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Transformation of Jatropha Seed to Biodiesel by In Situ Transesterification

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Abstract. The objective of this study was to investigate the in situ transesterification allowing to produce directly biodiesel from jatropha seed. Experiments were conducted using milled jatropha seed with moisture content of < 2% and mesh size of 20-35. The influences of amount of KOH catalyst, methanol to seed ratio, amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time were examined to define the best performance of biodiesel production yield and biodiesel quality. Generally, the methanol to seed ratio and amount of KOH affected biodiesel production yield and its quality. An increase of biodiesel yield and quality was observed as methanol to seed ratio and amount of KOH were increased. Highest biodiesel yield (76% with a FAME purity of 99.95%) and best biodiesel quality were obtained under methanol to seed ratio of 6:1 and amount of KOH of 0.075 mol/L in methanol. The acid value was < 0.3 mg of KOH/g, viscosity was < 3.5 cSt, and saponification value was > 210 mg of KOH/g. In addition, the amount of n-hexane to methanol and seed ratio affected biodiesel production yield. An increase of biodiesel yield was observed as amount of n-hexane to methanol and seed ratio was increased. The stirring speed, temperature and reaction time did not affected biodiesel yield. Highest biodiesel yield (89%) was obtained under amount of n-hexane to methanol and seed ratio of 3:3:1, stirring speed of 600 rpm, temperature of 40°C, and reaction time of 6 h. The effects of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on biodiesel quality were less important. In all experiments tested, the biodiesel quality was very good. The acid value was < 0.3 mg of KOH/g, viscosity was < 5.5 cSt, and saponification value was > 183 mg of KOH/g. The quality of biodiesel produced under optimal reaction condition was in accordance with the Indonesian Biodiesel Standard.

Keywords: *biodiesel; in situ; jatropha see; alkali; transesterification.*

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 jatropha cultivated land area is growing because this plant can be used to reclaim land, to prevent and/or control erosion, and it provides a new agriculture development mode without competition between food and non food uses.

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

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Jatropha curcas oil is regarded as a potential diesel substitute. Vegetable oils used as alternative fuel have numerous advantages. They are notably non toxic, safely stored and handled because of their high flash point. 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.

The preparation of biodiesel from various vegetable oils based on alkaline transesterification of triglycerides with polyhydric alcohol has been studied for several decades, and a major amount of industrial production has been achieved with this method [6,7]. However, the transformation of jatropha seed in oil industry requires extra-steps during the extraction and refining processes. As the cost of the vegetable oil production contributes to approximately 70% of the biodiesel production cost [8,9], 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.

On the other hand, the preparation of biodiesel based on in situ transesterification has been successfully carried out from various oilseeds [8-15]. In situ transesterification is a biodiesel production method that uses the original agricultural products as the source of triglycerides instead of purified oil for direct transesterification, and it works virtually with any lipid-bearing material. It can reduce the long production system associated with pre-extracted oil, and it maximizes ester yield.

The objective of this study was to investigate the in situ transesterification allowing to produce directly biodiesel from jatropha seed. The influences of amount of KOH catalyst, methanol to seed ratio, amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time were examined to define the best performance of biodiesel production yield and biodiesel quality.

2 Materials and methods

2.1 Materials

All trials were carried out using jatropha seed that was supplied by Indonesian Spices and Industrial Crops Research Institute (Sukabumi, Indonesia). The jatropha seed variety was the Lampung one. The oil content of the seed, expressed in relation to its dry matter content (standard NF V 03-908) was 39.4%, or 36.9% in relation to its wet basis. The seed moisture content at storage was 6.2% (standard NF V 03-903). Methanol (> 98% purity) and n-hexane (> 98% purity) were supplied by BRATACO Chemical Ltd (Indonesia). All solvents and chemicals for analysis were pure analytical grades that were obtained from Sigma-Aldrich, Fluka and J.T. Baker (Indonesia and France).

