

Rapid In Situ Transesterification of Papaya Seeds to Biodiesel with The Aid of Co-solvent

Elvianto Dwi Daryono*[‡], Erni Junita Sinaga**

*Department of Chemical Engineering, Faculty of Industrial Technology,
Institute Technology of National Malang, Indonesia

**Department of Industrial Engineering Diploma, Faculty of Industrial Technology,
Institute Technology of National Malang, Indonesia

[‡]Corresponding Author; Elvianto Dwi Daryono, Department of Chemical Engineering,
Institute Technology of National, Bendungan Sigura-gura No. 2 Malang (65145) Indonesia,
Tel. 0341-551431, elviantodaryono@yahoo.com, erni_junita@yahoo.com

Received: 29.09.2016 Accepted: 20.12.2016

Abstract- Methanol and co-solvent after being separated from the rest of the methyl ester had only discarded, but if reused will save the reactant and the co-solvent used. Variables of research is the reaction time is 3, 8, 13, 18, 23, 28 and 33 minutes and the mass addition of methanol and co-solvent residual is 0, 5 and 10% by weight. Papaya seeds that have been dried and pulverized size + 20/-30 mesh around 100 grams introduced in to the reactor and added methanol, THF and the catalyst NaOH and the reaction carried out according to the study variables and operating conditions. After the reaction was complete, added HCl 1 mol /L to pH 4 to stop the reaction and separated between cake and the filtrate. The filtrate was distilled at 70°C until no distillate dripping. Distillate was a mixture of methanol and co-solvent the rest of reaction to be used again in the reaction. Distillation residues incorporated into separating funnel and allowed to stand for 12 hours in order to form two layers. The bottom layer was glycerol and the upper layer as the methyl ester. Methyl ester concentration was analyzed by GC. The optimum conditions of the research on the mass addition of methanol and co-solvent remaining 10% and a reaction time of 8 minutes, methyl ester concentration of 99.39%, yield of 79.51%, density of 0.87 g/cm³, and acid value of 0.74 mg KOH/g. These results regards with SNI 04-7182-2006.

Keywords Methanol, co-solvent, reused, papaya seeds, methyl ester.

1. Introduction

Increased energy requirement, herculean task in extracting oil from oil well and cost of refining has undoubtedly lead to hike in oil prices. This increase will continue to occur each year in line with the development of technology and population. Fuel oil is a non renewable energy source that will eventually run out, so indispensable substitute fuels that are renewable one of which is biodiesel.

Indonesia has many kinds of oil-producing plants, one of which is the fruit of papaya. Papaya fruit is widely consumed as food and as raw material for the manufacture of cosmetics. Papaya fruit is not seasonal and available at all times. Papaya seeds only a small portion is used as a seed crop and largely discarded as waste. Among the composition of papaya fruit which has significant potential and is not yet widely used seeds. Papaya contains the seeds of about 15%. Oil content in the seeds of papaya of about 30.7% [1]. When compared with soybeans oil of 19.63%, sunflower seeds oil of 22.23%,

the oil content in the seeds of papaya bigger so very prospect was developed as a raw material for biodiesel. Oil on papaya seeds can not be used as a cooking oil because of the benzyl isothiocyanate compound carcinogenic [2]. Biodiesel production process is generally done in two phases: oil extraction of raw materials and oil into biodiesel transesterification stage. Vegetable oil extraction is generally done mechanically using expeller or hydraulic press which was followed by extraction with n-hexane.

The transesterification of vegetable oil into biodiesel is generally done through a process of chemical transformation by using methanol or ethanol and the acid or base catalyst. The second stage conducted separately and discontinuous, so that the biodiesel production process becomes less efficient and consumes a lot of energy. In addition, the oil production process from seed to burden 70% of the total production cost of biodiesel [3,4].

Many researchers investigated the in-situ technique for biodiesel production while no studies have been reported on

the co-solvent assisted in-situ methanolysis of papaya seeds to biodiesel. In situ transesterification of rapeseed get a yield of 80% with particle size of rapeseed 300-500 micron, reaction temperature of 60°C, reaction time of 1 h, ratio molar of methanol:oil is 571:1, concentration catalyst is 0,1 molal and the stirrer speed at 200 rpm [5].Georgogianni et al [6] conduct in situ transesterification of sunflower seeds and get a yield of 95% at the reaction temperature 60°C, a reaction time of 20 minutes, 2% NaOH catalyst, stirring speed of 600 rpm and the ratio of the mass of seeds:methanol = 1:10. In situ transesterification of cottonseed, conversion of 98% was obtained at a molar ratio methanol:oil = 135: 1, the reaction temperature 40°C, the reaction time of 3 hours, and the size of seeds 0.3 to 0.335 mm [7].

