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Short Communication

Supercritical fluid reactive extraction of *Jatropha curcas* L. seeds with methanol: A novel biodiesel production method

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ABSTRACT

The novel biodiesel production technology using supercritical reactive extraction from *Jatropha curcas* L. oil seeds in this study has a promising role to fill as a more cost-effective processing technology. Compared to traditional biodiesel production method, supercritical reactive extraction can successfully carry out the extraction of oil and subsequent esterification/transesterification process to fatty acid methyl esters (FAME) simultaneously in a relatively short total operating time (45–80 min). Particle size of the seeds (0.5–2.0 mm) and reaction temperature/pressure (200–300 °C) are two primary factors being investigated. With 300 °C reaction temperature, 240 MPa operating pressure, 10.0 ml/g methanol to solid ratio and 2.5 ml/g of *n*-hexane to seed ratio, optimum oil extraction efficiency and FAME yield can reach up to 105.3% v/v and 103.5% w/w, respectively which exceeded theoretical yield calculated based on *n*-hexane Soxhlet extraction of Jatropha oil seeds.

1. Introduction

When the price of crude oil dropped substantially to around USD 40 per barrel due to global economic crisis in early 2009, most of biodiesel production plants had to either shut down completely or cut down their production volume severely to avoid large monetary losses (Lim and Lee, 2010). The cheaper cost of mineral diesel has rendered biodiesel production no longer economically feasible. This incident has exposed the financial fragility of biodiesel in relation to fossil fuels' pricing mechanism. Thus, recent academic researchers have been focussing on investigating cost effective biodiesel production methods either via raw material or processing technology in order to become more competitive (Demirbas, 2008; Nielsen et al., 2008). Conventional biodiesel commercial production is based on the usage of edible energy crops such as rapeseed, soybean, oil palm and coconut. The high supply cost from these feedstocks which accounted more than 70% of the overall biodiesel production cost coupled with their competition as food sources have turned the attention to exploit other non-edible feedstocks such as Jatropha. Jatropha, which is suitable to be grown in non-arable land, has recently being hailed as a promising raw material for biodiesel production. However, its higher moisture and free fatty acid contents (15% FFA) have resulted in current commercial alkaline-based catalyst transesterification not being suitable to be employed (Berchmans and Hirata, 2008). The complicity of multi-stage processing involved (extraction, drying, degumming and deacidification) will add to the production cost and thus contribute negatively to the biodiesel cost effectiveness.

Recent publication indicated that reactive extraction of *Jatropha curcas* L. seeds using acidic catalyst (sulphuric acid) to produce biodiesel has the potential to reduce the high processing cost (Shuit et al., 2010). This method differs from conventional biodiesel production in which the oil-bearing solid energy crops will be in contact directly with alcohol instead of pre-extracted liquid oil. In this case, the alcohol will also act as an extraction solvent while esterification and transesterification proceed simultaneously in a single step. This process can reduce both the processing time and cost as the energy-intensive extraction phase (chemical solvent or physical pressing) is avoided. Meanwhile, biodiesel production from Jatropha oil via non-catalytic supercritical methanol had also been proven to be more superior in terms of reaction time, product separation, FAME yield and process complicity compare to conventional biodiesel processing (Hawash et al., 2009). Fluid in a supercritical phase can be considered as an intermediate between liquid and gas. This special state has attributed to several distinctive characteristics such as low viscosity, high diffusion coefficients, variation of density and dielectric constant as a function of pressure. Consequently, supercritical fluids (SCF) are excellent extraction solvents as well as chemical reaction reagents. Therefore, it will be interesting to investigate the potential of SCFs in direct contact with the oil-bearing solid materials for biodiesel production.

The main objective of this research is to determine the feasibility of non-catalytic supercritical reactive extraction using methanol to produce biodiesel from *J. curcas* L. seeds in a high-pressure

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batch reactor with *n*-hexane as co-solvent. Methanol was chosen since it has a milder supercritical condition (513.15 K, 8.1 MPa) and lower boiling point (338.15 K) for easier separation from the products. The effects of solid particle size of Jatropha seeds and reaction temperatures on the FAME yield and oil extraction efficiency were studied extensively to obtain a clearer picture of its suitability and future prospects.

2. Methods

2.1. Materials

J. curcas L. oil seeds used in this study were purchased from Misi Bumi Alam Sdn. Bhd., Malaysia. Methanol of 99.8% purity was purchased from HmbG Chemicals, Germany. Analytical grade *n*-hexane of 99% purity (Merck, Germany) was used as co-solvent. Methyl heptadecanoate (99.5% purity) as internal standard and standard references for methyl esters which include methyl palmitate, methyl stearate, methyl oleate and methyl linoleate were all obtained from Fluka Chemie, Germany.

