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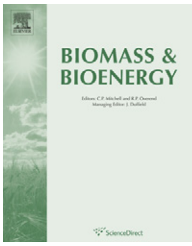

Parametric study and optimization of in situ transesterification of *Jatropha curcas L* assisted by benzyltrimethylammonium hydroxide as a phase transfer catalyst via response surface methodology

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ABSTRACT

In the present work, non-edible oil source, *Jatropha curcas* oil was used with base catalyzed methanol and ethanol to produce biodiesel using in situ transesterification assisted by Benzyltrimethylammonium hydroxide (BTMAOH) as a phase transfer catalyst (PTC). Experimental investigation showed that base catalyzed in situ transesterification reaction rate was enhanced with the use of BTMAOH as a PTC. During the experiment fast formation of biodiesel was observed in relatively shorter time for PTC assisted reaction as compared to the reaction in the absence of PTC. The effect of individual reaction parameters was investigated using response surface methodology (RSM). Optimum operating conditions were also found statistically. Weight fractions of 89 ± 0.7% fatty acid methyl esters (FAME) yield and 99.4 ± 0.4% fatty acid ethyl esters (FAEE) yield were produced at optimum reaction condition. The fuel quality of FAME and FAEE was investigated against the fuel quality specification set by ASTM D6751 and EN-14214 standards.

1. Introduction

Renewable fuels and chemical feedstocks are necessary to maintain sustainable development with zero net carbon dioxide emission and reduced environmental degradation. Currently, conversion of oils and fats to biodiesel by transesterification with alcohols receives wide attention. Transesterification is a very slow reaction as vegetable oil and methanol are sparingly soluble. Because of this, mass transfer rate seriously affects the reaction rate. In order to enhance the contact between two phases, several techniques such as co-solvent addition [1], ultrasonication [2], higher temperature and pressure or super critical methanol [3], super critical reactive extraction [4], microwave irradiation [5–7] were investigated. Zhang et al. [8] have investigated conventional transesterification of soybean oil assisted by phase transfer catalysis (PTC). In their research work, it was reported that PTC assisted base catalyzed transesterification reaction of soybean oil gave better biodiesel yield (>96.5%) in a relatively shorter reaction time as compared to the reaction conducted in the absence of PTC. PTC is a powerful technique to enhance reaction rate between two or more reactants in two or more sparingly miscible phases [9,10].

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Quaternary onium (ammonium and phosphonium) salts are commonly used as PTC as they are much cheaper than other candidates such as crown ethers and crepitates [9]. Zhong et al., [11], and Cai et al. [12], produced biodiesel from listea cubeba kernel oil in the presence of hexadecyl-trimethyl-ammonium bromide as a PTC in conventional transesterification reaction. They reported that in the presence of PTC the conversion of oil to methyl ester was 97.6%.

Cost of production of biodiesel needs to be reduced to make it a competitive substitute to petroleum-based diesel [13]. Harrington and D'Arcy-Evans [14] developed an "in-situ transesterification process" in which oil bearing sunflower seeds was used for the reaction instead of using oil that was already extracted from the seeds. This process reduces the expensive intermediary oil extraction step. It was observed that in-situ transesterification is more efficient than the conventional transesterification. Investigations on various edible oil seeds such as Haas et al. [15] on soybeans seeds and Georgogianni et al. [16] on sunflower seeds supported the observations of Harrington and D'Arcy-Evans [14]. However, usage of edible oil resources as a feedstock for biodiesel production has adverse effect on the price of food as well as biodiesel [17]. In view of this, usage of non-edible oil sources such as *Jatropha curcas L* [18] is drawing greater attention in recent times.

In the present work, catalytic effects of benzyltrimethylammoniumn hydroxide (BTMAOH) in 40% methanol solution and 40% ethanol solution as a PTC for in situ methanolysis and ethanolysis of *J. curcas L* seeds were investigated. Optimum operating conditions were determined through experimental design technique using response surface methodology (RSM).