In situ transesterification is the process by which oil extraction and transesterification of oil into biodiesel occurs simultaneously in one process. Weakness of the in situ transesterification reaction is a long time since the solubility of the oil in methanol is low. In situ transesterification needed large quantities of alcohol as solvent as well as reactant [8]. This obstacle can be overcome by adding a co-solvent. Co-solvent is a substance that serves to increase the solubility of the oil in methanol so as to form a single-phase reaction [9]. Co-solvent is highly soluble in alcohols, fatty acids and triglycerides. Based on the properties and economic value, is a co-solvent THF best because it is inexpensive, non-toxic, non-reactive and low boiling so easily separated together with methanol and can recycle back [10].

Research in situ transesterification of sunflower seed oil with a co-solvent DEM (Diethoxymethane), obtaining a product with FAME 97.7% and FFA 0.74% at a molar ratio of catalyst:oil = 0.5:1, molar ratio of methanol:oil = 101.39:1, molar ratio DEM:oil = 57.85:1, stirrer speed of 150 rpm, the reaction temperature of 20°C and a reaction time of 13 minutes [11]. In the in situ transesterification of Jatropha seeds get a yield of 99.8% with a size of jatropha seeds <0.355 mm, co-solvent n-hexane 10% vol. methanol, the reaction temperature of 60°C, reaction time of 24 hours, the ratio of methanol:seed is 7.5 ml/g and catalyst H₂SO₄ 15% [12]. In situ transesterification of castor seeds get a yield of 65.6% methyl ester in a reaction time of 2 hours, stirring speed of 300 rpm, the mass of 20 grams of castor seed, the catalyst KOH 1%, molar ratio of ethanol:oil is 60:1, the volume ratio of ethanol: n hexane = 20% of the volume of oil [13]. In situ transesterification copra using a mixture of methanol and THF, to get the highest yield of 96.7% at a reaction temperature of 60°C, a reaction time of 20 hours, the ratio of methanol/copra = 200 mL/100 g, the volume ratio of THF: methanol = 0.4, the ratio molar methanol: oil = 60:1 and the catalyst H₂SO₄ by 15 mL [14].

In the in situ transesterification of mahogany seeds, optimum conditions obtained at a molar ratio of oil:THF = 1:67.85, a reaction time of 23 minutes, the reaction at room temperature with a concentration of methyl ester of 69.28%, yield of 67.95% and density 0,8791 g/cm³ (meet SNI 04-7182-2006) [15]. In situ transesterification mahogany seed oil with a co-solvent n-hexane, yield of 88.18% was found in a mass ratio of seed:methanol:n-hexane = 1:3:4 and a

reaction time of 4 hours with a density of 0.8785 g/cm³ (meet SNI 04-7182-2006) [16]. In situ transesterification jatropha seeds, yield of 92%, concentration of FAME 98% and acid value 0.26 mg KOH/g was found in ratio of seed:n-hexane = 1:2, reaction time of 6 h, ratio molar of methanol:oil = 10.6:1, stirring speed of 200 rpm, reaction temperature of 50°C and 0.075 mol/L KOH in methanol [17]. In the research that has been done so far methanol and co-solvent residual reaction simply discarded. In this study will reuse the methanol and co-solvent for the rest of the in situ transesterification reaction papaya seed oil given residual methanol reaction is still quite a lot and the price of co-solvent which is relatively expensive. The study targeted to determine the optimum condition of in-situ methanolysis assisted with co-solvent of papaya seeds to biodiesel.

2. Material and Methods

Papaya seeds was collected from fruit vendors in Malang (Indonesia). Analytical reagent (AR) methanol (MERCK, 99.9%), THF (MERCK, 99.8%) and NaOH pellets (Riedel-de Haen, 99%). The fatty acid level, FFA level, moisture content are determined and found to be 22.59%, 0.5363% and 0.4%, respectively. Table 1 shows the fatty acid composition of papaya seed oil obtained from GC analysis, it has found papaya seed oil contain 19.4% saturated acid and 80.5% unsaturated acid.

Table 1. Fatty acid composition (%) of papaya seed oil

No.	Components	Composition (%)
1.	Myristic acid (14:0)	0.2
2.	Palmitic acid (16:0)	13.9
3.	Palmitoleic acid (16:1)	0.2
4.	Stearic acid (18:0)	4.9
5.	Oleic acid (18:1)	76.8
6.	Linoleic acid (18:2)	3.0
7.	Linolenic acid (18:3)	0.2
8.	Arachidic acid (20:0)	0.4
9.	Eicosenoic acid (20:1)	0.3

2.1. Pre-treatment of papaya seed

The seeds were washed with water at least 3 times to remove the gelatinous and 3 days of sun drying were required to completely dry 1 kg of fresh feed [18]. Papaya seeds after dried, pulverized size + 20/-30 mesh and analyzed moisture content. Papaya seeds powder was extracted oil with n-hexane for 33 minutes. Oil extraction results of its analysis % FFA.

