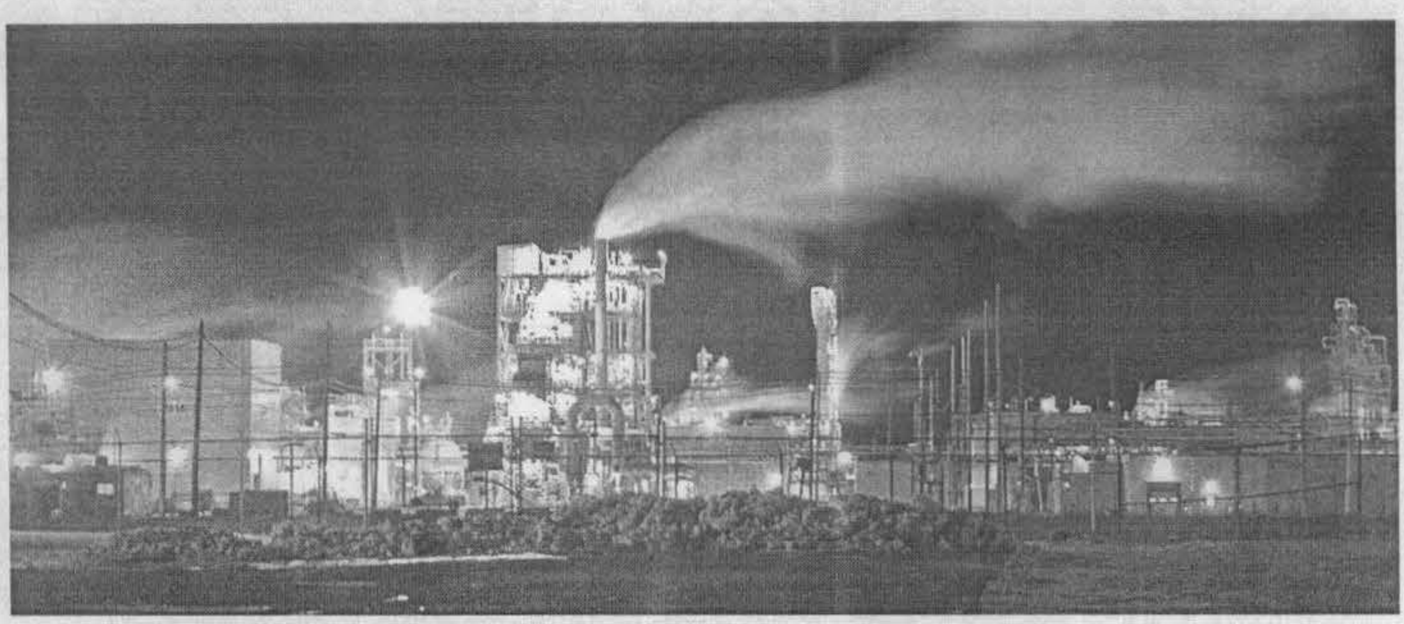
INTERNATIONAL SEMINAR ON CHEMICAL ENGINEERING
"SOEHADI REKSOWARDOJO 2011"

- PROCEEDING -



Theme: Bioenergy, Biobased Product and Process Development

Aula Barat & Aula Timur ITB
Bandung, Indonesia • 5 - 7 October 2011

PT PUPUK SRIWIDJAJA (Persero)

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International Seminar on Chemical Engineering
Soehadi Reksowardojo 2011