2.2 Experimental

In all trials, the moisture content and mesh size of jatropha seed were less than 1% and 35, respectively. To obtain a moisture content of less than 1%, the jatropha seed was dried at 60-70°C during 24-48 h. The dried jatropha seed was then milled using an electric grinder fitted with a mesh size of 35.

For the study of KOH amount effect and methanol to seed ratio effect on biodiesel production yield and biodiesel quality, 100 g of milled jatropha seed were mixed with methanol in which KOH was firstly dissolved. The amount of KOH and the methanol to

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seed ratio (v/w) were 0.05-0.1 mol/L in methanol and 2:1-6:1, respectively. The KOH amount used in this study was based on literature reported elsewhere [13]. 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, to accelerate the reaction and to perform 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 for the stirring speed, 60°C for the temperature and 4 h for the reaction time.

Upon achieving reaction period, the mixture was cooled to room temperature, and was vacuum filtered to separate the filtrate from a cake. The filtrate was then evaporated using a rotary evaporator to recover methanol and n-hexane, and allowed to settle to be separated into two layers. The lower layer was dark brown in color and contained glycerol, while the upper layer was yellow in color and contained the fatty acid methyl esters (crude biodiesel) and the unreacted triglycerides. The upper layer was then washed with water until neutrality, and dried at 105°C during 1 h. The mass of upper layer was measured, and the biodiesel production yield was calculated using the formula:

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

The cake was dried overnight at room temperature. The total volatile matter content (standard NF V 03-903) and the n-hexane extracted matter content (standard NF V 03-908) were the determined.

For the study of the operating conditions effects on biodiesel production yield and biodiesel quality, the experiments were conducted using KOH amount of 0.075 mol/L in methanol. The different operating conditions were examined by varying the amount of n-hexane to methanol and seed ratio (1:5:1, 2:4:1, 3:3:1), the stirring speed (200-600 rpm), the temperature (40-50°C) and the reaction time (4-6 h). Sample collection and analysis were performed according to procedure developed in the previous study. The randomized factorial experimental design with 2 replications and ANOVA (F-test at $\alpha = 0.05$) were applied to study the effects of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on biodiesel production yield and biodiesel quality using SAS software.

2.3 Biodiesel quality analysis

The quality parameters of biodiesel included acid value (standard NF T 60-204), saponification value (standard NI 01-3555-1998), iodine value (standard AOCS-Cd 1d-92), and viscosity (AOAC 974:07). Moreover, the fatty acid methyl esters content of biodiesel was determined by gas chromatography using the FAME method. The biodiesel produced under the optimal operating condition was completely characterized in accordance with the Indonesian Biodiesel Standard.

3 Results and discussion

The oil content of jatropha seed in this study was 39.4%. Such amount of oil in jatropha seed was in agreement with the results reported (22-48%) by a few researchers [4,16]. Jatropha oil used in this study was rich in oleic (39.44%) and linoleic (36.52%) fatty acids, such as other jatropha oils described by a few researchers in previous studies [1-5,16,17], and it contained 1.82% of free fatty acids. In alkaline transesterification, the free fatty acids quickly react with the catalyst to produce soaps that are difficult to separate.

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This may reduce the quantity of catalyst available for transesterification, lowering the ester production yield. Low free fatty acids content in the oil (less than 3%) is therefore required for alkali-catalyzed transesterification [18].

The simultaneous solvent extraction and in situ transesterification on biodiesel processing from jatropha seeds affected positively both biodiesel production 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 to extracted oils. Methanol proved to be a solvent not very efficient for oil extraction due to its immiscibility. However, the addition of a small quantity of a co-solvent such as n-hexane into the reaction mixture can improve significantly the mass transfer of oil into alcohol (methanol or ethanol) and also intensify the transesterification reaction between oil and alcohol [14,15,19,20]. n-Hexane is an efficient solvent for oil extraction from oilseeds. In the case of jatropha seed, its non-polarity can also limit the removal of free fatty acids and water from the seed [20]. In this study, the ratio of n-hexane added to seed was 1:1 (v/w) for all the experiments carried out.

