International Journal on
Advanced Science
Engineering
Information Technology

Vol.3 (2013) No. 3
ISSN: 2088-5334

Reactive Extraction of Jatropha Seed for Biodiesel Production: Effect of Moisture Content of Jatropha Seed and Co-solvent Concentration

M. Dani Supardan[#], Satriana[*], Fahrizal[*], Ryan Moulana[*]

[#] *Department of Chemical Engineering, Syiah Kuala University, Darussalam, Banda Aceh, 23111, Indonesia*
E-mail: m.dani.supardan@che.unsyiah.ac.id

[*] *Department of Agriculture Product Technology, Syiah Kuala University, Darussalam, Banda Aceh, 23111, Indonesia*
E-mail: satrianaa@yahoo.com, fahrizal_stp@yahoo.com, ryanmoulana@gmail.com

***Abstract*— Biodiesel is one among the promising renewable fuels, holding various advantages compared with fossil fuel. In this study, reactive extraction of jatropha seed for biodiesel production was investigated. The effect of moisture content of jatropha seeds and co-solvent concentration was examined to determine the best performance of the biodiesel production yield. The co-solvent used is hexane. Design of experiments (DOE) was used to study the effect of moisture content of jatropha seed and co-solvent of hexane concentration on the yield of biodiesel. Generally, the moisture content of jatropha seeds and co-solvent concentration affected biodiesel production yield. The experimental result also shows that the transesterification rate was improved when compared to the system without co-solvents. It was found that the production of biodiesel achieved an optimum level of 68.3% biodiesel yield at the following reaction conditions, i.e. moisture content of jatropha seed of 1% and hexane to oil ratio of 6.9 (w/w).**

***Keywords*— Biodiesel, co-solvent, jatropha seed, reactive extraction, moisture content.**

I. INTRODUCTION

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. Therefore, production of biodiesel from nonedible oils such as *Jatropha curcas* L. seeds and waste cooking oil would be a potential solution to this issue. Among these choices, jatropha seed has recently been hailed as the promising feedstock for biodiesel production because it can be cultivated in dry and marginal lands, and thus it does not compete for arable land that would have otherwise being planted with food crops [1]. Also, *Jatropha curcas* oil, due to the presence of toxic phorbol esters is considered a non-edible oil. Besides, its oil yield is comparable to that of palm oil but much higher as compared to other edible oil crops such as rapeseed, sunflower, and soybean. The role of *Jatropha curcas* as a substitute for diesel is very remarkable.

Biodiesel is produced through different techniques such as direct/oil blends, microemulsion, pyrolysis and transesterification. However, the most notable way to produce biodiesel fuel is through transesterification reaction. Transesterification is the reaction of triglycerides and low molecular weight alcohols such as methanol and ethanol to fatty acid alkyl esters in the presence of catalyst. Methanol is the most favored alcohol because it is less costly and easily obtainable. Transesterification reaction is catalyzed by either homogeneous catalyst (sodium hydroxide, potassium hydroxide, sulfuric acid, hydrochloric acid, etc.) or heterogeneous catalyst (enzymes, alkaline transesterification earth metal reaction compounds, titanium silicates, anion exchange resins, guanidine heterogenized on organic polymers) [2]. Enzymes-catalyzed procedures, using lipase as catalyst, do not produce side reactions, but the lipases are very expensive for industrial scale production and a three-step process is required to achieve a high conversion [3]. Acid catalyzed process is useful when a high amount of free fatty acids are present in the vegetable oil, but the reaction time is very long even at the boiling point of the alcohol, and a high molar ratio of alcohol is needed. In the base catalyzed procedure, some soap is formed and it acts as phase transfer catalyst, thus helping the mixing of the reactants. Base catalyzed process is strongly affected by the mixing of the reactants and/or by efficient heating that produces tiny droplets, thus increasing the reaction area.

The conventional methods for producing biodiesel from jatropha and other types of oil seeds involve various stages such as 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 [4]. Hybrid or simultaneous processes that combine reaction and separation operations in one unit have received much attention, recently, due to investment and energy cost savings, and the possibility of overcoming thermodynamic limitations imposed by reversible reactions or kinetic restrictions in irreversible reactions when separation of products is carried out in situ. Reactive extraction is a process that involves reaction and separation of liquid phases in the same unit simultaneously. Phase separation can occur naturally in the reactive system or can be introduced deliberately by adding a solvent. The technology increases yield and selectivity in a system with multiple reactions, reduces recycle streams and formation of waste streams, and facilitates purification of products that are difficult to separate by conventional technologies [5]. In reactive extraction process, 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 [6,7].