Table of Contents

CRE-05	Synthesis Of Bioetbe: The Advantage Of Solid Acid Catalyst Fo Synthesis A New Component Of Gasoline
CRE-06	Determination Of Kinetic Rate Of N-Hexane Oxidation Over Pt/Γ-Al2o3 In A Fixed Bed Reactor
CRE-07	Effect Of Process Conditions On The Characteristics Of Carbon Nanotubes By Catalytic Decomposition Of Methane Over Ni-Cu-Al Catalyst
CRE-08	Effect Of Temperature On Ethanol Electro-Oxidation On Carbon Supported Pt, Ptru And Ptsn Catalysts
CRE-09	Hydrogren Peroxide Study On Photocatalytic Decolourization Of Reactive Orange 16 Dye
CRE-10	Ceramic Membrane Contactor To Recover Iodine From Brine Water
CRE-11	Evaluation Kinetics Of Hydrodesulfurization Dibenzothiophene Using Nimo / Γ-Al$_2$o$_3$ Catalyst
CRE-12	Characterization Of Γ-Alumina Catalyst Support Prepared From Belitung Kaolin
CRE-13	Determining Rate Parameters Of Langmuir-Hinselwood Type Kinetics For Methane Oxidation Over Pt/Γ-Al2o3 In A Fixed Bed Reactor
DSC-01	Cfd Modeling Of High Performance Vane – Cyclone Mist Eliminator
DSC-02	Dynamic Modeling For Propylene Homopolymerization In Industrial Loop Reactors
DSC-03	Performance Evaluation Of Multicomponent Distillation Control System Using Steady State And Dynamic Process Modelling Case Study: Debutanizer Column
DSC-04	Dynamic Simulation Of Anti Surge Control For Two Stage Centrifugal Gas Compressor
DSC-05	Computer Aided Product Design Of Green Diesel From Biofuels
DSC-06	Scaled D-Optimal Design A Novel Approach For Improving Parameter Precision
DSC-07	Tuning Method Application Of Level Controller In Process Control Laboratory, Chemical Engineering Department, Politeknik Negeri Malang
DSC-08	Control Strategy For Outlet Temperature Of Heat Exchanger Networks By Using Pid And Mpc
DSC-09	Geometry Effects Of Upstream Conditions On The Internal Flow Characterictics In Shell And Tube Heat Exchanger
DSC-10	Simulation Process Water Treatment For Boiler
DSC-11	Supply Chain Modeling And Control System Design Of Fuel Oil Transfer Through Pipeline
DSC-12	Design And Control A Methanol Synthesis Process In A Multi Tube Plug Flow Reactor With Recycle Using Pi, Pid Controllers And Mpc

DSC-13	Simulation And Optimization Of Coupling Reaction Of Methanol Synthesis And Isopropyl Alcohol Dehydrogenation
EDU-01	Tanggapan Pendidikan Teknik Kimia Terhadap Perkembangan Perancangan Produk Kimia
EDU-02	A Chemical Engineering Laboratory Module On Soap Production
EDU-03	Teaching Chemical Product Design ar Universitas Indonesia
EST-01	Application Of Biofilm System In Treating Palm Oil Mill Effluent (Pome)
EST-02	A Feasibility Study Of Pome Pretreatment Using Wild Algae
EST-03	Index Based Inherent Safety Asessment At Early Stage Of Process Design
FST-01	Alternative Method Using Co2 For Tofu Perservation
KEY-01	Oleochemical Products
KEY-02	Current Status And Issues Of Biofuels
MST-01	Aluminum Corrosion In Citric Acid Solution
MST-02	An Experience Of Scalling-Up Paste Glue Production Of Gummed Tape From Laboratory Scale Experimental Data
MST-03	Physical Characteristics Of Biodegradable Foam From Mixed Hominy Feed And Cassava Starch
MST-04	Synthesis And Characterization Of Natrium Lignosulfonate
MST-05	Natural Rubber Powder Production From Latex: Equipment Design And Modeling
MST-06	Synthesis And Characterization Of Cellulose Based Superabsorbent Polymer Composites
MST-07	Development Of Non Petroleum Base Low Ift Surfactant For Improving Oil Recovery
MST-08	Accelerated Chamois Leather Tanning Process Using Hydrogen Proxide As An Oxiding Agent
MST-09	Factorial Design Analysis Of Compost Granulation
MST-10	Structure-Property Relationship In Layered-Silicate / Flexible Polyrethane Foam Nanocomposite
MST-11	Utilization Of *T.Ferrooxidans* Bacteria Activity In Producing Bioelectricity With Membrane Technology
POS-01	Accelerated Chamois Leather Tanning Process Using Hydrogen Proxide As An Oxiding Agent