2.1. Method used for production of biodiesel from papaya seeds

Alkaline transesterification has used for the production of biodiesel as it FFA less than 1% [19]. Sodium hydroxide was used as a catalyst because it is cheaper and reacts faster than acid catalyst [20].

3. Experimental Design

3.1 Variabel design methodology

The operating conditions of research that the molar ratio of oil:NaOH = 1:0.5, the molar ratio of oil:methanol = 1:101.39, molar ratio of oil:THF = 1:67.85, reaction at room temperature ($\pm 27^{\circ}\text{C}$), reaction time (3, 8, 15, 18, 23, 28 and 33 minutes) and mass addition of methanol and co-solvent remainder (0, 5, and 10% by weight of methanol and co-solvent beginning).

3.2 Experimental procedure

Incorporating 100 grams of dried papaya seeds, methanol, THF, and NaOH in the reactor and carrying out the reaction at room temperature ($\pm 27^{\circ}\text{C}$) and set the stirrer speed of 150 rpm. Selection of room temperature was done to save energy and compared with the results Zeng et al. [11] who obtain optimum conditions at a temperature of 20°C . Controlling the temperature of the reaction was done by looking at the temperature of the thermometer on the reactor and the evaporation of methanol and THF prevented by condenser. Selection of stirrer speed of 150 rpm based on the optimum conditions obtained Zeng et al. [11]. NaOH pellet catalyst was used in a molar ratio of oil: NaOH = 1: 0.5, the molar ratio of oil: methanol = 1:101.39, and the molar ratio of oil: THF = 1: 67.85 and a reaction time of 33 minutes. To stop the reaction that neutralized the NaOH catalyst by

adding HCl 1 mol / L to pH 4 on the outcome of the reaction [10]. Results reaction and the cake were separated by the filter paper. Results reaction then be distilled at 70°C until no distillate dripping. Separation of residual methanol and co-solvent THF can be done easily because the boiling point adjacent [10]. Distillate is methanol and co-solvent residual, while the residue was a mixture of methyl esters, oils, glycerol and catalyst. Distillate that will be used for the in situ transesterification reaction papaya seed oil further.

The operating conditions of research that the molar ratio of oil:NaOH = 1:0.5, the molar ratio of oil:methanol = 1:101.39, molar ratio of oil:THF = 1:67.85, reaction time (3, 8, 15, 18, 23, 28 and 33 minutes) and mass addition of methanol and co-solvent remainder (0, 5, and 10% by weight of methanol and co-solvent beginning). The reaction was performed in a stirred tank reactor at room temperature under the conditions of operation research. To stop the reaction that neutralized the NaOH catalyst by added HCl 1 mol / L to pH 4. The reaction results and papaya seeds were separated by the filter paper.

Results reaction then be distilled at 70°C until no distillate dripping. Residues included in separating funnel for 12 hours to form two layers are then separated. Brown undercoat were glycerol and the results of the neutralization reaction, while the top layer was a brownish orange. Methyl ester was washed at least six times with warm water before drying and settling. The upper layer methyl ester was orange color weighed as heavy rough, then analyzed the concentration of methyl esters by GC to obtain the yield. The highest yield of each variable mass addition of methanol and co-solvent residual analyzed density and acid value.

