated energy cost is 1.874 MJ per kg of biodiesel produced for transesterification of 5250 kg/h of oil using the conventional biodiesel process. At the optimal FAME conversion of 99.0 ± 1.1% and reaction conditions of 10.3 M ratio of methanol to WSLO, 6.5 h reaction time and 60 °C temperature, an equivalent biodiesel throughput would require 5820 MJ/h for excess methanol recovery and approximately 7448 MJ/h for the biodiesel purification. Estimated energy cost at the optimal conditions for the WSLO transesterification was 2.527 MJ/kg, which was about 35% higher than the conventional process using refined vegetable oil. In terms of the actual biodiesel production, the vegetable oil feedstock can contribute up to 70–95% of the total biodiesel production costs [18], while the cost of energy and utility account for less 10% [19]. The 35% increase in the energy and utility would be negligible compared to cost of the refined vegetable oil feedstock. Therefore, producing biodiesel for WSLO would reduce the production cost and improve the process economic.

Sharks' livers comprise 25–30% of their body weight [20]. The WSLO (Waste Shark Liver Oil) is obtained by exposing the liver to the sun until it melts, so that the oil can be collected. The major constituents of WSLO are triglycerides (TG), diacylglycerol ethers (DAGE), and squalene [21].

Generally, sharks form 50% of the by-catch in the deep water fisheries of New Zealand and Australia, yet most of the sharks are discarded and the liver oil is unutilised [21]. Historically, the discarded WSLO was used to proof wooden boats [22], but now these applications are no longer required as modern boats are made of fibreglass. The excess WSLO derived from these discarded shark livers in the fishing industry could instead be processed to obtain valuable products like biodiesel, squalene, and omega-3 PUFAs –including EPA and DHA. While the TG components of the WSLO can be converted to biodiesel using existing biodiesel processing technologies, the squalene, EPA and DHA can be extracted and sold as value-added products through a biorefinery process.

This study investigates the productions of FAME from WSLO using H_2SO_4 and NaOH catalysis. The biodiesel processes developed in this study was optimised using the Design of Experiment (DoE), by a response surface method. DoE is a statistical tool used to evaluate, and optimise, the relations between variables and system responses. The advantage of DoE lies in minimising the number of experimental trials required to cover a particular parameter space.

2. Materials and methods

2.1. Materials

The feedstock used for this study was WSLO obtained from the Carcharhinidae family. The oil was sourced from Sur, Sultanate of Oman, which is one of the largest collection centres for WSLO in Oman. Sulfuric acid (H_2SO_4, 98% purity, Sigma-Aldrich, UK) was used as an acid catalyst and granulated sodium hydroxide (NaOH, 97% purity, Sigma-Aldrich, UK) as an alkali catalyst. The alcohols used were anhydrous methanol (99.8% purity, Sigma-Aldrich, UK). Methyl heptadecanoate (99% purity, Sigma-Aldrich, UK) was used as an internal standard for gas chromatography (GC) analysis of the FAME produced. Acetic acid (99.5% purity, Sigma-Aldrich, UK) and sodium carbonate (99.5% purity, Sigma-Aldrich, UK) were used for quenching the reactions. A standard grain FAME Mix—10 mg/mL in dichloromethane, part number: CRM47801, from Sigma-Aldrich, UK—was used for identifying the FAME peaks in the chromatogram.

2.2. Characterisations of the waste shark liver oil

The WSLO was characterised for its water and FFA contents, lipid classes, as well as the fatty acid profile. The water content analysis was performed using a Karl Fischer Titration with HYDRANAL - coulomat AG as a titration reagent in a C30 Karl Fischer Titrator (Mettler Toledo, UK). The titration reagent was titrated until a steady background end point of 20 μL/min was achieved, followed by additions of about 0.2 g of the WSLO sample using a 1 mL syringe. The added samples were then titrated until a stable endpoint was achieved, to determine the water content of the WSLO. FFAs and lipid classes in the WSLO, such as the triglycerides (TG), diglycerides (DG) and monoglycerides (MG), were determined using Iatroscan MK-6s. The Iatroscan thin-layer chromatography (TLC)–flame-ionisation detection is a widely used technique for determination of lipid-classes and FFA contents.

The fatty acid profile of the WSLO was obtained by converting it into FAME via complete transesterification with methanol and then analysing using the BS EN 14103:2003 standard [23]. The WSLO transesterification was carried in a batch reactor at 18:1 M ratio of alcohol to oil, 6 wt % H_2SO_4, 60 °C and mixing was 720 rpm. Samples were collected at 30min intervals from the reaction mixture and analysed for FAME profile using a gas chromatography (GC), with the methyl heptadecanoate as an internal standard. This was continued until no further increase in FAMEs was observed. The FAME peaks were identified by their retention times using the grain FAME, and the FAME profiles quantification were done using peak areas of the internal standards based on the method BS EN 14103:2003 [23] as shown in Equation (3), where (A) is the peak area of a specified FAME, A_i is the peak area of methyl heptadecanoate, C_i is the concentration (mg/mL) of the methyl heptadecanoate solution, V_i is the volume (mL) of the methyl heptadecanoate solution, and m is the mass (mg) of the sample. The average molecular weight of the WSLO, as well as the average molecular weights of the TG, DG and MG, were calculated using the obtained fatty acid profile. The calculated WSLO molecular weight was used to determine the exact amount of alcohol required for the transesterification reaction: