Energy 71 (2014) 346–354

Contents lists available at ScienceDirect

Energy

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

Esterification of jatropha oil via ultrasonic irradiation with auto-induced temperature-rise effect

Cesar Augusto Andrade-Tacca [a], Chia-Chi Chang [a], Yi-Hung Chen [b], Do-Van Manh [c], Ching-Yuan Chang [a,d,*], Dar-Ren Ji [a], Jyi-Yeong Tseng [a], Je-Lueng Shie [e]

[a] Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan
[b] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan
[c] Danang Environmental Technology Center, Institute of Environmental Technology, Vietnam Academy of Science and Technology, Da Nang City, Viet Nam
[d] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan
[e] Department of Environmental Engineering, National I-Lan University, I-Lan 260, Taiwan

ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form
31 March 2014
Accepted 21 April 2014
Available online 21 May 2014

Keywords:
Jatropha oil
Esterification
Ultrasonic irradiation
Methyl ester
Acid value

ABSTRACT

Auto-induced temperature-rise effects of ultrasonic irradiation (UI) on the esterification performance of jatropha oil (JO) were studied. Comparisons with other methods of mechanical mixing (MM) and hand shaking mixing were made. Major system parameters examined include: esterification time (t_E), settling time (t_S) after esterification and temperature. Properties of acid value (AV), iodine value (IV), kinematic viscosity (KV) and density of JO and ester product were measured. The esterification conversion efficiencies (η) were determined and assessed. Sulfuric acid was used to catalyze the esterification using methyl alcohol. For esterification without temperature control, η at $t_E = 10$ and 30 min for UI of 56.73 and 83.23% are much higher than those for MM of 36.76 and 42.48%, respectively. At $t_E = 10$ min, the jatropha oil esters produced via UI and MM respectively possess AV of 15.82 and 23.12 mg KOH/g, IV of 111.49 and 113.22 g I_2/100 g, KV of 22.41 and 22.51 mm^2/s and density of 913.8 and 913.58 kg/m^3, showing that UI is much better than MM in enhancing the reduction of AV. The t_E exhibits more vigorous effect on AV for UI than MM. The UI offers auto-induced temperature-rise, improving the mixing and esterification extents.

1. Introduction

It is known that the sources of fossil fuels are limited. An extensive use will result in their complete depletion. Therefore, renewable energy sources have become very desirable [1–5]. Biodiesel, which is made from renewable biological sources such as animal fats and vegetable and plant oils [6,7], has been used as an alternative diesel fuel. It is composed of simple mono-alkyl esters (such as methyl ester). It has recently attracted much attention in many countries because of its availability, renewability, non-toxicity, biodegradability and less air pollutants emissions especially the reduction of emission of carbon dioxide into the environment [8,9]. Biodiesel can be manufactured by transesterification process using source oils to react with alcohol in the presence of the catalyst to form fatty acid alkyl esters (FAAEs) (i.e., biodiesel) and glycerol [10].

Inedible woody oil plants, such as *Jatropha curcas* Linaeus (yielding jatropha oil (JO)) and *Vernicia fordii* (bearing tung oil) are promising biomaterials around the world [11]. *J. curcas* is widespread in arid, semi-arid and tropical regions of the world. It is a drought-tolerant and hardy shrub growing quickly and can be used to prevent and or control erosion, to reclaim land and to grow as a live fence [12].

The conventional method for biodiesel production from jatropha oil involves an esterification treatment before the transesterification. The esterification is a reversible reaction where free fatty acid (FFA) is converted to alkyl esters via acid catalysis. The simplified form of this chemical reaction is presented by the well known equation as:

$$R_1\text{-COOH (FFA)} + R_2\text{-OH (Alcohol)} = R_1\text{-COO-}R_2 + H_2O \quad (1)$$

The transesterification is sensitive to the FFA content in raw jatropha oil. The increase in FFA content will reduce the formation rate [13] and yield [14] of fatty acids methyl esters (FAMEs). Further, the high content of FFA of raw jatropha oil such as 18.29 wt.% (standard deviation $\sigma_{n-1} = 0.28$ wt. %) encountered in this work

* Corresponding author. Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan. Tel./fax: +886 223638994.
E-mail address: cychang3@ntu.edu.tw (C.-Y. Chang).

http://dx.doi.org/10.1016/j.energy.2014.04.066
0360-5442/

may also induce the saponification possibility during transesterification [12–14]. Usually, the acid value (AV) of FFA is firstly reduced in esterification. Berrios et al. [15], Deng et al. [16], Jain et al. [17] and Corro et al. [18] have recommended the application of esterification pretreatment before transesterification process, when the FFA content of an oil or fat is high, in order to avoid the saponification and the reductions of the yield and formation rate of FAMEs. The saponification may also hinder the separation of the ester from glycerin.

The esterification treatment greatly reduces the AV of raw oil which saves the operation cost and processing time. Kywe and Oo [19] carried out the production of biodiesel in pilot plant using raw jatropha oil with an FFA of 8.8 wt. % and produced biodiesel with an FFA of 0.5 wt. %. Deng et al. [16] studied a two-step process using acid esterification to remove the FFA of jatropha oil followed by base transesterification with the application of ultrasonic irradiation (UI). They reported that FFA was reduced from 5.25% to 0.61% at 60 °C using H_2SO_4 for 60 min reaction time in the first step. Chen et al. [12] examined the acid esterification and base transesterification with mechanical mixing (MM), obtaining a jatropha oil biodiesel with AV of 0.12 mg KOH/g. Corro et al. [18] reported a novel solar esterification treatment by solar radiation employing Zn filings as solid catalyst with followed base transesterification, indicating that the AV was reduced from 18.5 to 0.38 mg KOH/g in the jatropha oil biodiesel.

