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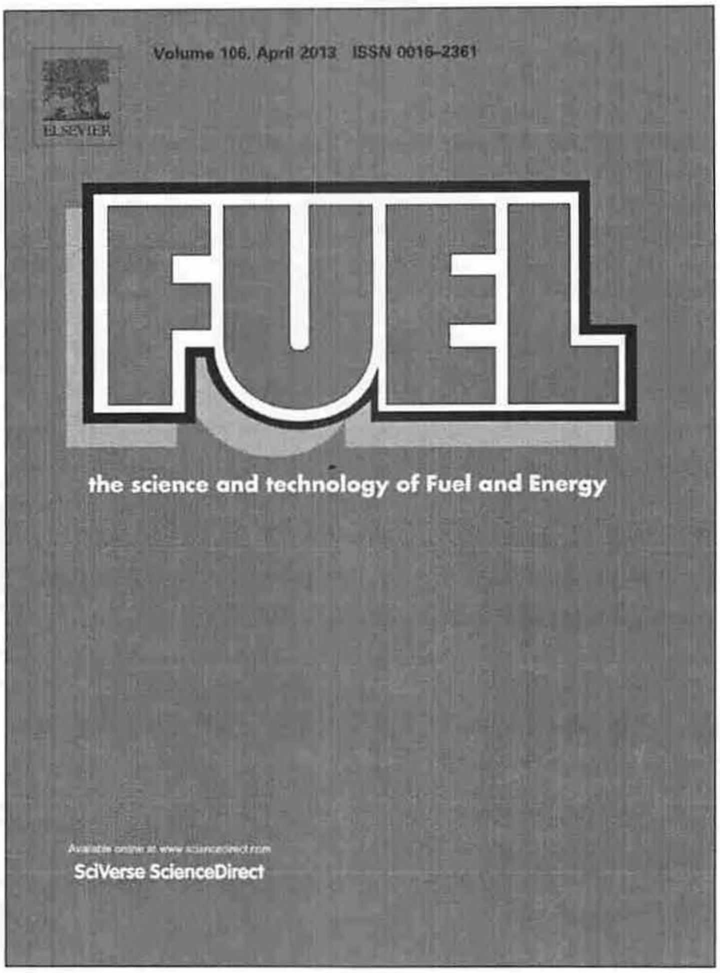

Volume 106, April 2013 ISSN 0016-2361

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Fuel 106 (2013) 111–117

Contents lists available at SciVerse ScienceDirect

Fuel

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

I. Amalia Kartika [a,*], M. Yani [a], D. Ariono [b], Ph. Evon [c,d], L. Rigal [c,d]

[a] Department of Agroindustrial Technology, FATETA-IPB, Darmaga Campus, P.O. Box 220, Bogor 16002, Indonesia
[b] Department of Chemical Engineering, FTI-ITB, Ganesha 10 Road, Bandung 40132, Indonesia
[c] Université de Toulouse, INP, LCA (Laboratoire de Chimie Agro-Industrielle), ENSIACET, 4 allée Émile Monso, BP 44362, Toulouse 31030 Cedex 4, France
[d] INRA, LCA (Laboratoire de Chimie Agro-industrielle), Toulouse 31030, France

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.

ARTICLE INFO

Article history:
Received 31 March 2011
Received in revised form 10 October 2012
Accepted 9 January 2013
Available online 31 January 2013

Keywords:
Biodiesel
Jatropha seed
In situ transesterification
Solvent extraction

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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* Corresponding author. Tel.: +62 251 8621974; fax: +62 251 8625088.
E-mail address: ikatk@yahoo.com (I. Amalia Kartika).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.01.021

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 only fatty acid methyl esters). Taking into account the fact that components contained in the crude biodiesel are not only fatty acid methyl esters, such formula may lead to a potential source of error.

Each experiment was conducted twice to give an average biodiesel yield with corresponding standard deviation. After the filtrate separation, the cake was not washed with methanol to take out the esters, meaning that it still contained a part of the fatty acid methyl esters produced during the in situ transesterification. It was directly dried overnight at room temperature, and the total volatile matter content and the *n*-hexane extracted matter content (i.e. weight loss upon *n*-hexane extraction) were then determined according to standards [33,34], respectively. All determinations were carried out in duplicate.

The effect of three other operating conditions (stirring speed, temperature and reaction time) on biodiesel yield and biodiesel quality was studied in the second stage. The corresponding experiments were conducted using a methanol to seed ratio of 6:1 (v/w) and 0.075 mol/L KOH in methanol. The stirring speed, the temperature and the reaction time were 700–900 rpm, 40–60 °C and 3–5 h, respectively. Sample collection and analyses were performed using the same procedure as for effect of methanol to seed ratio and amount of KOH on biodiesel yield and biodiesel quality. Each experiment was duplicated, and biodiesel yield was taken as the average with corresponding standard deviation. The randomized factorial experimental design with ANOVA (*F*-test at $p = 0.05$) was used to study the effects of stirring speed, temperature and reaction time on biodiesel yield and biodiesel quality using SAS software.