POS-02	The Process Of Analyzing Cu Is A Solution On Toward A Green Chemistry
POS-03	Pengembangan Model Pembelajaran Praktikum Kimia Melalui Dry Lab Pada Pembelajaran Jarak Jauh
RET-01	Degradation Of Biodiesel During Storage According To Total Acid Number And Viscosity
RET-02	Production Of Biohydrogen From Synthetic Tapioca Wastewater In Anaerobic Process
RET-03	Characteristic Of Gas-Liquid Contactor For Absorption Of Toluene Using Oils
RET-04	Measurement Of Auto-Oxidation Kinetics Of Methyl Oleate-Methyl Laurate Mixture As A Biodiesel Model System
RET-05	Enzymatic Hidrolisis Of Rice Straw With Alkaline Pretreatment For Hidrogen Production
RET-06	Producing Absolute Ethanol With Distilation And Adsorbtion By Molecular Sieve 3a
RET-07	Production Of Biodiesel By Enzymatic Transesterification Via Non-Alcohol Route Using Immobilized Biocatalyst In Column Technology Packed
RET-08	Proses Produksi Etanol Grade Bahan Bakar Dengan Proses 'Wet Adsorption-Distilation'
RET-09	Biohydrogen Technological Innovation Into Electrical Energy By Fuel Cell Technology
RET-10	Biomass To Liquid In Indonesia: Ft-Fuel Or Methanol
RET-11	Biogas Production From Glycerol Derived From Biodiesel Manufacturing
RET-12	Transformation Of Jatropha Seed To Biodiesel By In Situ Transesterification
RET-13	Biodiesel Production From Palm Fatty Acid Distillate (Pfad) Using Reactive Distillation
RET-14	The Stability Of Coal-Oil Mixtures As An Alternative Fuel Oil Using Dimensionless Number Analysis
RET-15	Determination Of Minimum Trace Metals (Nickel And Cobalt) Requirements For Obtaining Optimum Biogas Production In The Fermentation Of Palm Oill Mill Effluent
RET-16	Studies On The Reaction Kinetics Of Anaerobic Fermentative Hydrogen Production By Enterobacter Aerogenes
RET-17	Preparation, Characterization, And Activation Of Catalyst Nio/Al2o3 For Synthesis Of Diesel-Like Hydrocarbon From Jatropha Oil Through Catalytic Pyrolysis
RET-18	Esterification Of Palm Fatty Acid Distillate With Ethanol
RET-19	Natrium Hydroxide (Naoh) As Alkaline Hydrolysis On Pretreatment Of Biogas Production From Water Hyacinth (*Eichornia Crassipes*)
RET-20	Closed Loop Double Stage Husk *Jatropha*digester