The UI method uses less amount of catalyst, reduces the esterification time, while offers an excellent mixing with effective emulsification and mass transfer. The rate of ester formation is significantly enhanced, due that the esterification reaction is controlled by mass transfer which is improved by UI. The UI also generates heat with an increase of temperature offering a positive influence on esterification. Therefore, the UI gives esterification conversion efficiency (η) higher than the conventional mechanical mixing promoting the biodiesel yield, in addition to its wide availability, low cost, non-contamination and easy implementation.

In the above-mentioned studies, the reaction temperatures were held constant for mechanical mixing MM as well as UI. One should note that UI may also induce the heating effect. This can increase the temperature and thus in turn enhance the reaction extent. The application of UI should keep the advantage of simultaneous temperature rise. Hence, this study was aimed at examining the auto-induced temperature-rise roles of UI during the esterification of jatropha oil. Effects of major system parameters on the esterification performance emphasized on the reduction of AV were elucidated. These include esterification time (t_E), settling time (t_S) and reaction temperature (T).

2. Materials and methods

2.1. Materials

Jatropha oil was supplied by Ozone Environmental Technology Co., Yi-Lan County, Taiwan, with acid value AV = 36.56 ($\sigma_{n-1} = 0.56$) mg KOH/g, iodine value (IV) = 102.23 ($\sigma_{n-1} = 4.87$) g I_2/100 g, kinematic viscosity (KV) at 40 °C = 31.30 ($\sigma_{n-1} = 2.27$) mm^2/s and density (ρ_{LO}) at 15 °C = 918.45 ($\sigma_{n-1} = 0.24$) kg/m^3. Its molecular weight (MW) is 871.5 g/mol [20]. Methyl alcohol of anhydrous assay with purity of 99.8% and sulfuric acid of 96.7% purity were obtained from Mallinckrodt, Phillipsburg, NJ and Sigma–Aldrich, St. Louis, MO, respectively.

2.2. Esterification procedures

The acid catalyzed esterification pretreatment was carried out in a 500 mL batch reactor without and with cooling/heating systems. The cooling and heating were, respectively, operated by a refrigerated and heating bath circulator, model B10/-40, Firsteck Scientific Co., Taipei, Taiwan. A sample of 183.82 g jatropha oil was employed for a batch test. The sample was mixed with methanol with molar ratio of methanol to oil (M/O) = 11 and sulfuric acid as a catalyst with wt. % relative to oil (m_C) = 0.92 wt. %. The total sample volume (V_L) was 300 mL. The mixed sample was immediately subjected to the UI by an ultrasonic probe (Model 300 W, from Hoyu Technology Co., Taipei, Taiwan) operated at 25 kHz with power (P_{WUI}) at 90% (270 W) of its maximum power (300 W). The esterification times t_E for UI (t_{UE}) were conducted at 5, 10, 15 and 30 min. Different settling times t_S of 5, 10, 15, 20, 30, 40 and 1440 min at ambient temperature were kept after UI to allow post esterification reaction. The reaction temperature of sample (inside the reactor) during the esterification reaction was measured by a thermal couple (Firstteck Scientific, model-B403, Taipei, Taiwan).

After esterification, the sample was generally settled for proper t_S of 10 min unless otherwise specified. The reaction was then terminated by washing with saturated sodium chloride solution. After the mixture was settled for 3 h, it was separated into three layers. The lower, middle and upper layers of (1), (2), and (3), respectively, are (1) salt water, (2) mixture of glycerol, residual catalyst, methanol and soap, and (3) jatropha oil crude ester, which can be drawn out easily from the top of the separation funnel. The jatropha oil crude ester was then kept in the refrigerator waiting for analysis and avoiding its decomposition.

For the comparison of UI with sole mechanical mixing MM, the same experimental conditions, except the temperature, were carried out for MM with stirring speed (r_S) of 250 rpm. Cases for mechanical mixing examined include (1) without temperature control with initial temperature at ambient temperature (Case MNAT), and (2) with temperature in sample controlled by employing external heating using water bath of 65 °C (Case MHFT). The esterification times t_E for mechanical mixing (t_{ME}) were tested for 2, 5, 10, 15 and 30 min.

2.3. Analysis

The properties of crude jatropha oil ester such as AV, IV, KV and ρ_{LO} were measured according to the standard methods suggested by Manh et al. [9], Chen et al. [12] and Van Gerpen et al. [21]. These methods along with those of flash point and cetane number are outlined in Table 1 and may be further referred to Biofuel Systems [22] and TBOS (Taiwanese Bureau of Standards, Metrology and Inspection) [23]. Standard deviations σ_{n-1} were presented to reflect the errors of the data.

The acid values AV of initial jatropha oil JO and those after esterification treatment were determined according to ASTM D664 standard method employing an automatic potentiometric titration system using potassium hydroxide solution. The quality control of AV is important since the AV increases when the fuel itself deteriorates. The acid value is a measure of free fatty acids which can lead to corrosion and are symptom of water in the fuel or fuel oxidation.

The iodine value IV was measured following ASTM D1959 standard test method by an automatic potentiometric titration system with iodine. The IV is expressed in grams of iodine for the amount of halogens linked with 100 g test sample. The most important application of the IV is to determine the amount of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. A higher IV means that more unsaturated fatty acid bonds are present in a fat.

Kinematic viscosity KV was analyzed employing a Cannon–Fenske style glass capillary viscometer. The resistance to flow of a