In the present study, the use of reactive extraction process for the production of biodiesel from jatropha seed is presented. The main objectives of this study was to study the effect of process parameters, i.e. the moisture content of jatropha seed and the co-solvent concentration (hexane to oil weight ratio).

II. Experimental Procedure

The jatropha seed was kindly provided by a local farm around Banda Aceh, Indonesia. The hexane used was of 99.9% purchased from Fisher Scientific. The methanol used throughout this study was of technical grade.

Initially, fresh jatropha seed was blended and sieved to a size of <1mm. It was then weighed and dried in the oven at 76 °C repeatedly until constant weight was achieved. The dried seed was then sieved again to obtain fine particles of ≤0.355 mm in size. To determine the maximum amount of oil that can be extracted from the seed using the conventional method, a Soxhlet extractor with excess nhexane as the solvent was utilized. After the extraction process, hexane was removed using a rotary evaporator, and the extracted oil was measured. The oil content in jatropha seed was found to be 23.3%. This value will be used in the calculation of yield. The moisture content of the Jatropha seeds was determined using the oven method according to ISTA (International Seed Testing Association) rules.

Sodium hydroxide of 0.9 g was dissolved in methanol of 400 ml, and then the mixture was placed in a 1000 mL beaker glass and placed in a constant temperature water bath. The mixture was heated to the desired temperature (45^{o}C), using a heated circulating water bath. After desired temperature achieved, 42 g of ground and sieved jatropha seed with specified moisture content was transferred to the beaker glass and the reaction was carried out at the desired temperature for 120 minutes. The mechanical stirring experiment with agitation speed of 600 rpm was performed for reaction system.

After reaction for the desired time, the solid residue was separated from the liquid 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 gas chromatography-mass spectrofotometry (GC-MS) analyses. The experimental procedure is presented in Figure 1.

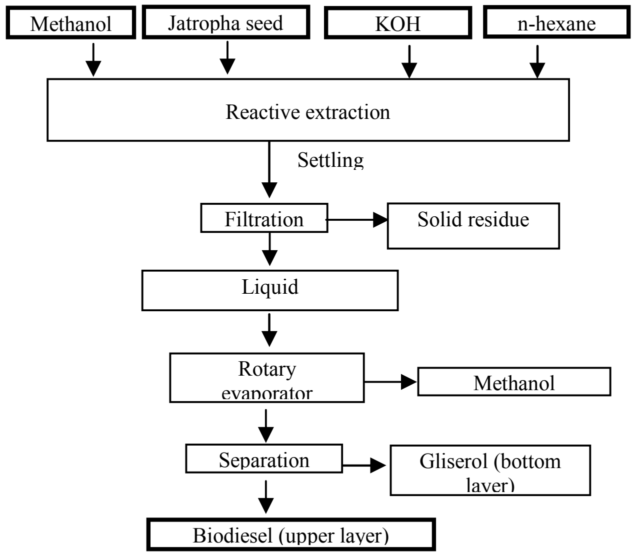

Figure 1. Experimental procedure

The effect of reactive extraction process parameters on the yield of biodiesel was studied using Design of Experiments (DOE). The process parameters studied include moisture content of jatropha seed and the amount of co-solvent of hexane. The DOE selected was response surface method (RSM) coupled with a three-level Factorial using Design Expert version 7.1.6 (Stat-Ease, Inc.) software.

III. Results And Discussions

Water content is an important factor in the alkaline-catalyzed transesterification of vegetable oil. Fig. 2 shows the effect of process parameter on yield of biodiesel. As shown in Fig. 2, the yield of biodiesel increased with decrease of moisture content of jatropha seed for various hexane to oil weight ratio. Alkali-catalyzed transesterification are greatly affected by the presence of water which makes the reaction partially change to saponification, leading to soaps formation [2]. Also, Haas [8] noted that water inhibits transesterification reactions since it competes with the alcohol (reactant), thereby transforming the required ester transfer reaction into ester hydrolysis, and leading to formation of free fatty acids.

