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Esterification of jatropha oil by sequential ultrasonic irradiation with auto-induced temperature rise and dosing of methanol and sulfuric acid catalyst

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ABSTRACT

The esterification of jatropha oil applying sequential ultrasonic irradiation (UR) with auto-induced temperature rise followed by adding a mixture of methanol/sulfuric acid catalyst (M/C) dose in a high temperature interval was studied. Comparisons with various doses of 5, 10, 16.6 and 25 mL in different temperature intervals of 93.32 to 100 °C, 108.9 to 120 °C and 128.5 to 140 °C were made. System parameters examined include: esterification times (t_E) for UR, 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 jatropha oil and ester product were measured. The esterification conversion efficiencies (η) were determined and assessed. An η of 99.35% was obtained in temperature interval of 108.9 to 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% in temperature interval of 75 to 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 jatropha ester produced via sequential UR and dose 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 UR and dose at higher temperature interval can give higher reduction of AV compared with 36.56 mg KOH 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 UR, temperature higher than boiling point of methanol used and micro-mixing and emulsification caused by UR/cavitation improve the esterification extent.

1. Introduction

World populations continue to increase every year meaning that the world energy demand also increases in the same way. Most energy resources are non-renewable energy *e.g.* fossil fuels [1]. Nowadays, oil price, the shortage of fossil fuel, and environmental problems are the global issues that have been widely concerned. Biodiesel, as a source of renewable energy, is one of the attractive options to solve this crisis for many countries to improve energy security supply and reduce the impacts of oil dependency. Biodiesel is made from biomass sources such as vegetable oils or animal fats [2,3]. It is chemically known as simple mono-alkyl ester (such as methyl ester) [4] and has recently attracted much attention in many countries because of its availability, renewability, non-toxic, biodegradability and less gas emissions reducing the emission of carbon dioxide [5,6]. Biodiesels can be prepared by transesterification processes combining vegetable oils with alcohol in the presence of the catalyst to form fatty acid alkyl esters (FAAEs) (*i.e.* biodiesel) and glycerol [7].

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 [8]. *J. curcas* is an inedible oil bearing plant that is widespread in arid, semi-arid and tropical

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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 [9,10].

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 reactants including FFA and alcohol are catalyzed by acid to form the alkyl ester and water. 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 FFA content in raw jatropha oil. The increase in FFA content will reduce the formation rate and yield of fatty acids methyl esters (FAMEs) [11,12]. Further, the high content of FFA of raw jatropha oil such as of 18.25 wt% may also induce the saponification possibility during transesterification. Usually, the AV of FFA is first reduced in esterification. Baroutian et al. [13], Berrios et al. [14], Corro et al. [15], Deng et al. [16] and Jain et al. [17] 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 the reductions of the yield and formation rate of FAMEs. Gole and Gogate [18], Lu et al. [19] and Veljkovic et al. [20] recommend that the oils going to alkaline transesterification should contain no more than 1% of FFA. 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 [21] carried out the production of biodiesel in pilot plant using raw jatropha oil with a FFA of 8.8 wt% and produced biodiesel with a FFA of 0.5 wt%. Deng et al. [16] have studied the acid catalyzed esterification and base transesterification of jatropha oil by ultrasonic irradiation (UR) reducing the AV from 10.5 to 1.2 mg KOH/g. Chen et al. [9] studied the effect of acid esterification with mechanical mixing and base transesterification obtaining a jatropha-oil biodiesel with AV of 0.12 mg KOH/g. Corro et al. [15] reported a novel solar esterification treatment by solar radiation with Zn filings as solid catalyst and base transesterification, indicating that the AV was reduced from 18.5 to 0.38 mg KOH/g on jatropha-oil biodiesel obtained. Worapun et al. [22] reported the two step catalyzed transesterification process coupled with UR at room temperature and reported 98% of conversion to biodiesel.

The role of UR in liquid phase and the physical and chemical effects of ultrasound and cavitation on the system can be referred to the studies of Peters [23], Gonzalez-Garcia et al. [24], Shah et al. [25], Kuppa and Moholkar [26], Parkar et al. [27] and Choudhury et al. [28,29]. Introduction of ultrasound in liquid medium induces sinusoidal variation of bulk pressure and thus cavitation. Cavitation bubbles grow from the nuclei and undergo expansion, compression and collapse stages. At bubble collapse, the energy concentration is intense, resulting in high temperature (~4727 °C) and pressure (~494 atm) inside the bubble [26]. Note that a pressure higher than 1000 atm was indicated by Gole and Gogate [30]. Regarding the transient bubble collapse, Kumar et al. [31–33] further reported that enormous heating and cooling rates ($>10^9$ K/s) occurs and is locally concentrated during the implosive compression of cavitation bubbles. At the above said high temperature and pressure at the transient bubble collapse, the dissociation of vapor molecules entrapped in the bubble generates radicals, which are released into the bulk liquid as the bubbles are fragmented at maximum compression. Sonochemical reaction is induced by the radicals. Mechanisms of physical effects of ultrasound and cavitation include micro-streaming, micro-turbulence, shock waves and micro-jets. These effects contribute the vigorous convection in the bulk liquid, reducing the mass transfer resistance while increasing the contacting surface of reactants. Only the chemical while both chemical and physical effects of cavitation are important for homogeneous and heterogeneous reaction systems, respectively. Noting the instability and short diffusion distance of radicals, Kuppa and Moholkar [26] pointed out that the sonochemical effect of these radicals generated from cavitation bubble collapse is only significant with the presence of radical conserving agent in the medium or of high concentration reactant at the position of bubble collapse. They thus concluded that without radical conserving agent, the promotion effects on the reaction system cause by the UR and cavitation are essentially physical but not sonochemical. For the system of ultrasound-enhanced liquid–liquid heterogeneous permanganate oxidation investigated by Kuppa and Moholkar [26], the physical effects of ultrasonic cavitation result in the formation of fine emulsion between immiscible phases that decreases the mass transfer resistance. Parkar et al. [27] studied the ultrasound-assisted acid catalyzed soybean-oil biodiesel production. They also found that the main physical effect of sonication is fine emulsification that induces large interfacial area for reaction that predominate the effect of specific rate constant. The physical effects of cavitation of micro-convection and shock waves are more vigorous at low temperature. Choudhury et al. [28] examined the mechanistic aspects of UR assisted heterogeneous catalyzed transesterification process of jatropha oil. They indicated that the sonication of reaction mixture does not alter the chemistry of the process and the enhancement is only of physical effect limited by the mass transfer. As for the UR enhanced CaO catalyzed soybean-oil biodiesel production, Choudhury et al. [29] identified that the needed convection in the 3-phase heterogeneous reaction system is contributed by the ultrasonic micro-streaming. Veljkovic et al. [20] further revealed that recent developments in sonotechnique improves the use of ultrasonic irradiation as new, more efficient mixing tool based on the emulsification of the immiscible liquids reactants by micro-turbulence generated by radial motion of cavitation bubbles.

In addition to the above said mechanistic characteristics of UR, it also induces temperature-rise effect. The increase of temperature certainly enhances the reaction rate and thus the yields of products. Although UR can induce the heating effect increasing the temperature, however, its enhancing effect would be partly offset by the endothermal reaction and the dose of reactants. In this study, sequential applying UR 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 UR. 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

J. 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 mm^2/s and density (ρ_{LO}) at 15 °C = 918.1 kg/m^3. Its molecular weight (M_W) is 871.5 g/mol [34]. 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

The acid catalyzed esterification pre-treatment was carried out in a 500 mL batch reactor without cooling/heating systems.