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Reduction of FFA in jatropha curcas oil via sequential direct-ultrasonic irradiation and dosage of methanol/sulfuric acid catalyst mixture on esterification process

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ABSTRACT

Production of jatropha-ester (JO-ester) from jatropha oil (JO) under sequential direct-ultrasonic irradiation (UI) with auto-induced temperature rise followed by adding a mixture of methanol/sulfuric-acid catalyst (M/C) dose between high temperature intervals was studied. Comparisons with various doses of 5, 10, 16.6 and 25 mL at different temperature intervals of 108.9–120 °C, 100–120 °C, 85–120 °C and 75–120 °C respectively were performed. System parameters examined include: esterification times (t_E) for UI, settling time (t_S) after esterification and temperature (T). Properties of acid value (AV), iodine value (IV), kinematic viscosity (kV), density (ρ_{LO}) and water content (m_w) of JO and JO-ester product were measured. The esterification conversion efficiencies (η) were determined and assessed. An η of 99.35% was obtained at temperature interval of 108.9–120 °C with 5 mL per dose for 20 doses and t_E of 167.39 min (denoted as Process $U_{120\text{-}5}$), which is slightly higher than η of 98.87% at temperature interval of 75–120 °C with 25 mL per dose for 4 doses and t_E of 108.79 min (noted as Process $U_{120\text{-}25}$). The JO-ester obtained via sequential UI with adding doses of 5 mL possess AV of 0.24 mg KOH/g, IV of 124.77 g I_2/100 g, kV of 9.89 mm^2/s, ρ_{LO} of 901.73 kg/m^3 and m_w of 0.3 wt.% showing that sequential UI and dose at higher temperature interval can give higher reduction of AV compared with 36.56 mg KOH/g of original oil. The effects of t_S and t_E on AV are of minor and moderate importance, respectively. The combined effects of auto-induced temperature-rise of UI and temperature higher than boiling point of methanol used improve the mixing and esterification extent.

1. Introduction

World population has continued to increase every year meaning that world energy demand also increases in same way. Most energy resources are non-renewables e.g. fossil fuels [1]. Nowadays, oil price, shortage of fossil fuel, and environmental concerns are global issues that have been widely treated. Biodiesel, as renewable energy source, is one of the attractive options to solve this crisis for many countries to improve energy security supply and reduce the impact of oil dependency. Biodiesel is made from biomass sources such as vegetable oils or animal fats [2–4]. It is chemically known as simple mono-alkyl ester (such as methyl ester) [5] and attracted much attention in many countries because of its availability, renewability, non-toxic, biodegradability and less gas emissions reducing the emission of carbon dioxide [6,7]. Biodiesel can be prepared by transesterification processes combining vegetable oil with alcohol in the presence of catalyst to form fatty acid alkyl esters (FAAEs) (i.e., biodiesel) and glycerol [8].

Inedible woody plant oils, such as jatropha curcas linaeus oil (jatropha oil, denoted as JO or J) and tung oil are promising biomaterials around the world [9]. Jatropha curcas is an inedible oil bearing plant that 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 [10,11].

The conventional method for biodiesel production from jatropha oil involves an esterification treatment before the transesterification in order to reduce the high FFA content in jatropha oil, the esterification is a reversible reaction where free fatty acid (FFA) is

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converted to alkyl esters via acid catalysis. The reactants including FFA and alcohol are catalyzed by acid to form alkyl ester and water. The simplified form of this chemical reaction is presented by the well-known equation as [12]:

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

The transesterification is sensitive to FFA content in raw JO. The increase in FFA content will reduce the formation rate and yield of fatty acids methyl esters (FAMEs) [13,14]. Further, the high content of FFA of 18.25 wt.% in raw JO may induce the saponification during transesterification. Usually, the AV of raw JO is firstly reduced in esterification process. Baroutian et al. [15], Berrios et al. [16], Corro et al. [17], Deng et al. [18] and Jain et al. [19] have recommended the use of esterification pretreatment before transesterification process when the percentage of FFAs of an oil or fat is high, in order to avoid the saponification and reduction of the yield of FAMEs. Somnuk et al. [12], Gole et al. [20], Lu et al. [21] and Veljkovic et al. [22] recommend that the oils going to alkaline transesterification should contain no more than 1% of FFA. The saponification is giving way to formation of long chain soaps, whose tensile properties do not permit an effective separation of glycerin at the end of process. The saponification may also hinder the separation of ester from glycerin.