RET-21	Conversion Of Whey From Tofu Into Biogas By Anaerobic Batch Process
RET-22	Effect Of Blending Among Biodiesels On The Properties Of Oxidation Stability
RET-23	Drying And Pyrolysis Of Kraft Pulp Mill's Sludge Cake
RET-24	Steaming And Enzymatic Hydrolysis Of Empty Palm Oil Fruit Bunch To Produce Monosaccharides
RET-25	Biorefinery Preliminary Studies: Integration Of Slurry And Co2 Gas As Biomethane Digester Waste For Microalgae Scenedesmus Sp. Growth.
RET-26	The Hydrothermal Treatment For Production Of Solid Biofuel From Sugarcane Bagasse
SPT-01	Removal Of Ammonia Concentration (Nh4+-N) In Leachate Using Packed Coloumn Stripping Process For Biogas Raw Material
SPT-02	Vapour-Liquid Equilibrium Study For Benzene And Several Types Of Oil As Absorbent
SPT-03	Cfd Turbulence Model Of Tangential Cylindrical Cyclone For Droplets Removal From Gas Streams
SPT-04	Performance Of Slotted Pore Microfiltration Membrane To Separate Oil From Water
SPT-05	Bench- And Pilot-Scale Evaluation Of Co2 Removal From Natural Gas Stream Using Polypropylene (Pp) Hollow Fiber Membrane Contactors
SPT-06	Combination Of Ozonation And Absorption Through Membrane Processes To Remove Ammonia From Wasterwater
SPT-07	Recent Development And Potential Applications Of Electrodeionization (Edi)
SPT-08	Improvement Of Selectivity And Permeation Properties Of Ultrafiltration Membrane For Humic Acid Water Treatment : A Review
SPT-09	Trimethylamine Removal From Pure Methanol Using Ion Exchange Resin
SPT-10	Room Temperature Ionic Liquids For Propyne-Propylene Separations: Theoretical And Experimental Investigation
SPT-11	Pengaruh Suhu Dan Waktu Pengeringan Film Lateks Karet Alam Menggunakan Tepung Kulit Pisang Sebagai Pengisi
SPT-12	Intensification Of Bioproducts Purification: A Perspective On Hydrolysis Of Lactate Esters
SPT-13	Study On The Effect Of Moisture Content And Material Size Of Vetiver On The Yield And Quality Of Vetiver Oil (Vetiveria Zizanoides L.)
SPT-14	Purification Process Of Tofu Waste Water Factory
SPT-15	Produced Water Management Using Membrane Technologies

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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].

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 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.

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.

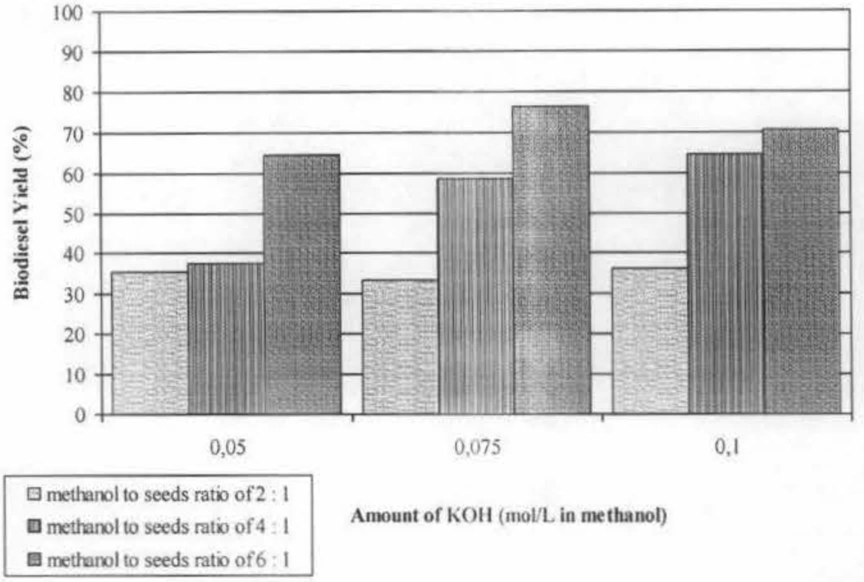

Figure 1 Influence of methanol to seed ratio and amount of alkali (KOH) catalyst on biodiesel production yield (%) (700 rpm for the stirring speed, 60°C for the temperature and 4 h for the reaction time).