Figure 1 shows that the methanol to seed ratio and the amount of alkali (KOH) catalyst affected generally the biodiesel production yield. As previously observed by a few researchers [9,12,13,20], an increase of both methanol to seed ratio and KOH amount increased the biodiesel production yield. For all the amounts of KOH tested, a systematic increase of the biodiesel production yield was observed when the methanol to seed ratio became higher than 2:1. In addition, increasing the amount of KOH from 0.05 to 0.075 mol/L increased significantly the biodiesel production yield. However, when the amount of KOH exceeded 0.075 mol/L, it had no significant effect on the biodiesel production yield. The highest biodiesel production yield (76% with a fatty acid methyl esters purity of 99.95%) was therefore obtained under methanol to seed ratio of 6:1 and KOH amount of 0.075 mol/L in methanol. By comparison, the optimal molar ratio for the conventional alkaline transesterification of different oils is of the order of 6:1 at 60°C [4,6,7,17,21]. Thus, the in situ transesterification of jatropha oil from seed used about 17 times more methanol than the conventional method. However, the excess reagents could be recovered for reuse.

The biodiesel produced by in situ transesterification of jatropha oil from seed had an excellent quality under a methanol to seed ratio of 6:1. The increase of KOH concentration did not improve significantly the biodiesel quality. The acid value and the viscosity remained stable at less than 0.3 mg of KOH/g of biodiesel and less than 3.5 cSt, respectively. The saponification value and the fatty acid methyl esters purity were high (> 190 mg of KOH/g of biodiesel and > 99.6%, respectively). These qualities were favorable for the use of such biodiesel as automotive diesel.

The quality of biodiesels produced by in situ transesterification of jatropha oil from seed under a methanol to seed ratio of less than 6:1 was relatively poor. The acid value and the viscosity were high (> 0.5 mg of KOH/g of biodiesel and > 8 cSt, respectively), while the fatty acid methyl esters purity was low (2-60%). The increase of the methanol to seed ratio and the increase of the amount of KOH in methanol improved the biodiesel quality. The acid value and the viscosity decreased, and the fatty acid methyl esters purity increased with the increase of the methanol to seed ratio and the increase of the amount of KOH in methanol. The saponification value remained stable at more than 190 mg of KOH/g of biodiesel as the methanol to seed ratio and the amount of KOH in methanol increased.

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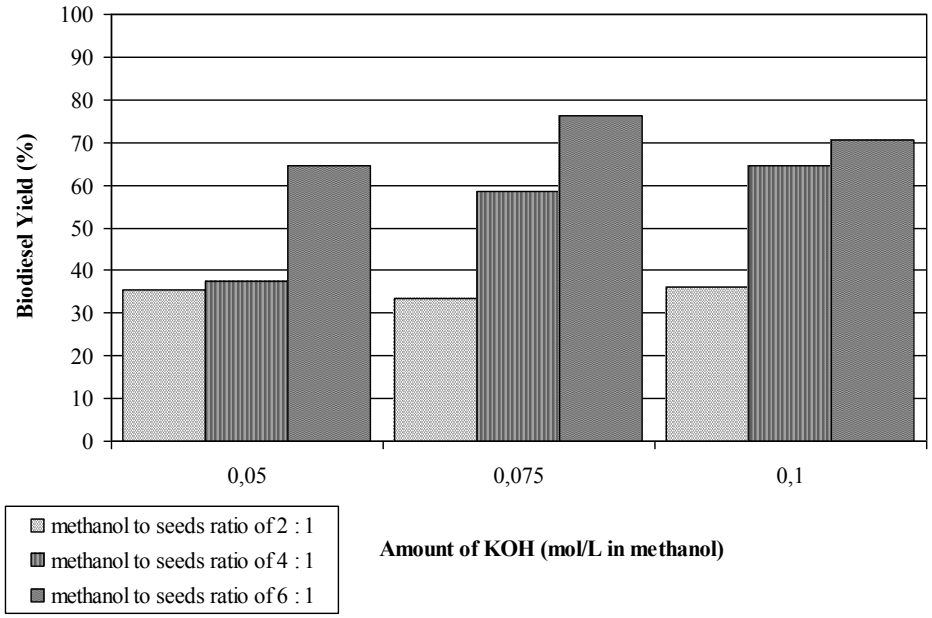