2.3. Analytical methods

Seed oil content was determined according to standard NF V 03-908 [34]. Ground seed was placed into an extraction thimble, and the oil was extracted using Soxhlet extraction apparatus with *n*-hexane for 6 h. The solvent was then evaporated using rotary vacuum evaporator, and the remaining oil was weighed. Seed oil content was expressed as percent by mass of the dry matter.

The fatty acid composition of oil extracted from jatropha seed was determined by gas chromatography (GC) using the following FAME method. The sample analyzed (i.e. the oil extracted from jatropha seed using the Soxhlet extraction apparatus and *n*-hexane as extracting solvent) was diluted in tert-butyl methyl ether (TBME) (concentration of around 20 mg/mL). A 100 μL aliquot of the prepared sample was then converted to methyl esters using 50 μL of 0.5 mol/L trimethylsulphonium hydroxide (TMSH) in methanol. The GC (VARIAN 3800) was equipped with a flame ionization detector using helium as carrier gas (1.2 mL/min). The sample injected (i.e. methyl esters) was separated in a CP Select CB (VARIAN) column (50 m × 0.25 mm). GC oven temperature was programmed at 185 °C for 40 min, then increased at a rate of 15 °C min^{-1} to 250 °C, and then maintained at 250 °C for 11.68 min. Injector temperature was programmed at 250 °C for 55 min, and detector temperature set at 250 °C.

The glyceride fraction content in jatropha oil and its composition (i.e. distribution between triglycerides, diglycerides, monoglycerides, and free fatty acids) was also determined by GC using the following method. 1.5 mg of the sample analyzed (i.e. the oil extracted from jatropha seed using the Soxhlet extraction apparatus and *n*-hexane as extracting solvent) was diluted in 1 mL of chloroform. 20 μL of silylation reagent (a mixture of 1 mL of N-methyl-N-trimethylsilyl-heptafluorobutyramide (MSHFBA) and 50 μL of 1-methyl imidazole) was added to a 180 μL aliquot of the prepared sample, and then heated at 103 °C for 3 min. The GC (Perkin Elmer) was equipped with a flame ionization detector using helium as carrier gas, and the injected sample was separated in a CP Sil 8CB (VARIAN) column (15 m × 0.32 mm). GC oven temperature was programmed from 55 °C to 360 °C at a rate of 45 °C min^{-1} to 80 °C, followed by 10 °C min^{-1}, and was then maintained at 360 °C for 16 min. Injector temperature was programmed from 55 °C to 340 °C at a rate of 200 °C min^{-1} and then maintained at 340 °C for 40 min, and detector temperature was set at 365 °C. Heptadecane was used as the internal standard. The peaks corresponding to the different glycerides and free fatty acids were identified by comparing the retention times of each detected component in the sample with the ones of pure glyceride and fatty acid standard compounds. To quantify each compound family (triglycerides, diglycerides, monoglycerides and free fatty acids) in the sample, a stock solution of triolein, diolein, monoolein and oleic acid added in the same proportions was prepared and then diluted to different concentrations. Stock solution and diluted solutions were used to obtain standard curves relating each peak area to the actual amounts of triolein, diolein, olein and oleic acid. For each of the four families above mentioned, the compound mass in the sample was obtained first by summing the peak areas from all same-family compounds, and then by relating area sums to standard curves. In each family, response factor of all the compounds was considered to be the same as the one of the corresponding oleic compound. The ratio between the sum of masses for triglycerides, diglycerides, monoglycerides and free fatty acids and the test sample mass was used to determine the glyceride fraction content in jatropha oil. The glyceride distribution between the four compound types was also calculated.

Once the biodiesel produced, its quality was analyzed. It includes the following parameters: (i) its acid value, expressed in mg of KOH/g of sample (standard NF T 60-204) [35], which is an indication of the free fatty acid content of the sample, (ii) its saponification value, expressed in mg of KOH/g of sample (standard NI 01-3555-1998) [36], which is the amount of alkali necessary to saponify a certain quantity of the sample, (iii) its iodine value, expressed as the number of centigrams of iodine absorbed per gram of sample (standard AOCS-Cd 1d-92) [37], which is a measurement of the unsaturations of the sample, and (iv) its viscosity, estimated using the AOAC 974:07 method [38] with an Ostwald viscometer, measured at 40 °C.