The classical method for production of biodiesel from high FFA via base-catalyzed transesterification need long reaction time with high temperature that will increase the cost and consume of energy however with esterification pretreatment the processing time and energy will be greatly reduced. Kywe and Oo [23] carried out production of biodiesel in pilot plant using raw JO with a FFA of 8.8 wt.% and produced biodiesel with a FFA of 0.5 wt.%. Deng et al. [18] studied the acid catalyzed esterification and base transesterification of jatropha oil by UI reported FFA reduction from 5.25 to 0.61 wt.% at 60 °C using H_2SO_4 as catalyst with reaction time of 60 min in the first step. Chen et al. [10] studied the effect of acid-esterification followed by base-transesterification under classical mechanical-mixing obtaining biodiesel with AV of 0.12 mg KOH/g. Corro et al. [17] reported a novel esterification treatment under solar radiation with Zn filings as solid catalyst followed by base-transesterification indicating AV was reduced from 18.5 to 0.38 mg KOH/g. Worapun et al. [24] reported the two step catalyzed transesterification process coupled with UI at room temperature and reported 98% of conversion to biodiesel. Boffito et al. [3] reported a biodiesel yield higher than 90% by ultrasound-assisted batch transesterification with pulsed UI performed in rosett cell reactor with a reaction time 15 times faster than classic mechanical stirred process.

The UI role on liquid phase and theirs physical and chemical effects of cavitation are referred from studies of Boffito et al. [3], Peters [25], Gonzales-Garcia et al. [26], Shah et al. [27], Kuppa and Moholkar [28], Choudhury et al. [29–30] and Parkar et al. [31]. Recently developments in sonotechnique [22] attracted great attention with the use of the use of UI as new, efficient mixing tool, based on emulsification of immiscible liquids (reactants) by microturbulence, which is generated by radial motion of cavitation bubbles. Although ultrasonic cavitation is a unique way to input energy into reactor through the physical effect of cavitation [27], such as nucleation, growth and transient collapse of tiny bubbles, which are driving by the ultrasound waves. Both of these effects could contribute with the kinetics enhancement and also with the reaction yield, however, in many situations, the influence of one of these effects is more dominant than the other. Therefore, determination of the physical effects of ultrasound cavitation is an important step of investigation in sonotechnique [28]. A combination of high speed liquid jets, high pressure (>1000 atm), high temperatures (>4727 °C) [32], and enormous heating and cooling rates ($>10^9\ \mathrm{Ks^{-1}}$) occurs and is locally concentrated during the implosive compression of cavitation bubbles [33–35], the principal physical effect of ultrasonic cavitation is formation of fine emulsion between immiscible phases (JO and mixture M/C) eliminating the mass transfer resistance [3], while the principal chemical effect is production of radicals through transient collapse of cavitation bubbles [28]. Choudhury et al. [29,30] have studied the physical aspects of UI assisted heterogeneous catalyzed transesterification and reported that the reaction mixture of sonication of does not change the chemistry of the process and the beneficial effect is only of physical nature, which is further limited by the intrinsic kinetics and mass transfer. Parkar et al. [31] reported that the major physical effect of sonication is fine emulsification that generates enormous interfacial area for reaction that overwhelms the effect of specific rate constant.

Although UI can induce temperature-rise effect, the increase of temperature certainly enhances the reaction rate and yield of products. However, its enhancing effect would be partly offset by the endothermic reaction and the dose of reactants. In this study, sequential applying UI and dosing of active reactants were employed to overcome the temperature decrease. Thus, the temperature decreased due to dosing may be regained by stopping the dose while applying UI. Effects of major system parameters such as esterification time (t_E), settling time (t_S) and reaction temperature (T) on the esterification performance especially on the reduction of AV were elucidated.

2. Materials and methods

2.1. Materials

Jatropha curcas oil was supplied by Ozone Environmental Technology Co., Yi-Lan county, Taiwan, with acid value AV = 36.5 mg KOH/g, iodine value (IV) = 105.68 g I_2/100 g, kinematic viscosity (kV) at 40 °C = 33.92 $\mathrm{mm^2/s}$ and density (ρ_{LO}) at 15 °C = 918.1 kg/$\mathrm{m^3}$. Its molecular weight (MW) is 871.5 g/mol [36]. Methanol (M) of anhydrous assay 99.8% and sulfuric acid (as catalyst denoted as C) of 96.7% purity were obtained from Mallinckrodt, Phillipsburg, NJ and Sigma–Aldrich, St. Louis, MO, respectively.

2.2. Esterification procedures

Direct sonication by inserting a probe directly into a sample vessel is the most common way to process a sample. Energy is transmitted from the probe directly into the sample with high intensity. The acid catalyzed esterification pre-treatment was carried out in a 500 mL batch reactor without cooling/heating systems, the experimental set-up for sequential UI esterification is illustrated in Fig. 1. The total reaction volume is 300 mL (oil + metahol + catalyst). A sample of 183.82 g (Wo) or 200 mL

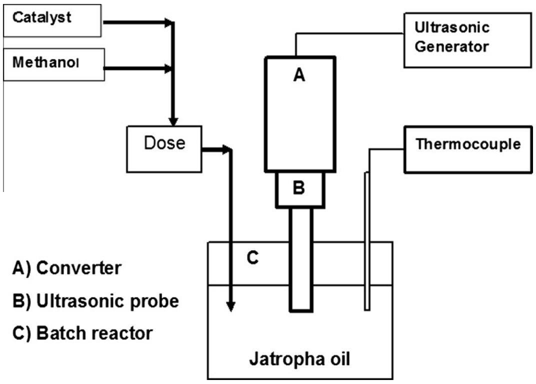

Fig. 1. Schematic diagram for sequential ultrasonic esterification.