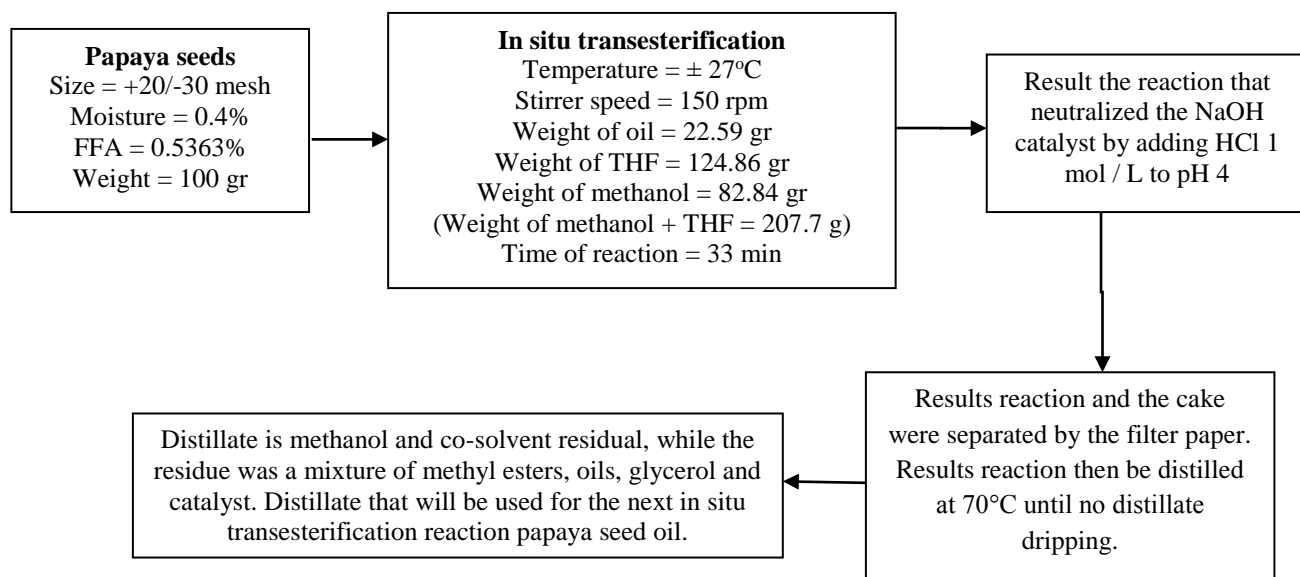


Fig.1. Set up diagram to get methanol and co-solvent THF residual.

Addition of methanol and co-solvent residual :
 0%, 5% (10.39 gr), 10% (20.77 gr)

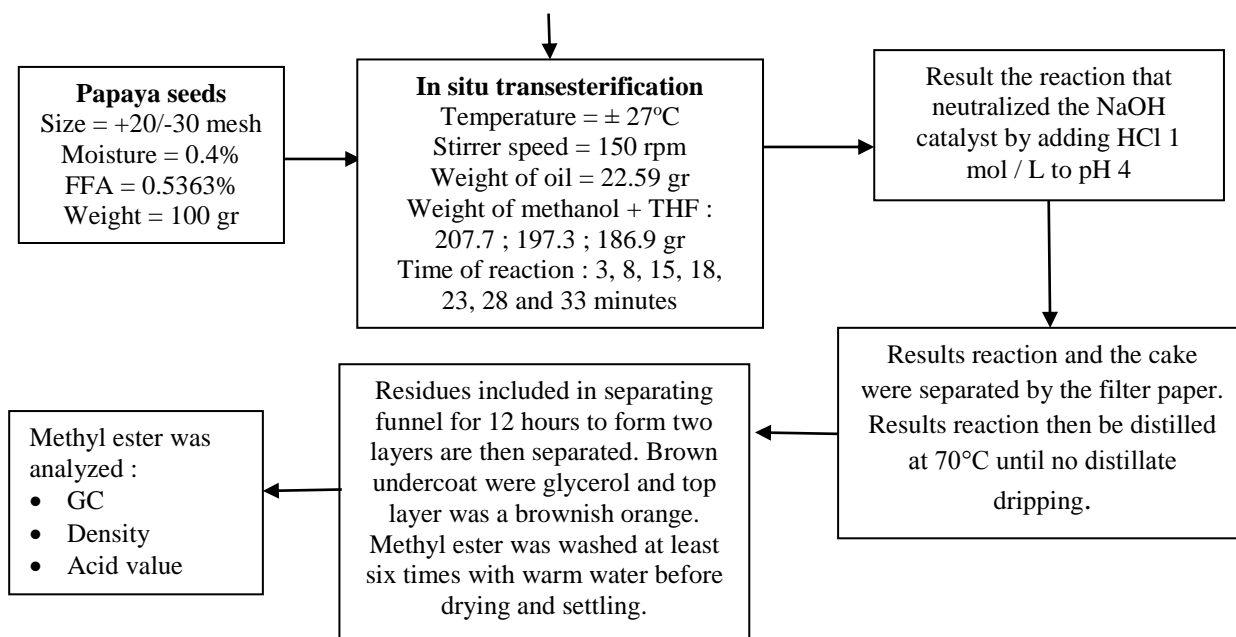


Fig.2. Set up diagram in situ transesterification papaya seed oil with addition of methanol and co-solvent THF residual

4. Results and Discussion

4.1 Psychochemical Properties of papaya seed oil

Papaya seeds after dried and pulverized, analyzed moisture content of 0.4% was obtained. Papaya seeds powder was extracted oil with n-hexane for 33 minutes. From the results obtained 56.4688 grams of oil extraction at 250 grams of dried papaya seeds. Oil extraction results of its analysis% FFA and FFA obtained 0.5363%, so it can be directly carried out in situ transesterification reaction.