In addition, the biodiesel fatty acid methyl ester content was determined by gas chromatography using the method described as follows. The sample was diluted in cyclohexane (concentration of around 8 mg/mL). The GC (Perkin Elmer Autosystem XL) was equipped with a flame ionization detector using helium as carrier gas, and the injected sample was separated in a VF-5 ms (VARIAN) column (15 m × 0.32 mm). GC oven temperature was programmed from 55 °C to 360 °C at a rate of 45 °C min^{-1} to 80 °C, followed by 10 °C min^{-1}, and was then maintained at 360 °C for 15 min. Injector temperature was programmed from 55 °C to 340 °C at a rate of 200 °C min^{-1} and then maintained at 340 °C for 35 min, and detector temperature was set at 365 °C. Methyl heptadecanoate was used as the internal standard. The peaks of different methyl esters were identified by comparing the retention time of each component in the sample with the peaks of pure methyl ester standard compounds.

The biodiesel produced under the optimal reaction conditions was completely characterized in accordance with Indonesian Biodiesel Standard [39]. All determinations were carried out in duplicate.

3. Results and discussion

In transesterification reactions with alkaline catalysts, the presence of water can cause ester saponification. Thus jatropha seeds with less than 1% moisture content were used in all experiments. Moreover, results from previous studies showed that this seed moisture content affected biodiesel yield [24,30,40], and that the latter increased as moisture content of jatropha seed was decreased [40]. In addition, this decrease in seed moisture content increased the amount of oil dissolved in methanol [30].

The oil content of the jatropha seed used in this study was 39.4 ± 1.5% relative to its dry matter content (standard NF V 03-908), and this agrees with the 22–48% results reported by some researchers [4,41]. The fatty acid composition of jatropha oil (FAME method) was palmitic (14.7 ± 0.2%), palmitoleic (0.9 ± 0.0%), stearic (7.4 ± 0.3%), oleic (39.4 ± 0.8%), linoleic (36.5 ± 0.9%), linolenic (0.7 ± 0.0%), arachidic (0.2 ± 0.0%), and gadoleic (0.2 ± 0.0%). Thus, the oil in this study was rich in oleic and linoleic fatty acids, like other jatropha oils described in the literature [1–5,41,42]. Its glyceride fraction content, i.e. the content of triglycerides, diglycerides, monoglycerides and free fatty acids in the oil, was 99.0 ± 0.5%, meaning that the unsaponifiable compounds such as sterols and tocopherols were minor compounds. It was composed of triglycerides (95.8 ± 0.2%), diglycerides (2.6 ± 0.1%) and monoglycerides (0.3 ± 0.0%), and it contained 1.4 ± 0.1% of free fatty acids. These are carboxylic acids released from triglycerides via lipase or oxidation. There is a high risk of oxidation of the jatropha oil inside the seed due to its high unsaturated fatty acid content, especially oleic and linoleic, and those containing one or more of the non-conjugated pentadiene system ($-CH{=}CH-CH_2-CH{=}CH-$) are especially sensitive [43]. In alkaline transesterification, the free fatty acids quickly react with the catalyst to produce soaps that are difficult to separate, and this may reduce the quantity of catalyst available for transesterification, lowering the ester production yield. Soaps produced could cause an increase in viscosity, and the appearance of gels, and also make the separation of glycerol difficult [30]. Low free fatty acid content in the oil (less than 3%) is therefore required for alkali-catalyzed transesterification [44]. An attractive way to control free fatty acids in the seed is by controlling its water activity (a_w) to a level that disables any undesirable reactions or enzyme activities. This means understanding seed characteristics and behavior in response to changes in environmental conditions, particularly relative humidity, which has been successfully applied to jatropha seed [45]. Thus, control of free fatty acids in the seed, can be achieved by proper handling and storage before oil extraction and in situ transesterification.

Simultaneous solvent extraction and in situ transesterification on biodiesel processing of jatropha seeds had a positive effect on both biodiesel yield and biodiesel quality. The main advantage of this combined process is that it allows solvent extraction to be applied to oilseeds and then in situ transesterification of the extracted oils. Methanol was not a very effective solvent for oil extraction due to its immiscibility. However, the addition of a co-solvent such as *n*-hexane into the reaction mixture can significantly improve mass transfer of oil into alcohol (methanol or ethanol) and also intensify the transesterification reaction between oil and alcohol [31,32,46,47]. *n*-Hexane is an efficient solvent for oil extraction from oilseeds and, in the case of jatropha seed, its non-polarity can also limit the removal of free fatty acids and water from the seed [47]. In this study, the ratio of *n*-hexane added to seed was 1:1 (volume/weight, expressed in mL/g) for all experiments.

