Fuel Processing Technology 128 (2014) 388–393

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Intensification of synthesis of biodiesel from palm oil using multiple frequency ultrasonic flow cell

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ARTICLE INFO

Article history:
Received 16 March 2014
Received in revised form 1 August 2014
Accepted 3 August 2014
Available online xxxx

Keywords:
Biodiesel
Intensification
Multiple frequency
Ultrasound
Transesterification
Cavitation

ABSTRACT

Biodiesel is one of the most promising alternatives for fossil fuels but the synthesis of biodiesel is hampered by significant mass transfer and equilibrium limitations along with higher energy requirements especially for the downstream processing. The present investigation focuses on the intensification of transesterification reaction for the generation of biodiesel using palm oil as the feedstock in the presence of KOH as a catalyst. For the first time, a triple frequency ultrasonic reactor (combination of 28–40–70 kHz) has been used for the intensification using palm oil with an objective of reducing the reaction time, molar ratio as well as possibly increasing the yield of biodiesel. The optimized parameters of reaction time, reaction temperature, and the obtained yield (%) in this ultrasound assisted system have been compared with the conventional approach of mechanical stirring. Also, within this ultrasound assisted approach, single, dual and triple frequency modes of operation have been compared to achieve an effective intensification. It has been observed that the cavitation effects were higher for the triple frequency operation as compared to the dual and single frequency operations. The maximum yield of biodiesel obtained with the triple frequency approach, at 3:1 molar ratio of methanol to oil with 1 wt.% potassium hydroxide as catalyst was 93% with a significantly reduced reaction time of 15 min as compared to 3 h required in case of conventional stirring to achieve 75% yield. The results of this investigation support that using multiple frequency ultrasonic irradiation is beneficial in intensifying the transesterification reaction.

1. Introduction

Biodiesel is among the promising alternatives for fossil fuels and is mainly produced from animal fats and vegetable oils but in recent years, use of various renewable sources including recycled oil or the waste cooking oil has been dominating due to the sustainability issues [1,2]. It is often claimed that biodiesel has several properties that are beneficial to the environment as compared to the traditional petroleum based fuels. Biodiesel is considered to be an excellent alternative for the petro-based diesel fuel based on the following factors [3–5]:

1. Antifoaming: Pure biodiesel (B100) has excellent anti-foaming properties which ensure faster filling of vehicles without any possible foam overflows or leaks.
2. Cetane number: Normally the Cetane number of biodiesel is in the range of 45–70, whereas for the petroleum diesel fuel it is in the range of 40–52.
3. Oxygen content: Biodiesel contains 11% oxygen that leads to smoother combustion, whereas diesel fuel doesn't contain any oxygen.
4. Cold flow properties: In petroleum diesel fuels, a large number of components are present and each of the components has its own crystallization temperature and thus solidification is a gradual process. Biodiesel is a much simpler mixture containing very few components so that the solidification is rapid.

Biodiesel is defined as a mixture of mono-alkyl esters of long-chain (C16–C18) fatty acids derived from vegetable oils or animal fats. Biodiesel can be produced from different varieties of feedstock such as vegetable oils (palm, soybean, peanut, cottonseed, sunflower, rapeseed, and coconut), animal fats (tallow) and used oils (e.g., frying oils). Methanol is the most commonly used alcohol for the production of bio-diesel though other alcohols like *iso*-propanol or ethanol may also be considered. The most commonly used technology for the production of biodiesel is the transesterification of triglycerides (oil) with alcohol giving fatty acid alkyl esters (biodiesel) as the main product and glycerin as the by-product. As the reaction is reversible, an excess amount of alcohol is required to shift the equilibrium to the product side. The variables that affect the transesterification process are reaction time, reaction temperature, intensity of mixing, ratio of oil to alcohol, concentration and type of catalyst and feedstock [6–11]. Often the transesterification reaction is severely limited by mass transfer giving much lower rates of reaction and hence there is always scope for

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http://dx.doi.org/10.1016/j.fuproc.2014.08.002
0378-3820/

intensification. In a range of techniques available for intensification, ultrasonic irradiation based approach could be considered as an effective one to assist and intensify the transesterification reaction. Passage of ultrasound through the liquid medium results in the formation of intense local conditions attributed to acoustic cavitation, which can be a very successful tool in enhancing the reaction rates in a variety of reactions [12]. The collapse of cavitation bubbles interrupts the phase boundary and causes emulsification due to the jets that impinge one liquid into another liquid [13]. Applying low frequency ultrasonic irradiation could be beneficial for the transesterification of triglyceride with alcohol. Ultrasonication can provide the mechanical energy for mixing and the activation energy for originating the transesterification process though the intensification will be mainly due to the mechanical effects leading to better mixing and the formation of fine emulsion [14,15]. Ultrasound assisted transesterification gives the advantages of shorter reaction period and hence less energy consumption along with using an effective molar ratio of methanol to oil as compared to conventional mechanical stirring [16,17]. Stavarache et al. [18] reported that conversion of vegetable oil to methyl esters was the highest for 1.0% (w/w) NaOH (i.e., 95% after 10 min at room temperature using ultrasonication of 28 kHz). Stavarache et al. [13] used ultrasonically driven continuous process for palm oil transesterification and reported more than 90% conversion using a catalyst (NaOH or KOH) concentration of 1 wt.% and a reaction time of less than 20 min. Hanh et al. [19] studied the effects of molar ratio, catalyst concentration and temperature on the transesterification of triolein with ethanol under ultrasonic irradiation and reported optimum conditions of ethanol to triolein for the formation of ethyl ester at 25 °C were 6:1 (mole ratio). It is important to note that all these studies were based on the use of single frequency ultrasonic irradiation at a laboratory scale of operation. The present work deals with the use of triple frequency reactor for the intensification of biodiesel synthesis from palm oil. The use of multiple frequency reactors for biodiesel synthesis has not been reported in the past and this forms the novelty of the present work. For the transesterification reaction, palm oil has been used as the starting feedstock due to its abundant availability in Malaysia. Malaysia is the largest exporter of palm oil in the world. About 40% of palm oil is mostly consumed into cooking oil, margarine, specialty fats and oleochemicals. Considering these proportions, palm oil could be a useful resource for the production of biodiesel without really inducing the food against energy conflict.

