Influence of co-solvent on reactive-extraction of *Jatropha curcas* L. seed for biodiesel production

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Abstract. In this study, experimental studies have been carried out to improve the yield of biodiesel by addition of co-solvent to enhance the miscibility of the phases and speed up the reaction rate. The co-solvent used are tetrahydrofuran and hexane. The experimental result shows that the transesterification rate was improved when compared to the system without cosolvents. The biodiesel produced in the experiment was analyzed by gas chromatography-mass spectrometry (GC-MS), which showed that methyl oleate was the highest compound in biodiesel.
Keywords: biodiesel, co-solvent, *jatropha curcas* seed, reactive-extraction

Introduction

Currently, the use of edible oil to produce biodiesel is not feasible in view of a big gap in demand and supply of such oils as food and they are far too expensive to be used. Obviously, the use of non-edible vegetable oils compared to edible oils is very significant. *Jatropha curcas* oil, due to the presence of toxic phorbol esters is considered a non-edible oil. The role of *Jatropha curcas* as a substitute for diesel is very remarkable. If *Jatropha curcas* is grown in large-scale plantations, it has the potential to create a new agricultural industry to provide low-cost biodiesel feedstock.

Jatropha curcas L. oil can be used as fuel in diesel engines directly and by blending it with diesel. Direct use of *Jatropha curcas* L. oil and/or the use of blends of the oil has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. Shah & Gupta (2007) reported the lipase catalyzed preparation of biodiesel from *Jatropha curcas* L. oil in a solvent free system. The main drawback of enzyme catalyzed process stems from the high cost of the lipases as catalyst (Wang *et al.*, 2008). Although lipase catalyzed transesterification offers an attractive alternative, the industrial application of this technology has been slow due to feasibility aspects and some technical challenges. Hawash *et al.* (2009) reported the transesterification of *Jatropha curcas* L. oil using supercritical methanol under different conditions of temperature (from 512 to 613 K), pressure (from 5.7 to 8.6 MPa) and molar ratio of alcohol to oil (from 10 to 43 mol alcohol per mol oil). The disadvantages of the supercritical methods stem mostly from high pressure and temperature requirement, high methanol to oil ratios that render the production expensive. Berchmans & Hirata (2008) and Lu *et al.* (2009) have been developed a technique to produce biodiesel from Jatropha curcas L. oil with high free fatty acids contents, in which two-stage transesterification process was selected to improve methyl ester yield. The first stage involved the acid pretreatment process to reduce the FFA level of crude Jatropha curcas L. oil and second was the alkali base catalyzed transesterification process. Although this is an effective method to deal with high FFA, the process seems rather complex.

The conventional methods for producing biodiesel from jatropha and other types of oil seeds involve various stages: oil extraction, purification (degumming, dewaxing, deacidification, dephosphorization, dehydration, etc.), and subsequent esterification or transesterification. These multiple biodiesel processing stages constitute over 70% of the total biodiesel production cost if refined oil is used as feedstock (Zeng *et al.*, 2009). Recently, some previous studies were shown that in situ extraction and esterification/transesterification, simply known as reactive extraction, is a feasible technology for the production of biodiesel using a single step that can cut the processing cost. In the reactive extraction process, extraction of oil and esterification/transesterification proceed in a single step in which the oil-bearing material contacts with alcohol directly instead of reacting with pre-extracted oil. In other words, alcohol acts both as an extraction solvent and as a transesterification reagent during reactive extraction, and therefore a higher amount of alcohol is required. However, reactive extraction eliminates the requirement of two separate processes, the costly hexane oil extraction process and the transesterification reaction process, thus reducing processing time, cost, and amount of solvent required (Shuit *et al.*, 2010, Kaul *et al.*, 2010). Furthermore, on the basis of a similar study reported in the literature (using soybeans), it was demonstrated that the reactive extraction process can be scaled up without encountering much problem in mass and heat transfer limitations (Haas & Scott, 2007).