As previously observed by some researchers [25,29,30,47], Fig. 1 shows that the methanol to seed ratio and the amount of alkali (KOH) catalyst affected the biodiesel yield. For the three levels of KOH tested, a systematic increase in biodiesel yield was observed when the methanol to seed ratio increased from 2:1 to 6:1. In addition, for a methanol to seed ratio of 2:1, the biodiesel yield remained relatively stable (between 35% and 38%), meaning that it did not depend on the amount of KOH in the methanol. Conversely, increasing the amount of KOH from 0.05 to 0.075 mol/L in methanol significantly increased the biodiesel yield when the methanol to seed ratio was at least 4:1. Thus, a methanol to seed ratio of only 2:1 was not sufficient for complete transesterification of the triglycerides released from jatropha seed. However, when the amount of KOH exceeded 0.075 mol/L in methanol, it had less effect on the biodiesel yield, with only a slight increase when the methanol to seed ratio was 4:1 (from 62% to 68%). For a methanol to seed ratio of 6:1, increasing the amount of KOH from 0.075 to 0.1 mol/L in methanol even caused a drop in yield (from 80% to 74%). Thus, 0.075 mol/L KOH in methanol is the optimal concentration of alkali catalyst. Excess catalyst gave rise to formation of an emulsion that increased the viscosity and led to the formation of a gel, lowering the ester production yield [48].

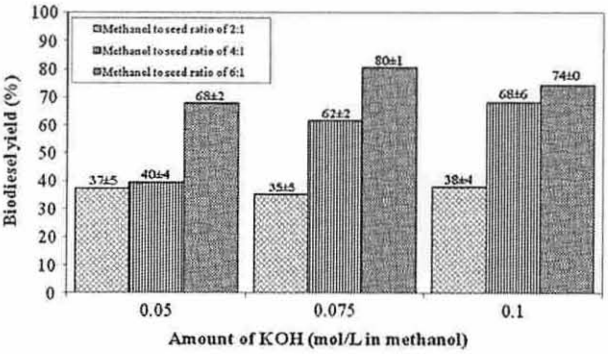

Fig. 1. Influence of methanol to seed ratio and amount of alkali (KOH) catalyst on biodiesel yield (700 rpm stirring speed, 60 °C temperature, and 4 h reaction time).

For the reaction conditions investigated (2:1–6:1 methanol to seed ratio, and 0.05–0.1 mol/L KOH in methanol), the best biodiesel yield (80% with a fatty acid methyl ester purity of 99.9%) was therefore obtained with a methanol to seed ratio of 6:1 (expressed in mL/g) and 0.075 mol/L KOH in methanol. For comparison, the optimal molar ratio for conventional alkaline transesterification of different oils is of the order of 6:1 (expressed in mol/mol) at 60 °C [4,22,23,42,48,49]. Thus, the in situ transesterification of jatropha oil from seed used about 17 times more methanol (lipid to methanol ratio of 1:104, expressed in mol/mol) than the conventional method (1:6). However, the excess reagents could be recovered for reuse.

Compared with acid-catalyzed in situ transesterification of jatropha oil from seed (over 12 h reaction time and 15 wt.% H_2SO_4) [31], the alkali-catalyzed process is faster and uses less reagents (4 h reaction time and 6.4 wt.% KOH). For 4 h reaction time, the yield obtained from acid-catalyzed in situ transesterification of jatropha oil from seed was only 40% [31] instead of 80% with the alkali-catalysed process described in this study. The greater yield with alkaline catalysis is consistent with its greater effectiveness in transesterification of triglycerides, and may also indicate better access of the transesterification reagent to the oil component of the seed, under alkaline conditions [25]. As observed in previous studies [25,30], alkaline alcohol could destroy intracellular compartments in oilseeds, allowing solubilisation and subsequent transesterification of triglycerides. In the present study, maximum ester yield (80% with a fatty acid methyl ester purity of 99.9%) was achieved with a reaction time of 4 h and 6.4 wt.% KOH (compared to the oil contained in the jatropha seed) or 0.075 mol/L in methanol. For comparison, the amount of catalyst (KOH) required for the conventional alkaline transesterification of different vegetable oils is 1% (based on oil weight) [48]. Thus, the in situ transesterification of jatropha oil from seed used about 6.4 times more KOH than the conventional method.

The biodiesel produced by in situ transesterification of jatropha oil from seed was of excellent quality using a methanol to seed ratio of 6:1 (Table 1). And, for this ratio, an increase in the amount of

Table 1
Crude biodiesel quality at different methanol to seed ratios and amounts of alkali (KOH) catalyst (700 rpm stirring speed, 60 °C temperature, and 4 h reaction time).