Figure 1 Influence of methanol to seed ratio and amount of alkali (KOH) catalyst on biodiesel production yield (%) (700 rpm for the stirring speed, 60°C for the temperature and 4 h for the reaction time).

Figure 2 shows the influence of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on the biodiesel production yield. Generally, the amount of n-hexane to methanol and seed ratio affected biodiesel production yield. An increase of biodiesel yield was observed as amount of n-hexane to methanol and seed ratio was increased. The stirring speed, temperature and reaction time did not affected biodiesel yield. Furthermore, the ANOVA applied to actual data (F-test at $\alpha = 0.05$) shows that the amount of n-hexane to methanol and seed ratio significantly affected the biodiesel production yield, while the temperature, the stirring speed and the reaction time did not significantly affect it. The biodiesel production yield at the amount of n-hexane to methanol and seed ratio of 1:5:1 was significantly different compared with those obtained at the amount of n-hexane to methanol and seed ratio of 2:4:1 and 3:3:1. On the other hand, the biodiesel production yields at the amount of n-hexane to methanol and seed ratio of 2:4:1 and 3:3:1were not significantly different. Highest biodiesel yield (89%) was obtained under amount of n-hexane to methanol and seed ratio of 3:3:1, stirring speed of 600 rpm, temperature of 40°C, and reaction time of 6 h.

For all the reaction conditions tested, the biodiesel quality was satisfactory. The acid value and the viscosity remained stable at less than 0.3 mg of KOH/g of biodiesel and less than 5.5 cSt, respectively. The saponification value was high (more than 183 mg of KOH/g of biodiesel). These qualities were favorable for its use as automotive diesel, and they were in accordance with the Indonesian Biodiesel Standard.

The ANOVA applied to actual data of acid and saponification values (F-test at $\alpha = 0.05$) shows that the amount of n-hexane to methanol and seed ratio, the temperature, the stirring speed and the reaction time did not significantly affected the acid and saponification values. The ANOVA applied to actual data of viscosity (F-test at $\alpha = 0.05$) shows that the amount of n-hexane to methanol and seed ratio significantly affected the

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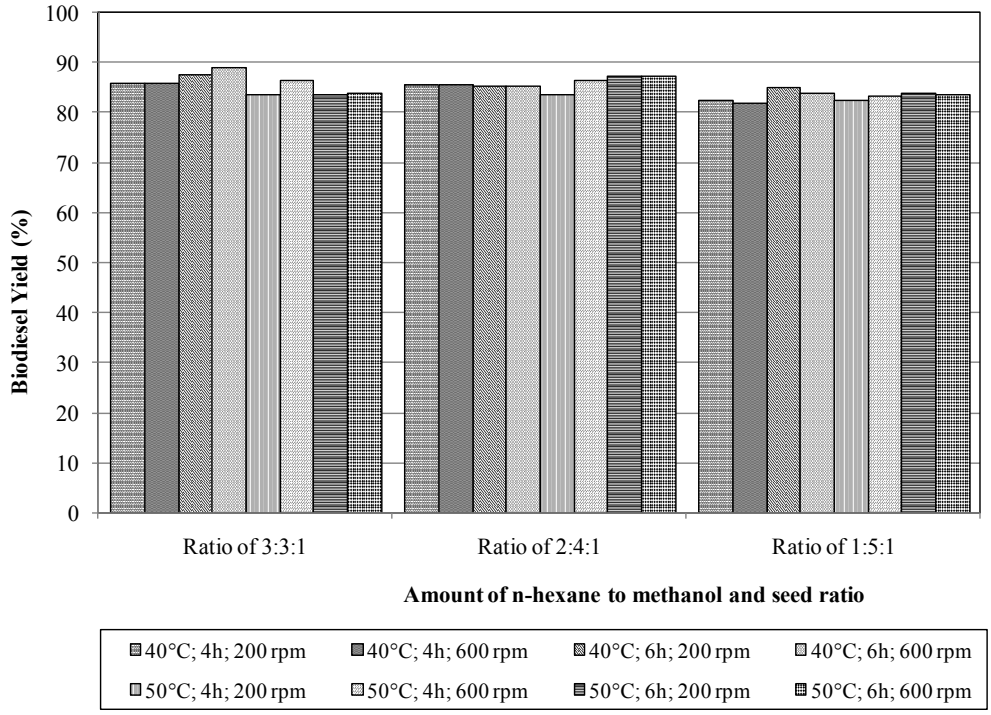