2.2. Preparation of *J. curcas* L. seeds

Laboratory Analytical Procedure (LAP) as provided by NREL (National Renewable Energy Laboratory, USA) (Hames et al., 2008), was utilized to ensure uniformity of the Jatropha solid content at ambient conditions. Jatropha samples were thoroughly mixed and placed in dry pan to a maximum depth of 1 cm. The samples were subsequently placed into a drying oven (Memmert UNB800, Germany) at 45 °C for 3 days. The oven-dried samples were cooled to room temperature before grounded using a chopper (Moulinex, France). Moisture content of grounded samples based on a 105 °C dry weight basis which was calculated by placing in the same oven at 105 °C repeatedly until constant weight was achieved. After drying, the Jatropha samples were then screened using a vibrator sieve shaker (Retsch, Germany). The sieving period was 15 min and three solid particle size fractions ($\leqslant 0.5$, $\leqslant 1.0$ and $\leqslant 2.0$ mm) were collected. For the oil content measurement, Soxhlet extractor with solvent *n*-hexane in excess was utilized. Jatropha seeds (20 g) from each solid fraction studied were extracted for 24 h before being evaporated in the rotary evaporator (Buchi, Switzerland) and the remaining oil was measured.

2.3. Experimental procedures

All the experimental runs for SCF reactive extraction to convert extracted oil from *J. curcas* L. seeds into biodiesel were carried out in a high-pressure reactor. The detail description of reactor is described elsewhere (Mazaheri et al., 2010). In a typical run, 20 g of blended and sieved Jatropha seeds were loaded into the 450 ml reactor together with 200 ml of methanol (solvent to seed ratio was fixed at 10.0 ml/g) and 50 ml of *n*-hexane (2.5 ml/g of co-solvent to seed ratio). Methanol would act both as an extraction agent and transesterification reagent while the addition of *n*-hexane was required to increase the oil solubility in the reaction mixture as well as separating the FAME from the glycerol in the later process (Georgogiannia et al., 2008; Shuit et al., 2010). The reaction mixture was first subjected to mechanical agitation at 400 rpm for 30 min at room conditions before being heated to the desired reaction temperature. The operating pressure and reaction time, which were not being studied independently were not controlled but correlated by the reaction temperature. The heating rate was adjusted so that the final temperature was always reached in the shortest possible time (45–80 min) after which the mixture would be quench immediately with cooling water to room temperature. Then, the reaction mixture was filtered and the solid residue was washed thrice with 30 ml of recycled *n*-hexane. In order to separate the FAME from glycerol and any *n*-hexane insoluble by-product from the SCF reactive extraction, the filtrate was stirred with 100 ml recycled *n*-hexane for 30 min before being transferred to separating funnel (Tizvar et al., 2009). The upper dark yellow colour layer was decanted after 1 h and excess *n*-hexane was evaporated to recover the FAME. The separation procedure was repeated twice for the lower dark brown colour layer to ensure complete separation of FAME from glycerol. The volume of the collected pure FAME sample was then measured and recorded for extraction efficiency calculation as shown below. Density of un-reacted oil and its methyl esters was considered to be equal since the difference was less than 5% at room temperature (Veny et al., 2009). This was validated by subjecting the post-reaction dried Jatropha seeds to Soxhlet extraction to determine the amount of leftover oil.

$$\text{Extraction efficiency }(\%) = \frac{\text{Final volume of collected FAME sample}}{\text{Total volume of oil in the original sample}} \times 100\% \tag{1}$$

2.4. Product analysis

The FAME samples were analyzed by using gas chromatography (GC) (Perkin–Elmer, Clarus 500) equipped with Nukol™ capillary column (15 m × 0.53 mm; 0.5 μm film thickness) and flame ionization detector (FID). Helium gas was used as the carrier gas with the initial oven temperature set at 110 °C (held for 0.5 min) and then increased to 220 °C (held for 8 min) at a rate of 10 °C/min. The temperatures of the detector and injector were fixed at 220 and 250 °C, respectively. Each sample of 1 μl, diluted with *n*-hexane and methyl heptadecanoate (internal standard), was injected into the column. Peaks of different methyl esters were identified by comparison with the peaks of pure methyl ester standard compound. The yield of FAME in the samples was calculated as shown in equation below.

$$\text{FAME yield }(\%) = \frac{\text{Total weight of methyl esters in collected FAME sample}}{\text{Total weight of oil in the original sample}} \times 100\% \tag{2}$$

3. Results and discussion

Moisture content of the *J. curcas* L. seeds subjected to drying at 105 °C was calculated to be at an average of 8.34 wt%. Total oil content in Jatropha seeds was discovered to vary according to different solid fractions (un-sieved: 37.8 wt%, <2.0 mm: 54.4, <1.0 mm: 62.4 wt% and <0.5 mm: 60.9). The distribution of oil inside the seeds was in agreement with those reported in the literature (Kumar and Sharma, 2008; Sayyar et al., 2009). Fig. 1 shows the effect of different temperatures and their corresponding pressures towards oil extraction efficiency with different range of solid particle sizes. In general, the oil extraction efficiency of *J. curcas* L. seeds increased with increasing temperature and pressure as higher temperature and pressure typically favoured the expulsion of oil from the shell (Berchmans and Hirata, 2008). The minimum oil extraction efficiency at lower temperatures (200–240 °C) was higher than 65% v/v for all solid fractions due to the contribution of *n*-hexane in the pre-stirring stage. Higher increment rate for oil extraction efficiency was discovered at temperature above 240 °C since supercritical fluid extraction began to take effect. Thus, it can be concluded that the effect of co-solvent is rather sig-