Methanol to seed ratio (v/w)	Amount of KOH (mol/L in methanol)	Acid value (mg KOH/g)	Saponification value (mg KOH/g)	Viscosity at 40 °C (10^{-6} m^2/s)	Composition (wt.%)				
					FAME	MAG	DAG	TAG	FA
2:1	0.05	1.48 ± 0.00	212 ± 4	24.1 ± 0.0	3.0 ± 0.1	0.2 ± 0.0	4.1 ± 0.1	91.7 ± 0.1	1.0 ± 0.1
2:1	0.075	1.48 ± 0.00	195 ± 1	21.9 ± 3.5	3.5 ± 1.5	0.1 ± 0.0	2.9 ± 0.2	91.9 ± 1.6	1.6 ± 0.3
2:1	0.1	0.81 ± 0.00	193 ± 1	21.9 ± 1.8	8.3 ± 0.8	0.1 ± 0.0	2.5 ± 0.1	88.3 ± 1.0	0.8 ± 0.0
4:1	0.05	0.27 ± 0.00	207 ± 4	21.5 ± 1.2	10.6 ± 1.0	0.3 ± 0.1	2.9 ± 0.1	85.4 ± 1.0	0.8 ± 0.0
4:1	0.075	0.27 ± 0.00	215 ± 1	8.1 ± 0.9	56.2 ± 3.5	0.2 ± 0.1	2.0 ± 0.0	40.9 ± 7.1	0.7 ± 0.1
4:1	0.1	0.27 ± 0.00	209 ± 0	3.7 ± 0.0	91.2 ± 0.8	0.1 ± 0.0	0.3 ± 0.1	8.1 ± 1.3	0.3 ± 0.1
6:1	0.05	0.27 ± 0.00	215 ± 2	3.5 ± 0.0	99.6 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.1
6:1	0.075	0.27 ± 0.00	212 ± 1	3.4 ± 0.1	99.9 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
6:1	0.1	0.27 ± 0.00	193 ± 1	3.5 ± 0.1	99.7 ± 0.5	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.1

FAME, fatty acid methyl esters; MAG, monoglycerides; DAG, diglycerides; TAG, triglycerides; FA, free fatty acids.

Table 2
Effect of operating conditions on process performance and crude biodiesel quality (6:1 methanol to seed ratio and 0.075 mol/L KOH in methanol).

Stirring speed (rpm)	Temperature (°C)	Reaction time (h)	Crude yield (wt.%)	Acid value (mg KOH/g)	Saponification value (mg KOH/g)	Viscosity at 40 °C (10^{-6} m^2/s)	Cake meal	
							Total volatile matter content (%)	*n*-Hexane extracted matter content (%)
700	40	3	81 ± 1	0.49 ± 0.10	198 ± 2	3.6 ± 0.0	10.2 ± 0.6	14.6 ± 2.8
800	40	3	82 ± 3	0.42 ± 0.10	190 ± 6	3.5 ± 0.0	9.8 ± 0.9	13.5 ± 0.5
900	40	3	83 ± 1	0.49 ± 0.10	201 ± 1	3.5 ± 0.0	11.3 ± 1.1	14.8 ± 0.5
700	50	3	83 ± 1	0.35 ± 0.10	197 ± 5	3.5 ± 0.0	10.7 ± 0.3	13.0 ± 0.7
800	50	3	81 ± 0	0.28 ± 0.00	200 ± 0	3.5 ± 0.0	11.3 ± 0.7	11.9 ± 1.4
900	50	3	82 ± 2	0.42 ± 0.00	200 ± 4	3.5 ± 0.0	10.0 ± 0.3	14.5 ± 2.1
700	60	3	77 ± 0	0.35 ± 0.10	205 ± 3	3.5 ± 0.1	9.8 ± 0.6	14.7 ± 1.7
800	60	3	83 ± 3	0.28 ± 0.00	199 ± 1	3.5 ± 0.0	11.1 ± 0.2	15.2 ± 3.0
900	60	3	85 ± 1	0.28 ± 0.00	200 ± 5	3.5 ± 0.0	10.1 ± 0.7	14.3 ± 1.7
700	40	4	79 ± 2	0.28 ± 0.00	197 ± 2	3.5 ± 0.0	11.2 ± 1.8	15.4 ± 0.3
800	40	4	76 ± 3	0.28 ± 0.00	203 ± 2	3.5 ± 0.0	10.4 ± 0.8	14.0 ± 0.9
900	40	4	83 ± 2	0.42 ± 0.00	201 ± 1	3.5 ± 0.0	10.9 ± 0.6	15.0 ± 0.5
700	50	4	86 ± 2	0.42 ± 0.00	194 ± 0	3.5 ± 0.0	11.8 ± 0.4	15.8 ± 2.4
800	50	4	83 ± 0	0.35 ± 0.10	194 ± 0	3.5 ± 0.0	11.5 ± 0.4	14.9 ± 0.0
900	50	4	84 ± 1	0.49 ± 0.10	202 ± 5	3.5 ± 0.0	9.7 ± 1.4	11.5 ± 2.0
700	60	4	76 ± 1	0.28 ± 0.00	200 ± 4	3.5 ± 0.0	10.6 ± 0.7	14.1 ± 0.9
800	60	4	85 ± 2	0.42 ± 0.00	196 ± 3	3.5 ± 0.0	10.7 ± 0.8	14.7 ± 0.0
900	60	4	75 ± 3	0.35 ± 0.10	200 ± 0	3.5 ± 0.1	9.1 ± 0.2	12.2 ± 2.9
700	40	5	84 ± 3	0.42 ± 0.00	196 ± 2	3.5 ± 0.0	10.0 ± 0.3	15.6 ± 0.8
800	40	5	83 ± 2	0.42 ± 0.00	198 ± 3	3.5 ± 0.0	10.6 ± 0.7	12.4 ± 0.1
900	40	5	84 ± 1	0.28 ± 0.00	201 ± 1	3.5 ± 0.1	11.9 ± 2.5	13.8 ± 1.2
700	50	5	85 ± 1	0.42 ± 0.00	200 ± 2	3.5 ± 0.0	10.0 ± 0.4	12.5 ± 1.3
800	50	5	87 ± 1	0.35 ± 0.10	199 ± 4	3.5 ± 0.0	10.5 ± 0.3	13.9 ± 1.8
900	50	5	85 ± 0	0.28 ± 0.00	198 ± 1	3.5 ± 0.0	9.4 ± 0.2	12.8 ± 1.4
700	60	5	80 ± 2	0.28 ± 0.00	206 ± 1	3.5 ± 0.0	10.8 ± 0.3	14.9 ± 0.8
800	60	5	76 ± 1	0.28 ± 0.00	203 ± 4	3.5 ± 0.1	10.2 ± 0.3	13.4 ± 3.3
900	60	5	76 ± 0	0.28 ± 0.00	200 ± 1	3.5 ± 0.0	10.5 ± 0.1	13.7 ± 0.8