2. Materials and methods

2.1. Materials

2.1.1. *Preparation and characterization of* J. curcas L *seeds*

Jatropha curcas L seeds were purchased from Agro Innaz Resources, Malaysia, a local jatropha seeds and oils supplying company. The source of jatropha seeds for this study was local from Luanti Baru Keningau accessions harvested from a jatropha pilot project conducted by the Institute of Agro-Biotechnology Malaysia at Luanti Baru village, Keningau, Sabah, Malaysia. The mature seeds were harvested manually from the plot. Immediately after the harvest, the seeds were sun dried for three days. The seeds were then separated from its coats and the uncoated seeds were again sun dried for additional three days to remove any moisture remained in the seeds. The dried seeds were then kept in ploy bags with internal plastic lining to avoid any contamination with moisture.

The seeds were then brought to Universiti Teknologi PETRONAS, Chemical Engineering Department, Oil and Gas Laboratory and stored in conventional oven adjusted at 30 °C to avoid any moisture contamination. The *Jatropha curcas L* seed shells were then manually broken and separated from the shell. The shell carefully removed from the kernels. Then the seed was grinded to fine particles using Panasonic MX-799S blender and dry mill. To keep the homogeneity, uniformity and accuracy of particle sizes range, the grinded seeds were screened using a vibrator sieve shaker for 20 min of sieving periods. Particle sizes in the range of 0.3–0.5 mm were collected for the in situ transesterification processes. The collected particles were further dried in conventional oven since it is necessary to reduce any moisture contamination of seed to avoid hydrolysis of triglyceride to FFAs which can consume the alkali catalysts to form unwanted soap. The prepared seeds were kept in amber-colored air tight bottles to eliminate moisture contact and prevent photo oxidation of the seeds. Mettler Toledo moisture analyzer (RH73) was employed to determine the moisture content of *J. curcas L* seed. The oil content of these particles was determined by using 20 g of seed with 150 ml of hexane as a solvent in a Soxhlet extractor. Hexane was vacuum evaporated to estimate oil content in the particles. The free fatty acid value and percentage were determined using AOCS official method Cd 3d-63, revised 2003 [19].

Methanol (CH_3OH, purity $\geq$99.7%), Ethanol (C_2H_5OH, purity $\geq$99.7%), n-hexane (CH_3 $(CH_2)_4CH_3$, purity $\geq$99%), sodium hydroxide (NaOH, purity $\geq$99%), potassium hydroxide (KOH, purity $\geq$85%), Iso-propanol ($CH_3CH_2OHCH_3$, purity $>$99.8%), benzyltrimethylammoniumn hydroxide (BTMAOH) in 40% methanol and ethanol solution ($C_{10}H_{17}NO$) were procured from Sigma Aldrich in Malaysia. Reagent grade acetic acid (CH_3OOH) and diethyl ether ($C_4H_{18}O$) were purchased from R & M chemicals, Malaysia. Gas chromatographic analytical grade chemical kits were purchased from Sigma Aldrich, Malaysia.

2.2. *In situ transesterification experiment*

Twenty grams of conditioned *J. curcas L* particles were prepared and placed in a two necks round bottom flask reactor. Required amount of alkaline methanol or ethanol was gently mixed with the desired amount of BTMAOH and preheated to the reaction temperature; then added to the reactor to start the reaction. The round bottom flask reactor was equipped with reflux condenser (to prevent loss of alcohol), magnetic stirrer and a thermometer. The flask was immersed in a silicon oil bath thermostat. After the reaction was completed, the reaction mixtures were cooled to room temperature. Vacuum Buchner funnel filter was used to separate the liquid from the solid residue. The solid residue was further washed with 20 ml methanol or ethanol to recover the remaining liquid in the solid residue. The liquid mixtures were diluted with distilled water to minimize further reactions. n-hexane (50 ml) was added to the liquid mixtures for faster clarification of the mixture into two phases. The top layer contains mixture of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE) and n-hexane while the bottom layer contains glycerol, methanol or ethanol, sodium hydroxide, BTMAOH, water and unspent oil. The top layer was recovered and then washed with warm (50–60 °C) water several times to remove contaminants. n-hexane and remaining traces of water were removed from the FAME or FAEE using vacuum evaporator. Each experiment was done in duplicate. The actual quantities of FAME and FAEE were measured and stored in a screw capped bottles for analysis. Maximum expected quantity of FAME and FAEE was estimated based on stoichiometery. The yields of FAME and FAEE were determined using the relation;