2. Materials and methods

2.1. Materials

The chemicals used include palm oil which was purchased from a local store; Methanol (99%), Potassium hydroxide (85%) and Phenolphthalein indicator obtained from Fisher Scientific, Germany and were of analytical grade and used as-received.

2.2. Triple frequency ultrasonic reactor

The schematic representation of hexagonal triple frequency ultrasonic reactor (Sonictron, Malaysia) has been shown in Fig. 1. The reactor was made of SS with the dimensions of 1000 mm × 600 mm × 1050 mm (length × width × height) with the operating capacity of 15 L. The operating frequencies of transducers are 28, 40 and 70 kHz with the rated dissipation power of 300 W per frequency setting. The two opposite plates in the hexagonal reactor mounted by six piezoelectric transducers have the same irradiating frequency. The set-up is also provided with cooling/heating coils by which temperature could be controlled and the reaction can be conducted at the desired temperature. Calorimetry experiments were performed on different frequency settings to obtain the actual power dissipated and energy efficiency of the system. Considering these three frequencies, there is a possibility of operating the system with seven frequency modes (28, 40, 70, 28–40, 40–70, 28–70 and 28–40–70 kHz).

2.3. Experimental procedure

Any water or moisture in the palm oil feed is likely to consume some of the catalyst and may slow down the transesterification reaction. Owing to this, palm oil was preheated at 110 °C which ensures complete removal of water, if present. In each experiment, 100 g of preheated oil with a mixture of methanol and potassium hydroxide at the selected mole ratios was taken in a glass reactor and was immersed in the water medium of triple frequency ultrasonic reactor. KOH at 1 wt.% of oil was premixed with methanol for all the experimental conditions. The frequencies employed were single frequencies (28, 40 and 70 kHz), double frequencies (28–40, 40–70 and 28–70 kHz) and triple frequency (28–40–70 kHz). In all seven different modes of operation were performed. The progress of reaction was monitored by taking the samples at regular intervals of 5, 10, 15, 30 and 45 min and subjected to analysis. The methanol to oil molar ratio considered were: 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 and 9:1. For comparison, the same reaction was also conducted under mechanical stirring by employing a catalyst concentration of 1%, maximum methanol to oil molar ratio of 9:1, a temperature of 60 °C and for a reaction period of 120 min. After completion of reaction, the mixture was transferred into a separating funnel to induce the phase separation. The FAME (fatty acid methyl ester) was formed in the upper layer whereas glycerol was formed in the lower layer. The traces of catalyst in the FAME layer were washed with warm water and then dried by subjecting it to 110 °C for 30 min.

2.4. Analysis

After the reaction, two distinct layers were observed; the top layer (translucent yellow) and the bottom layer (translucent brown). The top layer mainly consists of fatty acid methyl esters (biodiesel) and the bottom layer consists of glycerin. The biodiesel layer varied in its lucidity; appearing to be very cloudy in some of the batches to clear in others. Besides, no separation was observed in some of the batches. Following this, additional methanol was added to the reaction, as it is believed that sufficient methanol required for esterification might not be present in the system. To check the superficial quality of biodiesel, a visual analysis was made on the product after the initial transesterification reaction to see whether two distinct layers have been formed. Following the visual observation of two layers being found satisfactory, the separation of two layers was achieved based on the differences in the density. The weight of biodiesel layer was measured and used in the Eq. (1). to calculate the yield. We have calculated the yield of biodiesel (weight basis) based on the amount of biodiesel produced with respect to the amount of palm oil initially employed (both have been quantified by weighing them) as give below:

$$\text{Yield of biodiesel} = (\text{Weight of biodiesel formed}) / (\text{Weight of palm oil used initially for transesterification}). \quad (1)$$

2.5. Physicochemical characterization of palm oil

2.5.1. Iodine value

Iodine value is expressed as grams of iodine that can react with 100 g of fat or oil and can be used to quantify the degree of unsaturation of the fat/oil. The iodine value obtained for the palm oil was 56 g of I_2/100 g of oil.

2.5.2. Acid value

Acid value indicates the presence of free fatty acids or acids formed as a result of oil degradation and burning (during or after processing).