4.2 Fatty Acid Methyl Ester Composition

Methyl ester concentration data obtained from the GC analysis of the top layer of residue separation by distillation. GC analysis of the results of the methyl ester component consisting of methyl oleate, methyl palmitate, methyl heptadecanoate, methyl linoleate, methyl stearate, methyl myristate, methyl hexanoate, and methyl arachidate.

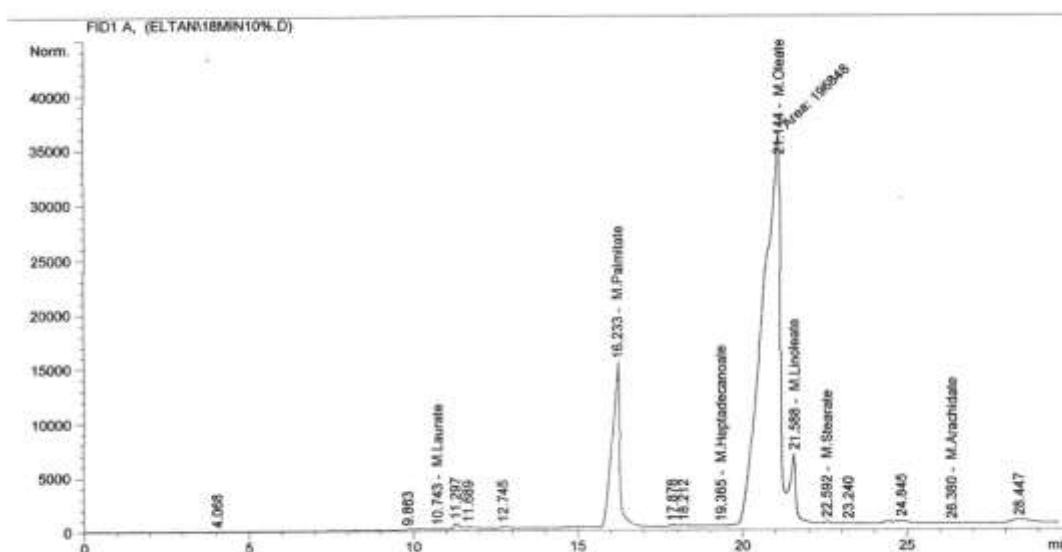


Fig. 3.GC result for in situ transesterification with time reaction 18 min and addition of spent of methanol and co-solvent 10%.

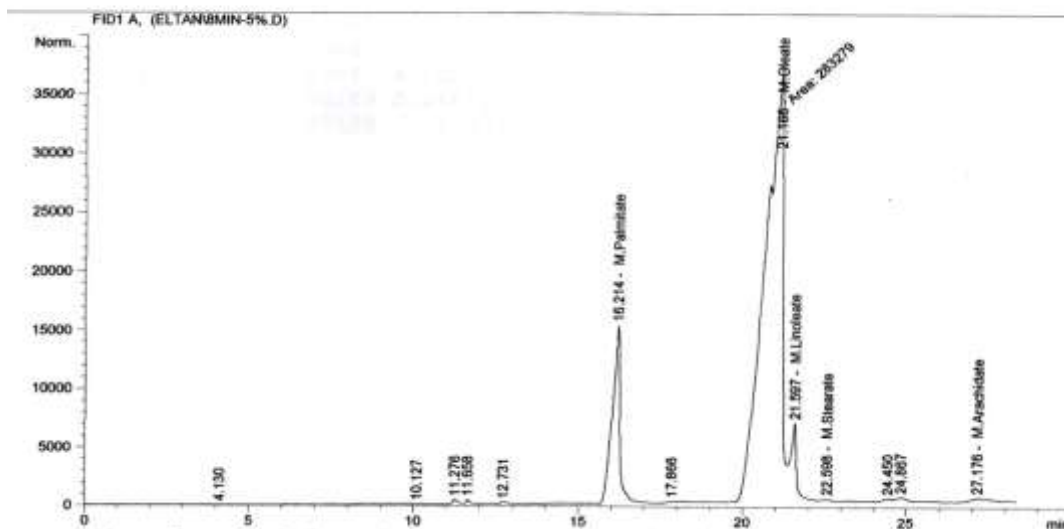


Fig.4. GC result for in situ transesterification with time reaction 8 min and addition of spent of methanol and co-solvent 5%.

