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Biodiesel production from jatropha seeds: Solvent extraction and in situ transesterification in a single step

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HIGHLIGHTS

- We investigate the biodiesel production directly from jatropha seeds.
- We examine influences of reaction conditions on biodiesel yield and its quality.
- Increasing methanol to seed ratio and alkali concentration will increase yield and quality.
- Increasing reaction temperature will increase yield.
- Temperature, time and stirring speed effects on biodiesel quality were less important.

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ABSTRACT

The objective of this study was to investigate solvent extraction and in situ transesterification in a single step to allow direct production of biodiesel from jatropha seeds. Experiments were conducted using milled jatropha seeds, and *n*-hexane as extracting solvent. The influence of methanol to seed ratio (2:1–6:1), amount of alkali (KOH) catalyst (0.05–0.1 mol/L in methanol), stirring speed (700–900 rpm), temperature (40–60 °C) and reaction time (3–5 h) was examined to define optimum biodiesel yield and biodiesel quality after water washing and drying. When stirring speed, temperature and reaction time were fixed at 700 rpm, 60 °C and 4 h respectively, highest biodiesel yield (80% with a fatty acid methyl ester purity of 99.9%) and optimum biodiesel quality were obtained with a methanol to seed ratio of 6:1 and 0.075 mol/L KOH in methanol. Subsequently, the influence of stirring speed, temperature and reaction time on biodiesel yield and biodiesel quality was studied, by applying the randomized factorial experimental design with ANOVA (*F*-test at $p = 0.05$), and using the optimum values previously found for methanol to seed ratio and KOH catalyst level. Most experimental runs conducted at 50 °C resulted to high biodiesel yields, while stirring speed and reaction time did not give significantly effect. The highest biodiesel yield (87% with a fatty acid methyl ester purity of 99.7%) was obtained with a methanol to seed ratio of 6:1, KOH catalyst of 0.075 mol/L in methanol, a stirring speed of 800 rpm, a temperature of 50 °C, and a reaction time of 5 h. The effects of stirring speed, temperature and reaction time on biodiesel quality were not significant. Most of the biodiesel quality obtained in this study conformed to the Indonesian Biodiesel Standard.

1. Introduction

Jatropha curcas is a drought-resistant shrub or tree belonging to the family *Euphorbiaceae*, which is cultivated in Central and South America, South–East Asia, India and Africa [1]. It is a plant with many attributes, multiple uses and considerable potential [2–4]. In Indonesia, the land area for jatropha plantation is increasing because this plant can be used to reclaim land, prevent and/or control erosion, plus it provides a new agricultural development mode with no competition between food and non-food uses.

The seed is the part of the jatropha plant with the highest potential for utilization. It contains between 40% and 60% oil, and between 20% and 30% proteins. The jatropha seed is generally toxic to humans and animals, with phorbol ester and curcin identified as the main toxic agents [1,5].

J. curcas oil is regarded as a potential alternative to diesel fuel, and vegetable oils have numerous advantages in this respect

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because they are safe to store and handle because of their high flash points. The fact that jatropha oil cannot be used for nutritional purposes without detoxification makes its use as an energy source for fuel production, very attractive [6,7].

In Indonesia, the availability of biofuel as a substitute for fossil fuel is urgently needed because national oil production has been falling over the past 5 years due to the natural decline of oil wells. The use of biodiesel from jatropha oil is a promising alternative because it is renewable, and environmentally friendly, and it can also be produced locally. Cultivating jatropha plants on land where no other crops can grow, and using its oil as an alternative energy source does not, at least in theory, reduce the availability of edible oils in the country.

Conventional industrial technology for the synthesis of biodiesel from vegetable oils involves isolation of the oil from the seed, refining, and then transesterification. Industrial oil extraction from oilseeds is usually done by mechanical pressing with a hydraulic or single expeller press, followed by solvent extraction. The combination of these operations produces oil extraction yields up to 98% in the case of sunflower, with residual oil content in cake meal between 0.5% and 1.5% [8]. The solvent extraction most commonly used today is by percolation with a countercurrent flow using hexane as extracting solvent [9–13]. Currently, twin-screw extrusion has been successfully carried out to extract oil from oilseeds [14–19], and to conduct mechanical pressing and solvent extraction of sunflower oil in a single step [20]. Highest oil extraction yield (98%) with best cake meal quality (residual oil content lower than 3%) was obtained using a screw rotation speed of 185 rpm, feed rate of 30 kg/h, and solvent-to-solid ratio of 0.55. Industrial oil refining normally includes many separate steps including degumming, neutralization, bleaching and deodorisation. These processes consume large amounts of energy, water and chemicals with much loss of neutral oil, and the production of large amounts of unwanted by-products [21].