KOH (from 0.05 to 0.1 mol/L in methanol) had no significant influence on the biodiesel quality which remained excellent. The acid value and the viscosity remained stable at less than 0.3 mg of KOH/g of biodiesel and less than 3.5 10^{-6} m^2/s, respectively. Saponification value and fatty acid methyl ester purity were high (more than 190 mg of KOH/g of biodiesel and more than 99.6%, respectively). These qualities would favor the use of such biodiesel as automotive fuel. The quality of the biodiesel obtained in this study was equivalent to that of one produced using the conventional method, and it conformed to the Indonesian Biodiesel Standard [39]. Moreover, the biodiesel quality was directly correlated to its yield. Indeed, best biodiesel quality was achieved with a methanol to seed ratio of 6:1 (Table 1) that also gave the best biodiesel yield (Fig. 1).

The quality of biodiesels produced by in situ transesterification of jatropha oil from seed with a methanol to seed ratio of less than 6:1 (Table 1) was relatively poor. Acid value and viscosity were high, whereas fatty acid methyl ester purity was low. Increasing the methanol to seed ratio and the amount of KOH in methanol improved the biodiesel quality. Acid value and viscosity decreased, and fatty acid methyl ester purity increased with an increase in methanol to seed ratio and amount of KOH in methanol. The saponification value remained stable at over 190 mg of KOH/g of biodiesel with increasing methanol to seed ratio and amount of KOH in methanol.

The influence of stirring speed, temperature and reaction time on biodiesel yield was studied using randomized factorial experimental design with three variables. For this study, methanol to seed ratio was 6:1, and KOH amount was 0.075 mol/L in methanol. The results obtained are shown in Table 2 and generally, stirring speed, temperature and reaction time affected biodiesel yield. But here, applying ANOVA to actual data (*F*-test at $p = 0.05$) shows that the effect of temperature on biodiesel yield was more significant than the two others. Five of the seven best yields corresponded to experiments conducted at 50 °C, with different stirring speeds (700–900 rpm) and different reaction times (4–5 h). Temperature can influence reaction rate and jatropha oil conversion, because intrinsic rate constants are largely dependent

Table 3
Jatropha crude biodiesel quality produced under optimal reaction conditions (6:1 methanol to seed ratio, 0.075 mol/L KOH in methanol, 800 rpm stirring speed, 50 °C temperature, and 5 h reaction time).

Parameter	Unit	Jatropha biodiesel	Biodiesel standard [39]
Density at 40 °C	g/cm^3	0.885	0.850–0.890
Viscosity at 40 °C	10^{-6} m^2/s	3.5	2.3–6.0
Flash point	°C	107	100 min
Pour point	°C	0	0 max [60]
Cloud point	°C	11	18 max
Acid value	mg KOH/g	0.35	0.8 max
Cetane number	-	47	51 min
Water and sediment content	wt.%	Trace (<0.05)	0.05 max
Sulfated ash content	wt.%	0	0.02 max
Iodine number	g iodine/100 g	107	115 max
HHV	MJ/kg	40	35 min [60]
Composition:	wt.%		
Fatty acid methyl esters		99.7	96.5 min [60]
Monoglyceride (MAG)		0.1	0.8 max [60]
Diglyceride (DAG)		0	0.2 max [60]
Triglyceride (TAG)		0	0.2 max [60]