4.3 Biodiesel yield and concentration of methyl ester

Methyl ester (FAME) yield was calculated using the following equation:

$$\text{Yield (\%)} = \frac{\text{Concentration of FAME} \times \text{weight of FAME}}{\text{Weight of initial papaya seed oil}} \times 100\%$$

4.3.1 Influence of mass addition of spent methanol and co-solvent and time of reaction to methyl ester concentration

Mass addition of methanol and co-solvent residual and reaction time greatly affect the concentration of methyl ester produced. Based on Fig. 5., can be seen that an increase in the concentration of methyl ester which was quite fast in the beginning of the reaction to the mass variable addition of methanol and co-solvent residual 0 and 5%. Methyl ester concentration reached about 50% in a reaction time of 3 minutes for the mass addition of methanol and co-solvent residual 0%, and reached a concentration of about 80% methyl ester in a reaction time of 3 minutes for the mass addition of methanol and co-solvent remaining 5%. On the mass of the addition of methanol and co-solvent remaining 10%, the methyl ester concentration of about 99% in a reaction time of 8 minutes.

Seen from Fig. 5., the highest concentration of methyl ester obtained in the mass addition of methanol and co-solvent remaining 10% with a reaction time of 8 minutes. On the mass of the addition of methanol and co-solvent concentration 0% residual methyl ester obtained high of 94.70% in a reaction time of 33 minutes. On the mass of the addition of methanol and co-solvent remaining 5% methyl highest concentration of 98.97% obtained at reaction time 18 minutes. On the mass of the addition of methanol and co-solvent remaining 10% methyl highest concentration of 99.39% obtained at reaction time 8 minutes. By increasing the mass of the addition of methanol and co-solvent the rest, we will get the concentration of methyl ester which was already high at the start of the reaction. This was because methyl ester from the previous reaction dissolved in

methanol and co-solvent the rest being used. On the mass of the addition of methanol and co-solvent residual 0%, has not achieved the optimum conditions for the concentration of methyl esters was increased. With the longer the reaction time, the more FAME obtained, because the longer solvent and co-solvent to extract oil from the seeds of papaya, then more and more oil produced in situ transesterification process. The addition of THF as a co-solvent to accelerating the reaction also helps to extract oil from the seeds of papaya.

On the mass of the addition of methanol and co-solvent remaining 5% at the optimum condition of reaction time 18 minutes, after which the concentration of methyl ester still declining. On the mass of the addition of methanol and co-solvent remaining 10% optimum conditions on reaction time 8 minutes, after which the concentration of methyl ester still declining. This was because at this time the reaction has reached equilibrium and if the reaction was continued then the equilibrium shifts toward the reactants for transesterification reaction was reversible.

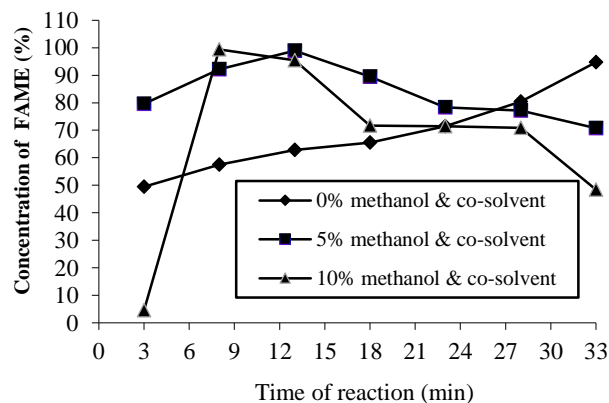


Fig.5. Effect of mass addition of spent methanol and co-solvent (%) and time of reaction (minutes) to the concentration of methyl ester (%)

Results of this study, highest concentration of methyl ester 99,39% obtained in the mass addition of methanol and co-solvent remaining 10%, and a reaction time of 8 minutes. Wong and Othman [21] get of fatty acid of the biodiesel from papaya seed oil was linoleic acid (67.4%), palmitic acid (29.5%) and stearic acid (3.1%). The GC-MS of papaya methyl ester identifies of linoleic acid and palmitic acid [22].

4.3.2. Influence of mass addition of spent methanol and co-solvent (%) and time of reaction (minutes) to the yield of methyl ester (%)

Mass addition of methanol and co-solvent residual and reaction time affects the yield of methyl ester produced. Based on Fig. 6., can be seen that there was an increase yield of methyl esters fast enough in the beginning of the reaction to the mass variable addition of methanol and co-solvent residual 0 and 5%. Yield reached 68% at the 3-minute reaction time for mass addition of methanol and co-solvent residual 0%, and the yield of methyl ester reached around 36% in a reaction time of 3 minutes for the mass addition of methanol and co-solvent remaining 5%. On the mass of the addition of methanol and co-solvent remaining 10%, a yield of about 79% methyl ester in a reaction time of 8 minutes.

Seen from Fig. 6., the highest yield of methyl ester obtained in the mass addition of methanol and co-solvent residual 0% with a reaction time of 33 minutes was 97.28%. On the mass of the addition of methanol and co-solvent remaining 5% yield of the methyl ester obtained high of 77.10% in a reaction time of 18 minutes. On the mass of the addition of methanol and co-solvent remaining 10% methyl ester yield high of 79.51% obtained at reaction time 8 minutes.