The preparation of biodiesel from various vegetable oils using alkaline transesterification of triglycerides with monohydric alcohol has been studied for several decades, and a large part of industrial production has been achieved using this method [22,23], although it requires extra-steps during the extraction and refining processes. As the cost of vegetable oil production accounts for approximately 70% of biodiesel production costs [24–26], there is a need for the development of a new biodiesel production process that is simple, compact, efficient, low-cost, and that consumes less energy.

Recently, the preparation of biodiesel using in situ transesterification has been successfully carried out with various oilseeds [24–32]. In situ transesterification is a biodiesel production method that uses the original agricultural products as the source of triglycerides, instead of purified oil, with direct transesterification, and works with virtually any lipid-bearing material. It reduces the time-consuming pre-extracted oil production system, and maximizes ester yield.

The conversion of jatropha seed to fatty acid methyl esters (FAME) by acid-catalyzed in situ transesterification has been successfully carried out [31]. Using seed size less than 0.355 mm and *n*-hexane as co-solvent under reaction conditions of 60 °C temperature, for 24 h, 7.5 mL/g methanol to seed ratio, and 15 wt.% of H_2SO_4, the FAME yield reached 99.8%. However, the conversion of jatropha oil to FAME by in situ alkaline transesterification has never been reported. Thus, a systematic study should be conducted to investigate and identify optimal reaction conditions for single step in situ alkaline transesterification combined with solvent extraction of jatropha oil.

The objective of this study was thus to investigate solvent extraction and in situ transesterification in a single step to produce biodiesel directly from jatropha seeds. The influence of methanol to seed ratio, amount of alkali (KOH) catalyst, stirring speed, temperature and reaction time was examined to identify the optimal reaction conditions and define best performance of biodiesel yield and quality.

2. Materials and methods

2.1. Materials

All trials were carried out using jatropha seeds (IP2 Lampung variety) supplied by the Indonesian Spices and Industrial Crops Research Institute (Sukabumi, Indonesia), and shells were removed manually before the study. Seed moisture content at storage was 6.2 ± 0.5% (standard NF V 03-909) [33]. Methanol (>98% purity) and *n*-hexane (>98% purity) were supplied by BRATACO Chemical Ltd. (Indonesia), and all analysis solvents and chemicals were pure analytical grades obtained from Sigma–Aldrich, Fluka and J.T. Baker (Indonesia and France).

2.2. Experimental

For all trials, moisture content determined by weight loss according to standard NF V 03-909 [33] and mesh size of jatropha seeds were less than 1% and 35, respectively. To obtain a moisture content of less than 1%, jatropha seeds were dried at 70–90 °C for 24–48 h, and then milled using an electric grinder fitted with a mesh size of 35.

The effect of methanol to seed ratio and amount of KOH on biodiesel yield and biodiesel quality was studied first. 100 g of milled jatropha seeds were mixed with methanol in which KOH had been dissolved. The methanol to seed ratio (v/w, expressed in mL/g) and the amount of KOH in methanol were 2:1–6:1 and 0.05–0.1 mol/L, respectively. The amount of KOH used in this study was based on literature values [30]. 100 mL of *n*-hexane (seed to *n*-hexane ratio (w/v) of 1:1) was then added to increase oil miscibility in the mixture, accelerate the reaction and complete it in a single phase. The reaction was carried out in a three-necked 2000 mL round bottom flask equipped with a reflux system, a magnetic stirrer and a heater, under reaction conditions of 700 rpm stirring speed, 60 °C temperature and 4 h reaction duration.

At the end of the reaction period, the mixture was cooled to room temperature, and vacuum filtered to separate the filtrate from the cake. The filtrate was then evaporated using a rotary evaporator to recover methanol and *n*-hexane, and allowed to settle and separate into two layers. The lower layer was dark brown in color and contained glycerol, while the upper layer (crude biodiesel) was yellow in color and contained the fatty acid methyl esters, the unreacted glycerides (triglycerides, diglycerides and monoglycerides), and other impurities. Methanol and *n*-hexane may extract materials other than triglycerides, such as fatty acids and phospholipids. The crude biodiesel was then washed with water until neutrality, and dried at 105 °C for 1 h. The fatty acid methyl ester, triglyceride, diglyceride, monoglyceride and fatty acid contents in crude biodiesel after washing and drying were then determined by gas chromatography. The mass of crude biodiesel after washing and drying was measured, and the biodiesel yield was calculated from the equation:

$$\text{Biodiesel yield } (\%) = \frac{\text{Mass of crude biodiesel after washing and drying (g)}}{\text{Mass of triglycerides in jatropha seeds (g)}} \times 100$$

with Mass of triglycerides in jatropha seeds (g) = Mass of oil contained in jatropha seeds (g) × Glyceride fraction content in jatropha oil (%) × Triglyceride content in glyceride fraction (%). The biodiesel yield is calculated on the basis of a pure biodiesel (i.e. containing