Figure 2 Influence of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on the biodiesel production yield.

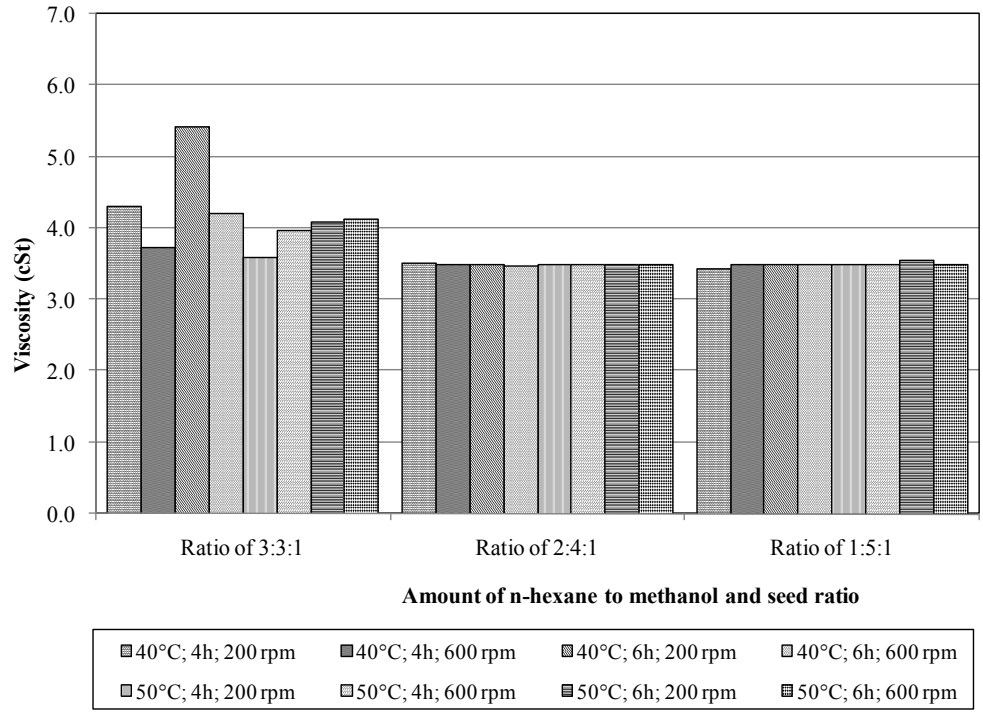

Figure 3 Influence of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on the viscosity of biodiesel.