on temperature [47]. A higher temperature can decrease the viscosities of oils, can increase the solubility of reactants, and can result in an increased reaction rate and a shorter reaction time [23]. In addition, high temperatures favor reactions with higher activation energy, and low temperatures those with lower activation energy [50]. However, in this study, results indicated that when reaction temperature was increased from 50 to 60 °C, biodiesel yield mostly decreased (from 86% to 76% with 700 rpm stirring speed and 4 h reaction time, and from 87% to 76% with 800 rpm stirring speed and 5 h reaction time, for example). Indeed, with a reaction temperature close to the boiling points of methanol and *n*-hexane, the methanol and *n*-hexane would partially vaporize and form some bubbles, which would restrain the reaction. This phenomenon was already observed during preparation of biodiesel from *J. curcas* oil produced by two-phase solvent extraction [47]. A reaction temperature of 50 °C for in situ transesterification of jatropha oil from seed led to the best biodiesel yields, and the highest one (87% with a fatty acid methyl ester purity of 99.7%) was obtained with 800 rpm stirring speed, 50 °C temperature, and 5 h reaction time.

Generally, reaction time is an important factor that affects alkali-catalyzed in situ transesterification, and triglyceride conversion increases at longer reaction time [23,25,29,30,47]. Nevertheless, within the 3–5 h reaction time investigated in this study, increasing this parameter did not systematically increase the biodiesel yield, as previously reported by Ozgul-Yucel and Turkay [51]. Instead, biodiesel yield remained relatively constant as the reaction time increased from 3 to 5 h, meaning that the equilibrium composition had already been achieved by the system after only 3 h. Normally, biodiesel yield reaches a maximum as reaction time increases (e.g. at a value less than 90 min for transesterification of isolated and refined vegetable oils), and then remains relatively constant with any further increase [23]. Moreover, a reaction time that is too long will lead to a reduction in the biodiesel yield, due to reverse transesterification reactions. A previous study [29] has shown that the alkali-catalyzed in situ transesterification reaction from sunflower seeds is extremely fast, requiring only 20 min for complete conversion.

In transesterification reactions, reactants initially form a two phase liquid system [50]. The reaction is diffusion-controlled, and poor diffusion between the two phases results in a slower rate. As methyl esters are formed, they act as a co-solvent for the reactants and a single phase system is formed. When the single phase is established, the mixing effect is insignificant and reaction rate is primarily influenced by reaction temperature. In this study, stirring speed did not affect the biodiesel yield, and this remained relatively constant as the stirring speed increased from 700 to 900 rpm, meaning that the lowest stirring speed of 700 rpm was sufficient to efficiently mix up the reactants before the establishment of the single phase.

For all the reaction conditions tested, the biodiesel quality was satisfactory (Table 2). The acid value and the viscosity remained stable at less than 0.5 mg of KOH/g of biodiesel and less than 3.6 10^{-6} m^2/s, respectively. The saponification value was high (more than 190 mg of KOH/g of biodiesel), and these qualities favor its use as automotive diesel, and conform to the Indonesian Biodiesel Standard [39].

ANOVA applied to actual acid and saponification values (*F*-test at $p = 0.05$) shows that temperature significantly affected them, while stirring speed and reaction time had no significant effect. The same tendency was previously observed for biodiesel yield, meaning that reaction conditions had exactly the same effect on both biodiesel yield and biodiesel quality.

ANOVA applied to actual viscosity data (*F*-test at $p = 0.05$) shows that stirring speed, temperature and reaction time did not significantly affect viscosity. Biodiesel viscosity remained relatively constant when stirring speed, temperature and reaction time increased.

The residual oil and fatty acid methyl ester contents in the cake meal were high (more than 11%, cf. Table 2). Although this quality was a disadvantage for direct utilization of the cake meal, it can be converted into usable energy by combustion, gasification or pyrolysis [52,53], or transformed into agromaterials [54–59].

The analysis of the biodiesel produced by solvent extraction and in situ transesterification of jatropha oil from seed under optimal reaction conditions (6:1 methanol to seed ratio, 0.075 mol/L KOH in methanol, 800 rpm stirring speed, 50 °C temperature, and 5 h reaction time) indicated that the product met the standard specification for biodiesel fuel in most regards (Table 3). Even if its cetane number (47) did not meet the Indonesian Biodiesel Standard specification (51 min) [39], it met the specification of ASTM D 6751 (47 min) [60].

4. Conclusion

This study showed that a new application for simultaneous solvent extraction and in situ transesterification of jatropha oil from seeds has been successfully carried out, and was a promising alternative technology for biodiesel processing from jatropha seeds. Biodiesel yield was 87% under the optimal reaction conditions with a FAME purity of 99.7%. Most of the quality of biodiesel produced from such conditions conformed to the Indonesian Biodiesel Standard. The process flexibility would allow different oilseeds to be treated and other co-solvents to be used. Moreover, the process compactness, its flexibility, and the lack of interdependence between the oil extraction from oilseeds and the transesterification of the extracted oil allow seed treatment capacities which are lower than those of the conventional method. These lower capacities could be adapted for treatment of local oilseed production, especially concerning specific varieties, to increase the added value of the oilseeds.