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

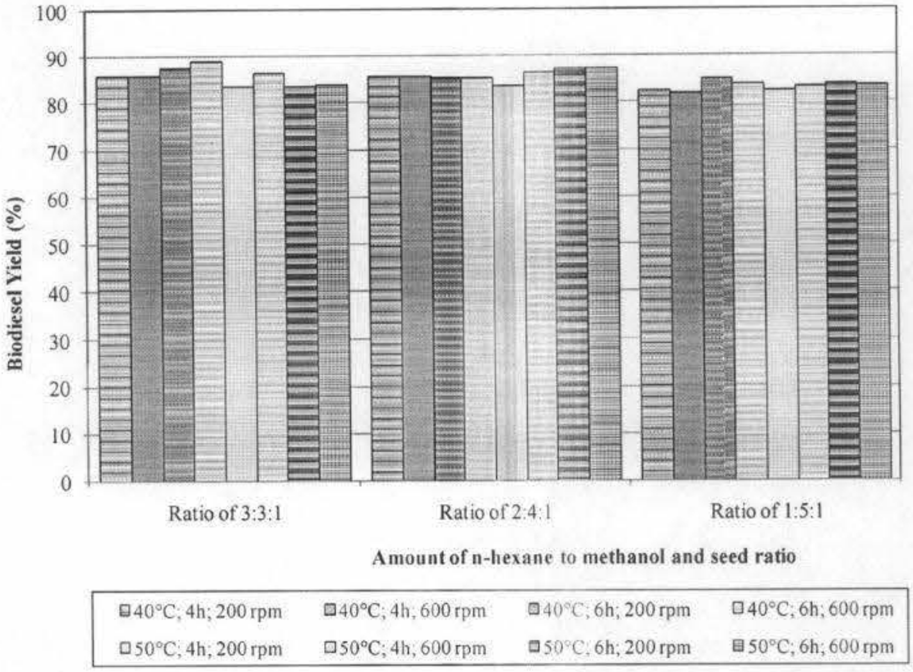

Figure 2 Influence of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on the biodiesel production yield.

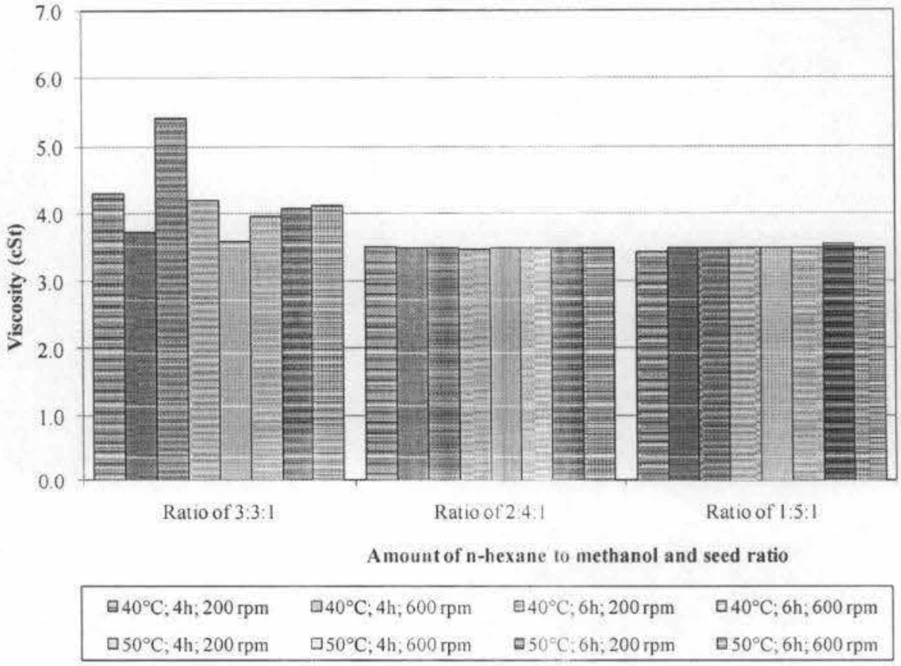

Figure 3 Influence of amount of n-hexane to methanol and seed ratio, stirring speed, temperature and reaction time on the viscosity of biodiesel.

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 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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Acknowledgement

The authors wish to thank DP2M DIKTI KEMENDIKNAS for financial support (Hibah Kerjasama Luar Negeri dan Publikasi Internasional).