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Mechanistic analysis of cavitation assisted transesterification on biodiesel characteristics

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ABSTRACT

The influence of sonoluminescence transesterification on biodiesel physicochemical properties was investigated and the results were compared to those of traditional mechanical stirring. This study was conducted to identify the mechanistic features of ultrasonication by coupling statistical analysis of the experiments into the simulation of cavitation bubble. Different combinations of operational variables were employed for alkali-catalysis transesterification of palm oil. The experimental results showed that transesterification with ultrasound irradiation could change the biodiesel density by about 0.3 kg/m^3; the viscosity by 0.12 mm^2/s; the pour point by about 1–2 °C and the flash point by 5 °C compared to the traditional method. Furthermore, 93.84% of yield with alcohol to oil molar ratio of 6:1 could be achieved through ultrasound assisted transesterification within only 20 min. However, only 89.09% of reaction yield was obtained by traditional macro mixing/heating under the same condition. Based on the simulated oscillation velocity value, the cavitation phenomenon significantly contributed to generation of fine micro emulsion and was able to overcome mass transfer restriction. It was found that the sonoluminescence bubbles reached the temperature of 758–713 K, pressure of 235.5–159.55 bar, oscillation velocity of 3.5–6.5 cm/s, and equilibrium radius of 17.9–13.7 times greater than its initial size under the ambient temperature of 50–64 °C at the moment of collapse. This showed that the sonoluminescence bubbles were in the condition in which the decomposition phenomena were activated and the reaction rate was accelerated together with a change in the biodiesel properties.

1. Introduction

Among the biofuels currently in use or researched, Free Fatty Acid Methyl Esters (FAME), which is also known as biodiesel is considered an ideal alternative to diesel due to their similarities and advantages [1]. Biodiesel is commonly generated through a three-step, consecutive and reversible reaction called "transesterification". Low mass transfer due to immiscible nature of reactants is the main weakness of transesterification [2,3]. Recently, ultrasound assisted transesterification has been confirmed as a green synthesis method that is fast and energy-efficient [4]. It is due to the ultrasound ability to enhance mass transfer between the immiscible reactants. In other words, ultrasound waves are sinusoidal mechanistic waves consisting of both expansion (negative) and compression (positive) pressure waves. Hence, irradiation of ultrasound waves generates vacuum micro-regions in the liquid called "sonoluminescence bubble" that are filled with reactants vapors. Mass transfer goes efficiently inside the micro-fine bubbles. "Cavitation" happens when bubbles grow (expansion) and collapse (compression) intensively [5]. This phenomenon assists the system to generate fine micro-emulsion through generation of micro streams, micro turbulent eddies and shock waves. Besides, the collapse is extremely energetic, resulting in generation of highly pressurized and over-heated regions called "hot spots" which induce the reaction [6].

Many authors have reported that low frequency ultrasound accelerates reaction rate in which higher conversion is achieved in transesterification within shorter reaction time compared to the other approaches [7–9]. Thermal decomposition can also be carried out in parallel with transesterification within these bubbles. Highly volatile hydrophobic molecules can easily and directly decompose in hot spots. Generally, biodiesel starts to decompose upon thermal stressing at 275 °C and above. The decomposition mainly involves (i) dimerization or polymerization reactions that form higher molecular weight components; (ii) isomerization reactions that transfer unsaturated *cis*-type FAMEs to *trans*-type FAMEs and (iii) pyrolysis reactions that break down FAMEs to form lower molecular weight FAMEs and hydrocarbons. These reactions occur

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at 300–425 °C, 275–400 °C and >350 °C, respectively [10]. Bruno and co-workers [11] observed that the polymerization and cracking of unsaturated FAMEs significantly influenced the volatility of biodiesel fuel. Imahara et al. [12] found that the cold flow properties of biodiesel produced under high temperature and pressure (350 °C and 43 MPa) increased slightly due to *cis–trans* isomerization. Lin et al. [10] investigated the influence of thermal stressing on biodiesel viscosity and cold flow properties at 250–425 °C. They demonstrated that *cis–trans* isomerization reactions had a minimal effect on biodiesel characteristics. Meanwhile, pyrolysis reactions reduced both viscosity and the crystallization onset temperature but polymerization showed the opposite effects. Xin et al. [13] observed that the oxidation stability of biodiesel made from waste cooking oils with high peroxide values was improved at temperature of 270 °C and pressure of 17 MPa compared to biodiesel produced from the same feedstock by conventional method at lower temperature and pressure.

Based on a detailed review done by Veljković et al. [6], despite a large quantity of researches on intensification of transesterification under irradiation of ultrasound energy, the quality of biodiesel produced in such conditions have not been well addressed. These characteristics influence flow injection and atomization of fuel as well as energy content of engine and its safety. In the current study, the authors tried to identify the physical mechanism of cavitation and provide a deep insight into the sonoluminescence transesterification that form conditions that may activate the thermal decomposition phenomena and influence the biodiesel characteristics. The principle aim is to find a link between the influence of thermal stressing and quality of biodiesel produced from alkaline transesterification of palm oil under ultrasound irradiation.