In a transesterification system, the mass transfer between the two phases of oil and alcohol becomes a significant factor that affects the reaction rate due to immiscibility of oil and alcohol phases. Although the miscibility of the two phases can be enhanced by increasing the temperature, however, 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 such as phospholipids, sterols, phenols, and vitamins can potentially dissolve in methanol. Based on this fact, a cosolvent could be added to enhance the miscibility of the phases and speed up the reaction rate. The influence of cosolvent of hexane to oil weight ratio on the yield of biodiesel obtained for various moisture content of jatropha seed is presented in Fig. 2. In the experimental range studied, it can be concluded that the use of co-solvent provided more yield of biodiesel when compared to the system without co-solvents. Gryglewicz [9] previously suggested the addition of an appropriate reagent to promote alcohol solubility in the oil and enhanced the transesterification reaction rate.

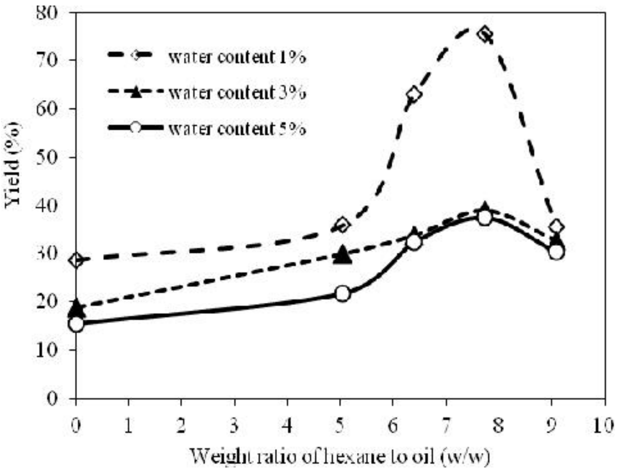

Figure 2. Effect of process parameter on yield of biodiesel

As shown in Fig. 2, the yield of biodiesel reached its maximum at weight ratio of hexane to oil of 7.6 for all of water content of jatropha seed. When the weight ratio of hexane to oil was lower than 7.6, the yield 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 [10]. Excessive addition of cosolvent into the reaction system could reduce the transesterification rate and increase the operating cost. Beyond a certain n-hexane to oil weight ratio, the excessive addition of hexane into the reaction system decreased the transesterification rate due to a dilution effect on the reagents. So the optimum loading amount of n-hexane to oil weght ratio was found to be 7.6:1. Qian et al. [11] reported that the optimum loading amount of n-hexane to oil weight ratio was found to be 3:1.

Based on the observations from single factor experiments, the range of each independent variable (moisture content of jatropha seed and hexane to oil weight ratio) that influence biodiesel yield were selected. Table 1 indicates the actual values of the process parameters used and the complete design matrix. The result was then analysed using analysis of variance (ANOVA). The predicted values were obtained from model fitting technique and were seen to be sufficiently correlated to the observed values. Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA showed that the process was most suitably described with quadratic polynomial model. The following quadratic model equation (in coded factors) that correlates the yield of biodiesel to the various process parameters is given by Eq. (1).

$$\text{Yield (g)} = 40.65 - 12.3A - 5.08B + 6.35AB + 12.35A^2 - 10.9B^2 \quad (1)$$

Based on calculation results, the F test (Fisher) on Eq. (1) gives an F value of 7.87 and a "prob > F" value of 0.013, indicating that the developed model is significant. Besides that, R^2 is close to unity, 0.8676, indicating that the developed model equation successfully captured the correlation between the process parameters to the yield of biodiesel for reactive extraction process of jatropha seed.

TABLE I
EXPERIMENTAL DESIGN MATRIX AND RESULTS

Moisture content, A [%]	Hexane to oil ratio, B [w/w]	Biodiesel yield [%]
5	8.9	30.4
3	7.6	38.9
3	7.6	38.9
5	6.3	32.4
3	6.3	33.8
1	8.9	35.6
5	7.6	37.5
1	6.3	63.0
1	7.6	75.5
3	8.9	32.7
3	7.6	38.9
3	7.6	38.8

The graphical representation of the regression Eq. (1), and the contour plot are presented in Fig. 2. Two variables within the experimental range were depicted in one 3D surface plot. Shape of the contour plot indicated different interaction between the variables. As shown in Fig. 3, the biodiesel yield increased with decrease of moisture content of jatropha seed. When moisture content was set, biodiesel yield was found to increase with increase of hexane to oil weight ratio from 6.3 to 7.6, but beyond 7.6, biodiesel yield decreased with increasing hexane to oil weight ratio.

The optimal values of the selected variables were obtained by solving the regression equation of Eq. (1). This model was employed to find the value of the process variables that gives maximum yield biodiesel. The predicted optimal value, that obtained from the model equation for reactive extraction of jatropha seed to produce biodiesel are moisture content of of jatropha seed of 1% and hexane to oil weight ratio of 6.9. The model predicts that the maximum yield biodiesel that can be obtained under these optimum conditions of the variables is 68.3%.

