Fuel Processing Technology 116 (2013) 241–249

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

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

Ultrasound assisted interesterification of waste cooking oil and methyl acetate for biodiesel and triacetin production

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 14 July 2013
Accepted 14 July 2013
Available online xxxx

Keywords:
Biodiesel
Waste cooking oil
Interesterification
Process intensification
Ultrasound

ABSTRACT

Intensification of the interesterification reaction of waste cooking oil with methyl acetate using potassium methoxide as a catalyst has been carried out using ultrasonic horn (frequency of irradiation of 22 kHz and rated power of 750 W). Experiments have been performed at different operating parameters viz. reaction temperature (30, 40 and 50 °C), oil to methyl acetate molar ratio (over the range of 1:4 to 1:14), catalyst concentration (0.5, 1.0 and 1.5% by weight of oil) and amplitude of ultrasound (40, 50, 60 and 70%) with an objective of understanding the effect of important operating parameters on the extent of conversion of waste cooking oil to the ester. It has been observed that maximum yield (90%) of biodiesel from waste cooking oil using sonochemical reactors was observed at a molar ratio of 1:12, catalyst concentration of 1.0% and temperature of 40 °C. It is also observed that higher conversion was obtained in the presence of ultrasound as compared to the conventional method. Kinetic studies have been carried out to determine the rate constant by fitting the obtained experimental data to a second-order rate equation. It has been observed that rate constant increases with an increase in temperature and the activation energy is found to be 56.97 kJ/mol.

1. Introduction

Biodiesel is generally referred to as fatty acid esters, which can be essentially synthesized from oils or fats using the esterification based reactions. Biodiesel has several advantages over petroleum derived diesel such as biodegradability, non-toxicity, lower harmful emissions, higher flash point, excellent lubricity and superior cetane number [1]. Moreover, biodiesel is essentially free of sulfur and the engines fuelled by biodiesel emit significantly fewer particulate matters, residual hydrocarbons (due to near complete combustion) and less carbon monoxide as compared to the engines operating on conventional petrobased diesel [2]. Due to the depletion of petroleum reserves and increased environmental concerns, synthesis of alternative fuels has been a significant point of interest to the researchers. Overall, biodiesel has a huge potential to replace exhaustible fossil fuel, ensuring the sustainability of human development and energy sources [3]. It is, however, estimated that the cost of biodiesel is approximately 1.5 to 2 times higher than that of the petroleum based diesel fuel [4]. The reasons for the higher price of biodiesel are as follows: a) 70–95% cost of biodiesel synthesis process is from the cost of raw materials such as food grade vegetable oils [5] b) low rates of reaction due to mass transfer limitations in the heterogeneous reaction system and c) difficulty in the separation of biodiesel from the side product and unreacted alcohols giving lower yields.

The production cost of biodiesel can be reduced by using waste cooking oil (WCO) as a starting raw material, which is less expensive than pure vegetable oil and also by employing interesterification process instead of the more commonly used transesterification process for biodiesel production. The interesterification of oils and fats with methyl acetate provides a promising alternative to transesterification because of the formation of triacetin instead of glycerol. This complex reaction is composed of three consecutive reversible reactions, which are shown in Scheme 1 [6]. Triacetin is used mainly as a plasticizer and a gelatinizing agent in polymers and explosives and as an additive in tobacco, pharmaceutical industries, and cosmetics. Recent studies have also shown that triacetin may be added to the formulation of biodiesel (up to 10% by weight) and the blended biodiesel still meets the quality standards set by ASTM D6451 and EN 14214 because of its mutual solubility [7]. Interesterification has been mostly studied in the presence of enzymes [8–10] or under supercritical conditions [3,11–14]. Supercritical and enzymatic methods of interesterification have their own disadvantages. The main disadvantages of supercritical method include (a) operations at very high pressures (20–40 MPa); (b) requirements of high temperatures (350–400 °C) resulting in much higher heating and cooling costs; (c) high oil: methyl acetate ratios (usually set at 1:42) [12] and finally the supercritical method entails higher costs for the evaporation of the unreacted methyl acetate. The drawbacks of enzymatic route of interesterification are significantly higher production costs [15] as well as difficulty in manufacturing at larger scales due to the need for a careful control of the reaction parameters and inherent slowness of the reaction [16].

Based on this analysis, it can be established that there is a need to develop sustainable process intensification technology for biodiesel production from WCO sources based on interesterification with an