By increasing the mass of the addition of methanol and co-solvent the rest, will be obtained yield of methyl ester getting down, it is because the solubility of methanol and co-solvent remainder being used more and more down. On the mass of the addition of methanol and co-solvent residual 0%, has not achieved the optimum conditions for the methyl ester yield was increased. On the mass of the addition of methanol and co-solvent remaining 5% at the optimum condition of reaction time 18 minutes, after which the methyl ester yield decreased.

On the mass of the addition of methanol and co-solvent remaining 10% optimum conditions on reaction time 8 minutes, after which the methyl ester yield decreased. This was because at this time the reaction has reached equilibrium and if the reaction was continued then the equilibrium shifts toward the reactants for transesterification reaction was reversible.

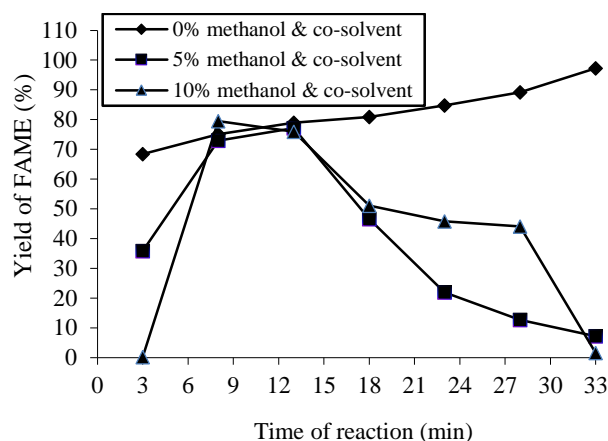


Fig.6. Effect of mass addition of spent methanol and co-solvent (%) and time of reaction (minutes) to yield of methyl ester (%)

Results of this study, highest yield of methyl ester 79.51% obtained in the mass addition of methanol and co-solvent remaining 10%, and a reaction time of 8 minutes. Charvet et al. [18] get a 62.4% yield on the two-step conversion FAME (esterification and transesterification) papaya seed oil. Transesterification was carried out at a temperature of 60-65°C for 1 hour in a molar ratio of oil:methanol 1:6 and catalyst NaOH 1% by weight of the oil [18]. Wong and Othman [21] get a yield of 96% on the enzymatic transesterification of papaya seed oil with a molar ratio methanol:oil 6:1, reaction time of 24 hours at room temperature.

4.3.3. Influence of mass addition of spent methanol and co-solvent to density and acid value

Mass addition of methanol and co-solvent residual and time of reaction were effected to the acid value and density of methyl ester. Analysis of the acid value and density of biodiesel were done at the optimum condition of each variable. Table 2 shows that the higher the mass of the addition of methanol and co-solvent residual, the greater acid value. This was because with the increasing mass addition of methanol and co-solvent residual, the more the rest of the FFA soluble than previous reaction, causing the acid value high. All the density of the resulting methyl esters meets the specifications SNI 04-7182-2006 (from 0.85 to 0.89 g/cm³). On the mass of the addition of methanol and co-solvent remaining 10% and a reaction time of 8 minutes were the best condition, obtained density and acid number which fulfills SNI 04-7182-2006 (max. 0.8 mg KOH/g).

Table 2. Data density and the acid value of methyl ester

Mass of the addition of methanol and co-solvent residual(%)	Time of Reaction (min)	Density (g/cm ³)	Acid Value (mg KOH/g)
0	33	0.89	0.44
5	13	0.86	0.67
10	8	0.87	0.74

5. Conclusion

The optimum conditions at the time the research showed the addition of methanol and co-solvent remaining 10% and a reaction time of 8 minutes, the concentration of methyl ester 99.39%, yield of 79.51%, density of 0.87g/cm³, and the acid value 0.74 mg KOH/g. These results regards the specifications SNI 04-7182-2006 with density from 0.85 to 0.89 g/cm³, a maximum acid value of 0.8 mg KOH/g and the concentration of methyl ester of at least 96.5%. From the results of the study proved that by using methanol and co-solvent residual reaction can still be produced biodiesel that meets the standards of biodiesel.

Acknowledgements

The authors thank to DIKTI (Direktorat Jenderal Pendidikan Tinggi) through Hibah Bersaing programme for generous financial support and Department of Chemical Engineering, Faculty of Industrial Technology, Institute Technology of National Malang, Indonesia for the facilities and support.