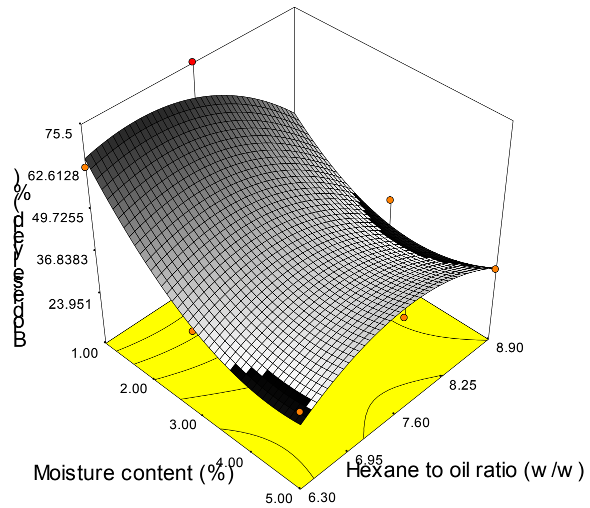

Fig.3. Combined effect of moisture content of jatropha seed and hexane to oil weight ratio on yield of biodiesel

IV. Conclusions

The reactive extraction of *Jatropha curcas* L seed for biodiesel production was investigated in this study. Reactive extraction is a feasible technology for the production of biodiesel using a single step of extraction and reaction that can cut the processing cost. The transesterification rate was improved when compared to the system without co-solvent. Response surface methodology in conjunction with a three-level factorial was employed to statistically evaluate and optimize the biodiesel production process. It was found that the production of biodiesel achieved an optimum level of 68.3% biodiesel yield at the following reaction conditions, i.e. moisture content of jatropha seed of 1% and hexaneto oil ratio of 6.9 (w/w).

Acknowledgment

This work was supported by Directorate Higher Education of the Republic of Indonesia under the project Hibah Bersaing (Contract No. 141/UN11/A.01/APBN-P2T/2012) and Indonesia Toray Science Foundation under STRG 2011.

References

[1] K. Becker, and H.P.S. Makkar, “Jatropha curcas: a potential source for tomorrow’s oil and biodiesel,” Lipid. Technol. 20 (2008) 104–107.

[2] I.M. Atadashi, M.K. Aroua, A.R.Abdul Aziz, and N.M.N. Sulaiman, “The effects of water on biodiesel production and refining technologies: A review,” Renew. Sust. Energy Rev. 16 (2012) 3456–3470

[3] D. Wang, Y. Xu, and T. Shan, “Effects of oils and oil-related substrates on the synthetic activity of membrane-bound lipase from *Rhizopus chinensis* and optimization of the lipase fermentation media,” Biochem. Eng. J., 41 (2008) 30-37.

[4] J. Zeng, X. Wang, B. Zhao, J. Sun, and Y. Wang, Y, “Rapid in situ transesterification of sunflower oil,” Ind. Eng. Chem. Res., 48 (2009) 850–856.

[5] K.J. Dussan, C.A. Cardona, O.H. Giraldo, L.F. Gutiérrez, and V.H. Pérez, “Analysis of a reactive extraction process for biodiesel production using a lipase immobilized on magnetic nanostructures,” Biores. Technol., 101 (2010) 9542–9549

[6] S. Kaul, J. Porwal, and M.O. Garg, “Parametric study of jatropha seeds for biodiesel production by reactive extraction,” J. Am. Oil Chem. Soc., 87 (2010) 903–908.

[7] S.H. Shuit, K.T. Lee, A.H. Kamaruddin, and S. Yusup, “Reactive extraction and in situ transesterification of *Jatropha curcas* L. seeds for the production of biodiesel,” Fuel, 89 (2010) 527–530.

[8] M.J. Haas, “Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock,” Fuel Process. Technol. 86 (2005) 1087–96.

[9] S. Gryglewicz, “Rapeseed oil methyl ester preparation using heterogeneous catalyst,” Biores. Technol., 70 (1999) 249-253

[10] H.J. Kim, and B.S. Kang, “Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst,” Catal. Today, 93 (2004) 315–320.

[11] J. Qian, H. Shi, and Z. Yun, “Preparation of biodiesel from *Jatropha curcas* L. oil produced by two-phase solvent extraction,” Biores. Technol., 101 (2010) 7025–7031