Journal of Industrial and Engineering Chemistry 35 (2016) 14–19

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Short communication

Determining optimum pulse mode for ultrasound enhanced biodiesel production

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ARTICLE INFO

Article history:
Received 23 October 2015
Received in revised form 29 December 2015
Accepted 3 January 2016
Available online 8 January 2016

Keywords:
Pulse-sonication
Duty cycle
Energy consumption
Alcohol effect
Reaction temperature

ABSTRACT

This study evaluated the most suitable pulse mode (pulse ON–OFF pattern) for transesterification of waste cooking oil (WCO) using sodium hydroxide. Pulse sonication effect was investigated using ethanol, methanol, and ethanol–methanol mixtures to convert waste cooking oil into biodiesel. The importance of duty cycle (pulse-mode operation) and the role of reaction temperature during the conversion process were discussed. A maximum biodiesel yield of 99% was obtained for a pulse ON–OFF combination of 7 s–2 s at 150 W power output, and the optimum reaction conditions of 9:1 alcohol-to-oil molar ratio (50%-ethanol, 50%-methanol), 1 wt.% of NaOH, and 1.5 min reaction time.

Introduction

Ultrasound irradiation is one of the most promising techniques for biodiesel production. It reduces the process time and catalyst consumption. It can be cost-effective and energy-efficient because it requires only one-third to a half of the energy that is consumed by mechanical agitation [1–4]. In addition, ultrasonication enhances chemical reactions by providing the mechanical energy for mixing as well as the activation energy required for initiating the transesterification reaction [4]. Ultrasound cavitation phenomenon can increase the mass transfer between the oil phase and the reactant during the transesterification process [5]. In general, ultrasound replaces the conventional agitation and heating required to establish close contact between the two immiscible phases involved in the reaction, the triglycerides and the reactant (alcohol). According to Qian et al. [6] the wave frequency and specific ultrasonic energy influence biodiesel yields either under pulse or continuous sonication mode within the range of 20 and 48 kHz. The lower is the frequency; the higher will be the biodiesel yield [7].

Ultrasound in biodiesel production

A wide variety of ultrasonic devices are available to convert triglycerides into fatty acids or biodiesel. These devices may provide direct (applicator or horn) or indirect sonication (i.e. ultrasonic bath or tube type ultrasonicator). Direct sonication is the most effective method, and it has been proven to be more energy-efficient than mechanical mixing [8–10]. Ultrasound (US) is very effective at dispersing a material present in a solution and its application contributes to a more homogenous reaction mixture. The chemical effects of ultrasound originate from several acoustic phenomena where cavitation (formation, growth, and implosive collapse of bubbles in a liquid) is the most important [11]. The cavities or microbubbles are formed when ultrasound passes through the liquid which consist of both expansion (negative pressure) and compression (positive pressure) [12]. The collapse of cavitation bubbles causes acoustic microstreaming or formation of small eddies that increase the mass and heat transfer in the liquid and causes velocity gradients that result in shear stress [13]. The implosive bubble collapse produces intense local heating, high pressures, and very short lifetimes (less than a nanosecond) that releases a large amount of energy [14]. In ultrasound processing, the temperature of the bulk reaction does not necessarily represent the local microscopic temperature which leads to completion of the transesterification reaction [15,16]. Hot spots formed in the cavitating bubbles have equivalent temperatures of roughly 5000 K, pressures of about 1000 atm, and very high heating/cooling rates [15,16]. Thus, ultrasound can create extraordinary

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http://dx.doi.org/10.1016/j.jiec.2016.01.004
1226-086X/

reaction environment in otherwise low temperature reaction mixtures [17,18].

Pulse sonication mode

Several studies were reported on biodiesel production using ultrasound irradiation in continuous and/or pulse conditions. However, very few reports have specifically addressed the importance of using either pulse or continuous sonication [1,9] and the optimum ON/OFF time to reduce energy consumption during biodiesel production [19–22]. For instance, Hingu et al. [23] investigated the effect of pulse sonication using waste cooking oil. They reported that 2 s ON and 2 s OFF resulted in a conversion of 62%, 5 s ON and 1 s OFF increased the conversion to 65.5%, and at 1 min ON and 5 s OFF (for a reaction time of 40 min) the conversion was 89.5%. They reported that the yield was further increased to 94.5% after dry washing the esters. Their optimum conditions were 200 W, 1 wt.% catalyst, 45 °C temperature, and 6:1 alcohol to oil molar ratio. Martinez-Guerra and Gude [9] compared the use of pulse (5 ON, 1 OFF) and continuous sonication (using WCO) for different sets of reaction conditions. The optimum conditions for this study were 98% biodiesel yield for pulse sonication and 93.5% biodiesel yield for continuous sonication. Among others, Kumar et al. [24] reported on pulse sonication mode, for conversion of *Jatropha curcus* oil into biodiesel at pulse cycles of 0.3, 0.4, 0.5, 0.7, and 0.9 s cycles each second and the optimum condition was reported as 0.7 s cycle for a reaction time of 15 min. The maximum biodiesel yield was 98.5%, and reported that there was no significant change in biodiesel conversion after 0.7 s. Similarly in another study by Kumar et al. [25], pulse sonication was used to convert coconut oil into biodiesel. The optimum conditions were 1:6 oil to ethanol molar ratio, 0.75 wt.% KOH, ultrasonic irradiation pulse of 0.3 s cycle each second for a reaction time of 7 min, and a biodiesel yield of 98%. They concluded that ultrasonication reduces the processing time from the conventional heating of 1–4 h to 7 min, and the separation time was reduced from 5 to 10 h (conventional) to less than 30 min (US). Ultrasound helps reduce the amount of catalyst required due to increased chemical activity in the presence of cavitation. It also reduces the amount of excess alcohol [25], and increases the purity of glycerol [24]. Therefore, pulse sonication is proven to be more efficient than continuous sonication. However, the effect of pulse sonication on the purity of glycerol is not clear because the reaction involving free fatty acids and alkaline catalyst causes soap formation, which makes biodiesel purification process difficult depending on the amount of FFA [26]. For this reason, some researchers have studied enzyme catalysts. However, there are several disadvantages associated with enzyme catalysts [26]. For example, the cost of enzymes makes the biodiesel production cost-intensive, and enzyme catalysts require longer reaction time than base catalysts.