References

- [1] T.P.S.M. Abdulkarim, H.M. Ghazali, "Properties of Carica Papaya L. (Papaya) seed oil following extractions using solvent and aqueous enzymatic methods", *Journal of Food Lipids*, vol. 12, pp. 62-76, 2005.
- [2] P. Sammarphet, *Investigation of the papaya seed oil properties for development in to edible oil*, Master Thesis Mahidol University, 2006.
- [3] M. Bender, "Economic feasibility review for community-scale farmer cooperatives for biodiesel", *Bioresour.Technol.*, vol. 70, pp. 43-50, 1999.
- [4] M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, "A process model to estimate biodiesel production costs", *Bioresour. Technol.*, vol. 97, pp. 671, 2006.
- [5] R. Zakaria, A.P. Harvey, "Direct production of biodiesel from rapeseed by reactive extractive/in situ transesterification", *Fuel Processing Technology*, vol. 102, pp. 53-60, 2012.
- [6] K.G. Georgogianni, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, V. Gergis, "Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel", *Fuel Processing Technology*, vol. 89, pp. 503-509, 2008.
- [7] J. Qian, F. Wang, S. Liu, Z. Yun, "In situ alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal", *Bioresource Technology*, vol. 99, pp. 9009-912, 2008.
- [8] O.D. Samuel, O.U. Dario, "A critical review of *in-situ* transesterification process for biodiesel production", *The Pacific Journal of Science and Technology*, vol. 13 No. 2, pp. 72-79, November 2012
- [9] S. Mahajan, S.K. Konar, D.G.B. Boocock, "Standard biodiesel from soybean oil by a single chemical reaction", *JAOCs*, vol. 83, pp. 641-645, 2006.
- [10] D.G.B. Boocock, S.K. Konar, V. Mao, H. Sidi, "Fast one-phase oil-rich process for the preparation of vegetable oil methyl esters", *Biomass Bioenergy*, vol. 11, pp. 43-50, 1996.
- [11] J. Zeng, X. Wang, B. Zhao, J. Sun, Y. Wang, "Rapid in situ transesterification of sunflower oil", *Ind. Eng. Chem. Res.*, vol. 48, pp. 860-856, 2009.
- [12] S.H. Shuit, K.T. Lee, A.H. Kamaruddin, S. Yusup, "Reactive extraction and in situ of *JatrophaCurcas L.* seeds for the production of biodiesel", *Fuel*, vol. 89, pp. 527-530, 2010.
- [13] G. Hincapie, F. Mondragon, D. Lopez, "Conventional and in situ transesterification of castor seed oil for biodiesel production", *Fuel*, vol. 90, pp. 1618-1623, 2011.
- [14] D.S. Khang, L.F. Razon, C.F. Madrazo, R.R.Tan, "In situ transesterification of coconut oil using mixtures of methanol and tetrahydrofuran", *Chemical Engineering Research and Design*, vol. 92, pp. 1512-1518, 2014.
- [15] E.D. Daryono, A.C. Rengga, I. Safitri, "Production of process of methyl ester from mahogany seed oil with in situ transesterification using co-solvent THF (tetrahydrofuran)", *Reaktor*, vol. 15, pp. 51-58, 2014.
- [16] E.D. Daryono, "In situ transesterification of mahogany seed oil (*Sweitenia Macrophylla King*) become of methyl ester with co-solvent n-hexane", *Int.J.ChemTech Res.*, vol. 8, pp. 1026-1031, 2015.
- [17] I.A. Kartika, P. Evon, M. Cerny, O. Suparno, D. Hermawan, D. Ariono, L. Rigal, "Simultaneous solvent extraction and transesterification of jatropha oil for biodiesel production, and potential application of the obtained cakes for binderless particleboard", *Fuel*, vol. 181, pp. 870-877, 2016.
- [18] C.T.S.P. Charvet, M.R.J.V. Duya, A.V.G. Miller, L.F. Razon, "Evaluation of the biodiesel fuel properties of fatty acid methyl esters from Carica Papaya L", *The Philippine Agricultural Scientist*, vol. 94 No. 1, pp. 88-92, March 2011.
- [19] J.V. Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, "Biodiesel Production Technology", National Renewable Energy Laboratory (NREL), 2004.
- [20] Dharmesh Kumar N.B, M.C. Math, "Application of response surface methodology for optimization of biodiesel production by transesterification of animal fat with methanol", *International Journal of Renewable Energy Research*, vol. 6 No. 1, pp. 74-79, 2016.
- [21] C.S. Wong, R. Othman, "Biodiesel production by enzymatic transesterification of papaya seed oil and rambutan seed oil", *International Journal of Engineering and Technology*, vol. 6 No. 6, pp. 2773-2777, Dec 2014-Jan 2015.
- [22] P. Prabhakaran, C.G. Saravanan, C. Syed Aalam, "Effects of papaya methyl ester on DI diesel engine combustion, emission and performance characteristics", *International Research Journal of Engineering and Technology*, vol. 3 No. 2, pp. 319-325, Feb-2016.