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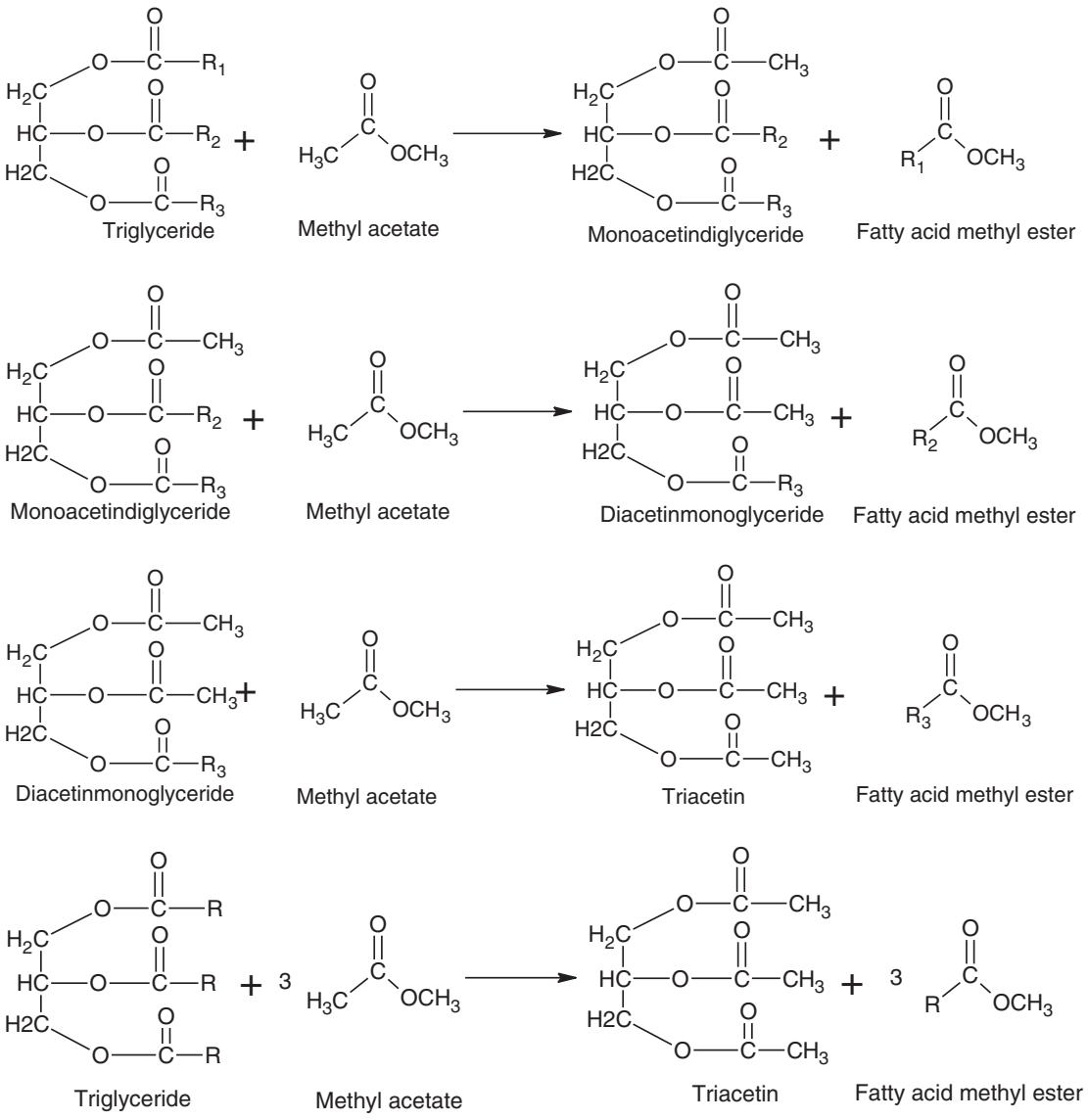
http://dx.doi.org/10.1016/j.fuproc.2013.07.004



Scheme 1. Interesterification reaction (Initial 3 equations show the individual steps whereas final equation gives the overall reaction).

objective of reducing the cost of processing. Cavitational reactors can offer a useful energy-efficient process intensification approach for biodiesel production as compared to other approaches for intensification such as microwave irradiation, oscillatory flow reactor, microchannel reactor, addition of co-solvent and supercritical uncatalyzed transesterification [17]. However, a careful study of the existing literature indicates that there has been absolutely no study related to the use of cavitational reactors for intensification of synthesis of biodiesel and triacetin using the interesterification reaction route. With this background, the present work deals with the intensification of interesterification reaction using sonochemical reactors, which are based on the generation of cavitation events due to the pressure fluctuations induced by the incident ultrasound waves. The interesterification reaction of pretreated WCO has been carried out in the presence of potassium methoxide as a catalyst using ultrasonic horn. Potassium methoxide has been selected as the catalyst for interesterification reaction due to the fact that it gives higher yield of biodiesel in interesterification reaction as compared to other catalysts such as potassium hydroxide, or PEGK (Polyethylene glycol complex with potassium). Experiments have been performed in the presence of potassium methoxide as a catalyst at different temperature, methyl acetate to oil molar ratio, catalyst concentration and amplitude to investigate the dependency of biodiesel yield from WCO. Kinetic constant as well as activation energy for the interesterification reaction have been also determined at optimum operating conditions. Also, the properties of the synthesized biodiesel from these methods have been evaluated in order to match with ASTM standards.

2. Material and methods

2.1. Materials

Waste cooking oil was procured from a local restaurant (Garnish Restaurant, King's Circle, Mumbai, India). Analysis of the WCO (Table 1) indicates that it is mainly composed of 91% unsaturated fatty acids (linoleic and oleic acids) and 9% saturated fatty acids (palmitic and stearic acid). Table 1 also shows the properties of waste cooking oil used as the starting raw material. Methyl acetate, potassium hydroxide pellets (LR grade), ortho-phosphoric acid, molecular sieves (3°A) used in the experimental work were procured from S.D. Fine Chem. Ltd., Mumbai. The weak anion-exchange resin (Indion 860) was obtained from Ion Exchange Ltd., Mumbai. Acetonitrile and acetone