Continuous sonication (pulse frequency equal to 1) can induce strong emulsion of alcohol and oil phases in a short time, while pulse sonication (pulse frequency less than 1) improves energy efficiency and enhances mass transfer even with heterogeneous catalytic transesterification reaction [27,28]. Pulse sonication can be used to convert any oil feedstock into biodiesel [8,24,25,27,29]. For example, Ahmad et al. [30] converted marine algae oil into biodiesel through pulse sonication for a reaction time of 25 min at pulses of 9.9 s ON and 5 s OFF. Saez-Bastante et al. [31] also used pulse sonication for different feedstock including coconut oils, palm oils, rapeseed oils, and soybean oils. They noticed that oils with high content of saturated fatty acids did not reach the expected yield (96.5% from oils with high unsaturated fatty acids). In this case, the pulse sonication was set to a 70% duty cycle (i.e. 70% time pulse ON). A wide range of pulse ON/OFF times were reported in many previous studies. None of the studies clearly identified the effect of pulse sonication which is the focus of this study. Therefore, this present work emphasizes the relevance of selecting an optimum pulse time during the transesterification reaction while using ultrasonication. In order to complete the experimental work, WCO, ethanol, methanol, and the mixture of ethanol and methanol along with sodium hydroxide as catalyst (NaOH) were used. Currently, WCO is the most feasible feedstock to produce biodiesel because it is non-edible, and it is considered an environmental hazard if not treated and disposed properly [15]. The following sections describe the effect of pulse time (ON and OFF conditions) on transesterification of WCO and discuss the various parameters involved in determining the appropriate pulse time for transesterification reaction.

Materials and methods

Materials

Waste cooking oil (WCO) was obtained from Perry Market Cafeteria located at Mississippi State University. Molecular weight of the oil (835 g/mol) was calculated by using Gas Chromatography-Flame Ionization Detector (GC-FID). Analysis of WCO revealed a composition of the following fatty acids: 50 wt.% linoleic, 27 wt. % oleic, 8.5 wt.% palmitic, 6.5 wt.% linolenic, 6 wt.% stearic acid, and 2 wt.% others. The average acid value was 4.1 mg KOH/g oil, which was determined according to the ISO 660 standard. The WCO did not require pre-treatment other than filtration prior to the transesterification process. Ethanol, methanol, and sodium hydroxide were purchased from Fisher Scientific. Methanol used in this study was of American Chemical Society (ACS) certified grade and ethanol was of reagent grade. The NO-MS100 ultrasonicator manufactured by Columbia International Technologies was used. It has a maximum output power capacity of 1 kW and an ultrasonic frequency of 20 kHz. The horn is made of titanium alloy with the following dimensions: 2.54 cm diameter tapered to 0.254 cm tip diameter.

Transesterification reaction

Pulse sonication of WCO transesterification reaction was carried out in a 100 mL batch reactor (beaker) equipped with an ultrasound horn and a digital temperature probe. The reaction temperature was measured at ten seconds time interval and a temperature profile was generated for each condition. The experimental conditions include: pulse time ON/OFF 3/1, 2, 3; 5/1, 2, 3; 7/1, 2, 3; 9/1, 2, 3; a reaction time of 90 s, 150 W of power output, 1% catalyst (wt./wt), triglycerides to reactant (methanol, ethanol, ethanol–methanol) ratio of 9:1; and 10 mL of waste cooking oil. The conditions were selected based on the optimum results obtain from our previous study [10]. For the transesterification process, the catalyst was pre-mixed with the reactant for approximately 10 to 15 min for methanol and 15 to 20 min for ethanol. Then, the WCO was added to the homogenous mixture of NaOH and methanol (and/or ethanol) to be later exposed to US irradiation for 90 s of reaction time and 150 W power output. Each reaction condition was repeated three times to calculate standard deviations and to ensure validity of the results. The standard deviation bars are not visible in the figures because they were insignificant, lower than 0.40 (indicates high reproducibility). In order to maintain constant mixture and consistent data, the horn tip was submerged 5–6 mm into the liquid.

Biodiesel purification

After completion of the transesterification process (formation of fatty acid alkyl esters, FAAE), the samples were left over night to settle. The biodiesel layer was separated from the glycerol layer by