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viscosity of biodiesel, while the temperature, the stirring speed and the reaction time did not significantly affect it (Figure 3). The viscosity of biodiesel at the amount of n-hexane to methanol and seed ratio of 3:3:1 was significantly different compared with those obtained at the amount of n-hexane to methanol and seed ratio of 2:4:1 and 1:5:1. On the other hand, the viscosity of biodiesel at the amount of n-hexane to methanol and seed ratio of 2:4:1 and 1:5:1were not significantly different. Lowest viscosity of biodiesel (3.45 cSt) was obtained under amount of n-hexane to methanol and seed ratio of 1:5:1, stirring speed of 200 rpm, temperature of 40°C, and reaction time of 4 h.

The analysis of the biodiesel produced by solvent extraction and in situ transesterification of jatropha oil from seeds under the optimal reaction condition (amount of n-hexane to methanol and seed ratio of 3:3:1, 600 rpm for the stirring speed, 40°C for the temperature and 6 h for the reaction time) indicated that the product met the standard specification for biodiesel fuel in most regards (Table 1).

Table 1 Jatropha crude biodiesel quality produced under optimal reaction condition (amount of n-hexane to methanol and seed ratio of 3:3:1, 600 rpm for the stirring speed, 40°C for the temperature and 6 h for the reaction time).

Parameter	Unit	Jatropha biodiesel	Biodiesel standard
Density at 40°C	g/cm^3	0.871	0.850-0.890
Viscosity at 40°C	cSt	4.21	2.3-6.0
Flash point	°C	107	100 min
Pour point	°C	0	0 max[b]
Cloud point	°C	11	18 max
Acid value	mg of KOH/g	0.20	0.8 max
Cetane number	-	62.5	48 min
Water and sediment content	%, wt	trace (< 0.05)	0.05 max
Sulfated ash content	%, wt	0	0.02 max
Iodine number	g of iodine/mg	75.26	115 max
HHV	MJ/kg	39.73	35 min

4 Conclusion

This study showed that the in situ transesterification of jatropha seed has been successfully carried out, and was a promising alternative technology for biodiesel processing directly from jatropha seed. Moreover, the n-hexane was an excellent co-solvent. This new technology allowed the solvent extraction to be applied to oilseed and the transesterification to the extracted oil at the same time and in the same machine.

The methanol to seed ratio and amount of KOH affected biodiesel production yield and its quality. An increase of biodiesel yield and quality was observed as methanol to seed ratio and amount of KOH were increased. Highest biodiesel yield (76% with a FAME purity of 99.95%) and best biodiesel quality were obtained under methanol to seed ratio of 6:1 and amount of KOH of 0.075 mol/L in methanol. The acid value was less than 0.3 mg of KOH/g, viscosity was less than 3.5 cSt, and saponification value was more than 210 mg of KOH/g.

The amount of n-hexane to methanol and seed ratio affected biodiesel production yield. An increase of biodiesel yield was observed as amount of n-hexane to methanol and seed ratio was increased. The stirring speed, temperature and reaction time did not affected biodiesel yield. Highest biodiesel yield (89%) was obtained under amount of n-hexane to methanol and seed ratio of 3:3:1, stirring speed of 600 rpm, temperature of 40°C, and

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reaction time of 6 h. The effects of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on biodiesel quality were less important. In all experiments tested, the biodiesel quality was very good. The acid value was less than 0.3 mg of KOH/g, viscosity was less than 5.5 cSt, and saponification value was more than 183 mg of KOH/g. The quality of biodiesel produced under optimal reaction condition was in accordance with the Indonesian Biodiesel Standard.

Finally, the biodiesel processing with in situ transesterification resulted in a biodiesel production yield and a biodiesel quality equivalent to those obtained with the conventional method. The flexibility of the process would permit to treat different seeds, and to use other co-solvents. In addition, the process compactness and its flexibility, the lack of interdependence between the oil extraction from oilseeds and the transesterification of extracted oils, and the minimization of investment costs allow seed treatment capacities lower than those of the conventional method. These lower capacities could be adapted to treat the local oilseeds productions, especially specific varieties, to increase the added value of oilseeds.

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