Several authors have suggested that methanolysis occurs only in the methanol phase. They suggested that addition of a cosolvent could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system (Boocock *et al.*, 1996; Guan *et al.*, 2009; Peña *et al.*, 2009). Thus, the aim of this research is to the influence of co-solvent on reactive-extraction of *Jatropha curcas* L. seed for biodiesel production.

Materials and Methods

The jatropha seed was kindly provided by a local farm around Banda Aceh. The hexane and tetrahydrofuran used were of 99.9% and 99% purity, respectively. The methanol used throughout this study was of 99.97% purity. All solvents were purchased from Fisher Scientific.

A known amount of sodium hydroxide was dissolved in 400 ml of methanol, and then the mixture was placed in a 500 mL round-bottom flask equipped with a condenser and an overhead stirrer and placed in a constant temperature water bath. The mixture was heated to the desired temperature (50^{o}C), using a heated circulating water bath. After desired temperature achieved, a 40 gram of ground and sieved jatropha seed (up to 60 mesh of size) was transferred to the round-bottomflask and the reaction was carried out at the desired temperature and reaction periods. The stirrer speed was maintained at 200 rpm for all of the experiment. It was important to ensure that there was no escape of methanol from the flask as losses of methanol to the atmosphere would distort the outcome of the parametric study.

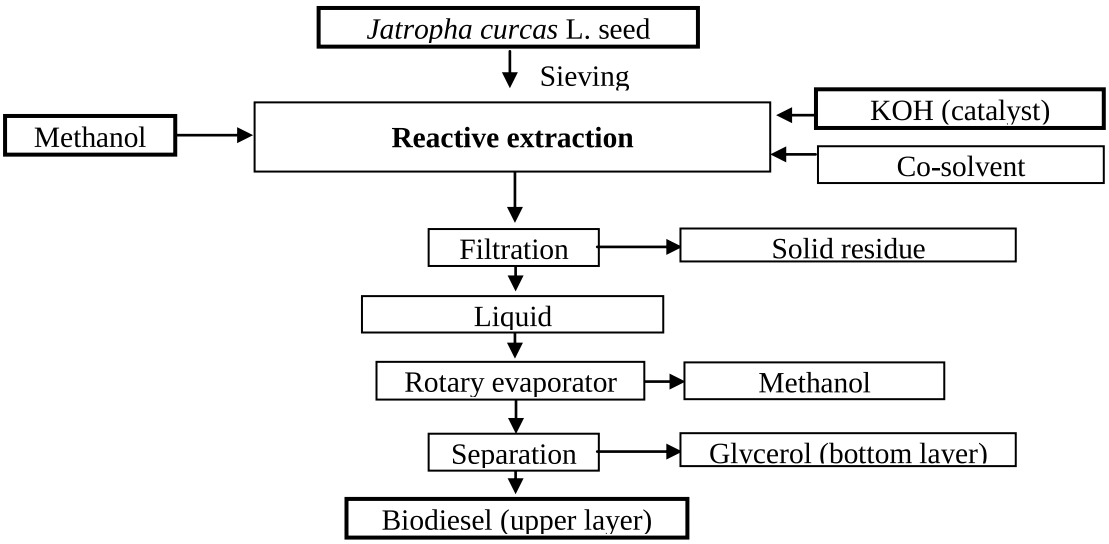

Figure 1. Experimental procedure

After operation for the desired time, the liquid was separated from the seed using vacuum filtration. The solid residue was washed repeatedly with methanol to recover any product that adhered to the seed and the excess methanol was removed using a rotary evaporator. After evaporation, two layers of liquid were formed. The upper layer contained the ester phase, while the bottom layer contained the glycerol phase. The layers were separated using a separating funnel, weighed, stored in sealed vial and ready for GC-MS analyses. The experimental procedure is presented in Figure 1.