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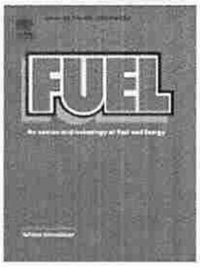

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Imprint: ELSEVIER

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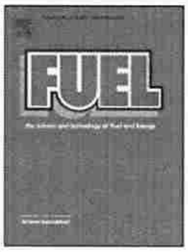

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Highlights

► Tyre blended with a high ash coal is a proper fuel in AFBC for electricity generation. ► Tyre offers a high calorific power (38.82 MJ/kg) and a low mineral content (3.30%). ► Zinc recovery (until 95%) from tyre ashes is viable for secondary metal production. ► Zinc recovery from fly ash is always greater than from bottom. ► Temperature and leaching time favours the extraction of zinc in acid lixiviation.

4 ☐ Tribological behavior of diesel fuels and the effect of anti-wear additives Review Article
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Highlights

► Main reason for the lubricity of diesel fuels is oxygen- and nitrogen-containing polar compounds. ► Anti-wear additive becomes the prime requirement to be mixed with desulfurized diesel fuel. ► Biodiesel and chemical polar compounds are the major class of lubricity additives. ► Anti-wear property of additives increases with increase in unsaturation and hydroxyl groups.

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Highlights

► DNS of a gas–solid 3d plane jet is carried out using the two-way coupling method. ► Effects of mass loading on modification of turbulence and particle are explored. ► A loading dependent asymmetric modulation of large scale vortex is observed. ► Modulation of turbulent kinetic energy and Reynolds stress is explored. ► Modification of particle dispersion characteristics by mass loadings is explained.

7 ☐ **Experimental study on fast pyrolysis of free-falling millimetric biomass particles between 800 °C and 1000 °C** Original Research Article
Pages 61-66
Li Chen, Capucine Dupont, Sylvain Salvador, Maguelone Grateau, Guillaume Boissonnet, Daniel Schweich
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Highlights

► Drop tube pyrolysis was tested at 800 °C and 950 °C on 350 to 800 μm wood particles. ► Solid size impacts pyrolysis time and char structure but not final products yields. ► Temperature significantly changes individual gas species yields. ► Particle shrinkage can be observed along pyrolysis under all conditions tested.

8 ☐ **Harvesting of Hartbeespoort Dam micro-algal biomass through sand filtration and solar drying** Original Research Article
Pages 67-71
Jacobus Brink, Sanette Marx
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Highlights

► Microalgae were harvested through sand filtration and solar drying. ► Volumetric harvesting yield of 4.6 kg L^{-1} a^{-1} was achieved. ► Aerial harvesting yield of 47.3 kg m^{-2} a^{-1} was achieved.

9 ☐ **Oxy-fuel combustion of millimeter-sized coal char: Particle temperatures and NO formation** Original Research Article
Pages 72-78
Jacob Brix, Leyre Gómez Navascués, Joachim Bachmann Nielsen, Peter Løvengreen Bonnek, Henning Engelbrecht Larsen, Sønnik Clausen, Peter Glarborg, Anker Degn Jensen

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Highlights

► Combustion of millimeter sized char particles in fixed bed reactor. ► Combustion in O_2/N_2 and O_2/CO_2 atmospheres up to 80 vol.% O_2. ► Particle temperatures determined by CCD camera. ► NO yields from char combustion determined.

10 ☐ **Investigation of deposition in aviation gas turbine fuel nozzles by coupling of experimental data and heat transfer calculations** Original Research Article
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Highlights

► Fuel deposits were generated experimentally and modelled by heat transfer model. ► Results showed that deposition is largerly dependent on fuel inlet temperature. ► Heated tube initial wall temperature had a lesser effect on deposit formation. ► Uncertainty analysis demonstrated the reliability of the heat transfer calculations. ► The heat transfer model was found sensitive to thermocouple measurement accuracy.

11 ☐ **Kinetic effect of hydrogen addition on natural gas premixed flames** Original Research Article
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Highlights

► Zheng and Yao's mechanism can capture spray combustion of fuel rich regions. ► Cylinder peak pressure is delayed by shifting diesel to dual-fuel combustion mode. ► IMEP and ITE are increased by applying higher amount of pilot fuel. ► Higher NO_x and CO levels are resulted by increasing pilot fuel quantity.

13 ☐ **Effect of biodiesel and its blends with diethyl ether on the combustion, performance and emissions from a diesel engine** Original Research Article
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Highlights

► To analyze the performance and emissions of a diesel engine fueled with biodiesel and its diethyl ether blends. ► BTE is higher with the addition of 5% diethyl ether to biodiesel (BD5). ► CO and smoke emissions are lower for BD5. ► A slight increase in NO_x emissions for BD5.

14 ☐ **Biodiesel production from jatropha seeds: Solvent extraction and in situ transesterification in a single step** Original Research Article
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