2. Methodology

2.1. Material and method

RBD (Refined, Bleached and Deodorized) palm oil was employed as the source of triglyceride. Its chemical composition and physical properties can be found in Table 1. Absolute methanol (99.99%) and hydrochloric acid (30 wt.%) for the pre-treatment step were purchased from Sigma Aldrich while potassium hydroxide pellets (99.99 wt.%) were purchased from Merck Companies, Malaysia. A mixture of fatty acid including palmitic, stearic, oleic, linolenic and linoleic methyl esters (called MSTFA) which was used as the HPLC standards in this study, was supplied by Supelco Company.

2.2. Experimental design

Central composite design (CCD) was employed to specify the effects of operational variables on conversion of oil to FAME. This type of design is desirable for sequential experiments to obtain proper information for examining lack of fit without a large number of design points [14]. The operational parameters included (i) temperature, in the range of 50–64 °C; (ii) MeOH:oil molar ratio, in the range of 6–12; (iii) concentration of catalyst, in the range of 1–2%; (iv) sonication power, in the range of 0–400 W; (v) mechanical stirring, in the range of 400–800 RPM and (vi) reaction time, in the range of 20–60 min. Each parameter was fixed and coded into levels: −1 (Minimum level), 0 (middle level) and +1 (Maximum level). Finally, 50 experimental runs including 10 axial points, 32 factorial points, and 1 replicable central point were designed. The central point was repeated 8 times in order to identify the experimental error. The employed design matrix with the related yield and biodiesel properties are reported in Tables 2 and 3 respectively.

Table 1
Properties of used palm oil.

Property	Value
Density at 15 °C	791.8 kg/m^3
Viscosity at 40 °C	33.60 mm^2 s^{-1}
Moisture content (%)	400 × 10^{-6} ppm
Acid value	51.8 ppm
Iodine value	0.151 mg/g

2.3. Biodiesel synthesis

A 300 ml stainless steel and a 400 ml glass flask were used as the reaction vessels. Both were equipped with a water bath to control the temperature; a condenser to inhibit the exhaust of evaporated methanol and a thermometer to record the reaction temperature. The sonication was carried out by a 24 kHz-ultrasonic processor, UP400S (Hielscher Ultrasonics). The mechanical stirring was done by an overhead stirrer (13516 IKA Eurostar 60 Digital). Both reactors were connected to a 220 V voltage regulator. Since ultrasonication generates heat, the temperature in the ultrasonic bath was controlled at about 2–10 °C below the reaction temperature.

The reactors were initially charged with favorable amount of palm oil and then heated to reaction temperature by the surrounding water. In the next step, a pre-provided and pre-heated solution of methanol and catalyst was added to the oil. Then, the stirring/sonication of the reaction started immediately and continued with the specified mixing intensity/sonication power and reaction time. After the stirring/sonification, the mixture was transferred to a separatory funnel for gravitational separation for 48 h. The methyl ester was then washed with diluted hydrochloric acid to neutralize the remaining alkaline catalyst before being washed by distilled water twice. Finally, the excessive methanol and water in the product were removed by rotary evaporation at 70 °C for 120 min.

2.4. Biodiesel analysis and characterization

The chemical compositions of biodiesel product and yield of reaction were determined by a gas chromatography (Agilent Technology gas chromatograph model GC 6890) equipped with cool-on column (DB-23, 60 mL, 0.250 mm ID, 0.15 μm film thickness). The results are summarised in Table 2. Helium was used as a carrier gas at the flow rate of 1.0 mL/min; nitrogen was used as a make-up gas at the flow rate of 25 mL/min and hydrogen was used as a fuel gas at the flow rate of 40 mL/min. The start-up temperature was 323 K, which was increased to 448 K at 25 K/min and further increased to 553 K at 5 K/min. 553 K was maintained for 5 min. The standard test methods according to ASTM Standard are applied to evaluate the quality of biodiesel [15]. The density of the biodiesel produced was analyzed (based on ASTM D4052-96) by a fully automatic density meter (Mettler Toledo model DM.40, *Switzerland*). The viscosity (based on ASTM D445-06) was measured by a fully automatic viscometer (Brookfield DV-II+PRO Viscometer). The pour and cloud point (based on ASTM D97-93 and D2500) were determined by a pour/cloud point tester (Normalab, model NTE 450, France) while flash point (based on ASTM D93-07) was determined by a Pensky–Martens Closed Cup Tester.

3. Mathematical model

The dynamic of sonoluminescence bubble along with the phenomena of liquid vaporization, diffusion, heat transfer and chemical reactions within the cavitation bubbles were simulated using Matlab to get a quantitative insight of the influence of ultrasound irradiation on a system (Mathworks Inc., USA).