Results and Discussion

Since the oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. Although the miscibility of the two phases can be enhanced by increasing the temperature, this is an energy-consumptive process. Methanol extracts some amount of material from the seed but very little is triglyceride. The poor triglyceride solubility in methanol is as expected, since methanol is a very polar solvent, whereas most triglycerides are non-polar long chain hydrocarbon molecules. However, various other compounds in the seed can potentially dissolve in methanol, e.g. phospholipids, sterols, phenols, and vitamins. Based on this fact, a cosolvent could be added to enhance the miscibility of the phases and speed up the reaction rate.

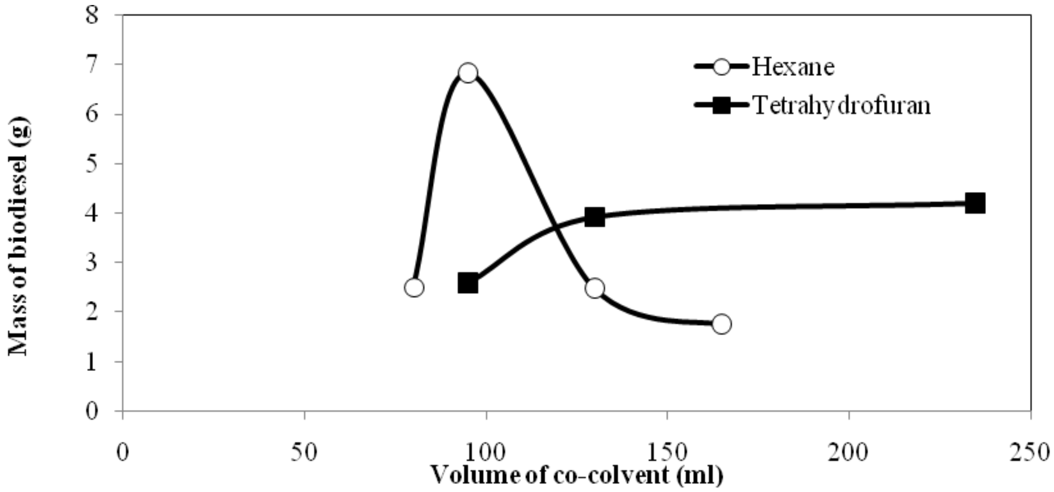

Figure 2. Influence of co-solvent on the mass of biodiesel

The influence of co-solvent of hexane and tetrahydrofuran on the mass of biodiesel obtained is presented in Figure 2. Hexane and tetrahydrofuran have influenced to the mass of biodiesel obtained in a different degree. In addition, the influence of hexane and tetrahydrofuran provided a different trend. Meanwhile, the comparison of mass biodiesel produced with and without co-solvent is given in Table 1. It can be concluded that the use of co-solvent provided more mass of biodiesel when compared to the system without co-solvents.

Table 1. Effect of co-solvent on the amount of mass of biodiesel.

Co-solvent	Mass of biodiesel (g)
None	1.71
Hexane*	6.83
THF **	3.92

* Volume of hexane added: 95 ml, ** Volume of THF added: 130 ml

As shown in Fig. 2, the mass of biodiesel reached its maximum at the volume of hexane of 95 ml. This indicates that excessive addition of hexane into the reaction system decreased the transesterification rate, due to a dilution effect on the reagents. When the volume of cosolvent was lower than 95 ml, the mass of biodiesel decreased because of the immiscibility of the oil and methanol. However, even when the cosolvent–methanol–oil system did not become homogeneous, the transesterification rate was improved when compared to the system without cosolvents. On the other hand, as a non-polar solvent, n-hexane can partly dissolve an amount of methanol. So n-hexane also can be used as a co-solvent in the transesterification to form biodiesel in order to accelerate reaction rate (Kim & Kang, 2004). Excessive addition of cosolvent into the reaction system could reduce the transesterification rate and increase the operating cost. Beyond certain n-hexane to oil volume ratio, the excessively added n-hexane diluted the *Jatropha curcas* L. oil concentration. So the optimum loading amount of n-hexane to oil volume ratio was found to be 4.2:1. Qian *et al.* (2010) reported that the optimum loading amount of n-hexane to oil weight ratio was found to be 3:1.

Boocock *et al.* (1996) suggested that addition of a cosolvent such as tetrahydrofuran could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system. As shown in Fig. 2, the mass of biodiesel obtained increase with increasing of tetrahydrofuran volume added. Tetrahydrofuran is a widely used solvent in the transesterification reaction system, but it tends to form peroxide on storage. In addition, excessive addition of tetrahydrofuran into the reaction system could increase a significant operating cost. For tetrahydrofuran, recycle of solvent is simplified because of the similar boiling points of tetrahydrofuran (67°C) and methanol (65°C).

The biodiesel obtained in the experiment is a clear yellow liquid. Compositions of samples were analyzed by GC-MS. The typical GC-MS total ion chromatogram of compound in biodiesel obtained by reactive extraction can be seen in Figure 3. The identified main compounds in the biodiesel are presented in Table 2. It can be clearly seen that the biodiesel obtained in the experiment mainly contained five fatty acid methyl esters. Therefore, it can be concluded that the composition of biodiesel was similar with the composition of fatty acid of jatropha oil. The GC-MS analysis indicated that the amount of methyl oleate was the highest in the biodiesel.

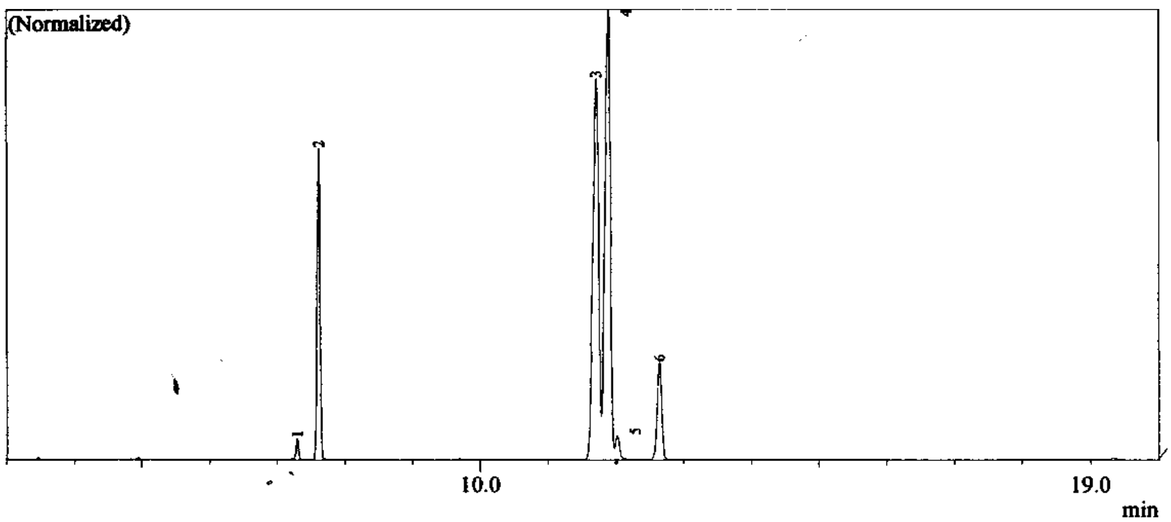

Figure 3. Typical GC-MS total ion chromatogram of compounds in biodiesel

Table 2. GC-MS result of biodiesel

Component	Composition (%)
methyl oleate	39.12
methyl linoleate	35.12
methyl palmitate	14.89
methyl stearate	7.54

Conclusions

The influence of co-solvent in the production of biodiesel from *Jatropha curcas* L seed using reactive-extractionon process was investigated in this study. The present study indicates that the type of solvent have a significant influence on the process. The transesterification rate was improved when compared to the system without cosolvents. Based on GC-MS analysis, methyl oleate was the highest compound in biodiesel.

Acknowledgements

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