9 772476 953012

Proceeding of the International Seminar on Science Education Volume III

ISSN: 2476-9533

PROCEEDING

International Seminar on Science Education
Volume III

Enhancing Interdisciplinary Practice of Science Education in the Realization of NGSS (Next Generation Science Standard)

Graduate School
Yogyakarta State University

Batik Yogyakarta Motif Semen Sido Mukti

Tugu Yogyakarta

October 28th, 2017

ISSN : 2476-9533
Volume 3, October 2017

PREFACE

Praise to Allah SWT for all the blessings and guidance given to us all, so that the program of the International Seminar on Science Education (ISSE) 2017 with the topic about Enhancing Interdisciplinary Practice of Science Education in The Realization of NGSS (Next Generation Science Standards) which held on October 28th 2017 at Rectorate Hall, Yogyakarta State University can be completed successfully.

This proceeding is presented in four sections: 1) Science; 2) Physics; 3) Biology Chemistry; and 4) General Education. This comprises number of papers that have been presented in the seminar, written by lecturers and students from Yogyakarta State University and other universities.

We owe many parties for the success of the seminar. Therefore, we would like to sincerely extend our gratitude to:

1. The rector of Yogyakarta State University, Prof. Dr. Sutrisna Wibawa, M.Pd for facilitating all the activities of the International Seminar on Science Education (ISSE) 2017;
2. The director of Graduate School of Yogyakarta State University, Dr. Moch. Bruri Triyono for providing all the facilities of the International Seminar on Science Education (ISSE) 2017;
3. The invited speakers for their willingness to share thoughts and insights on science teaching and learning in the seminar;
4. All committee members for the time, effort, and thoughts for the success of this activity; and
5. All presenters and participants who have come a long way to contribute to the success of the seminar.

However, we truth fully understand that some imperfections might be find in this proceeding and in the seminar. Thus, suggestions and constructive criticisms are very much welcome. Finally, we hope that this proceeding may contribute in science and science education

Yogyakarta, Oktober 28th 2017

Chair Person

Prof. Dr. I Gusti Putu Suryadarma, M.S

ISSN : 2476-9533
Volume 3, October 2017

TABLE OF CONTENTS

ISSN : 2476-9533
Volume 3, October 2017

ISSN : 2476-9533
Volume 3, October 2017

ISSN : 2476-9533
Volume 3, October 2017

ISSN : 2476-9533
Volume 3, October 2017

ISSN : 2476-9533
Volume 3, October 2017

3rd International Seminar on Science Education
Yogyakarta State University, Saturday 28th October 2017

ISSN : 2476-9533
Volume 3, October 2017

Synthesis Of Methyl Ester From *Pome* Assisted By Ultrasonic Irradiation And Cracking Using Zeolite Catalyst

Agus Sundaryono[1], M. Lutfi Firdaus[2], and Dewi Handayani[3]
[1]Graduate School of Science Education University of Bengkulu, Bengkulu, Indonesia
[2] Graduate School of Science Education University of Bengkulu, Bengkulu, Indonesia
[3]Under Graduate School of Chemistry Education University of Bengkulu, Bengkulu
[1]E-mail address: sundaryono_2005@yahoo.fr

Abstract. The purpose of this research is to convert the Palm Oil Mill Effluent (POME) into biofuel to find alternative energy as a substitute for petroleum-based energy supply. This study began with the synthesis of methyl esters, the synthesis of methyl ester was carried out in two stages of reaction: esterification with the aid of ultrasonic irradiation using acid catalyst and trans-esterification reaction with base catalyst. The result of the synthesis then cracked by heating at a temperature of 380 °C for 2 hours using natural zeolite catalysts that have impregnated by active metals, i.e. Cr/HZa and Ni/HZa catalysts. The Ni/HZa catalyst produced 2.4% hydrocarbons, equivalent oil gas, 14.1% short-chain methyl ester and 83.2% long-chain methyl ester. The Cr/HZa catalyst was able to crack methyl esters to produce hydrocarbons of 5.4%, equivalent oil gas, 15.19% short-chain methyl ester and long-chain methyl ester of 79.4%. Characteristics of biofuel that was resulted from catalytic cracking of methyl ester using Ni/HZa catalyst: density 0,799 g /mL, kinematic viscosity 1,391 cSt, fog point 1,67 °C, pour point 0°C, acid number 1,86 mg KOH/g oil and water content 0,932 %. Characteristics of biofuel resulted from catalytic cracking of methyl ester using Cr/HZa catalyst: density 0,795 g / mL, kinematic viscosity 1,322 cSt, fog point 1°C, pour point 0°C, acid number 1,68 mg KOH/g oil and water content 2,102%.
Keywords: ultrasonic irradiation, biofuel, methyl ester, zeolite-based catalyst, Palm Oil Mill Effluent

1. Introduction

In the period of petroleum thinning, a lot of research is done to get fuel from non-petroleum materials. Utilization of vegetable oil as a fuel is hampered because vegetable oil has an average viscosity of 10 up to 20 times higher than diesel oil. This problem can be solved by transesterification of triglycerides present in vegetable oils [1]. Transesterification is the reaction between oil and alcohol to produce a methyl ester [2]. Methyl esters are considered safe to use as biodiesel, because they are not toxic, lower in sulfur and more environmentally friendly [3]. The use of CPO as a fuel is still a problem, that is, the viscosity is too high when compared to diesel petroleum [4]. To overcome it, the CPO is converted to methyl esters [5],[6].

Catalytic cracking is the process of breaking long-chain hydrocarbon compounds into hydrocarbons with shorter chains assisted by a catalyst. The MgO catalyst in the cracking reaction of palm oil produces a hydrocarbon mixture of olefin and paraffin [7]. The Cu metal catalyst impregnated in ZSM-5 was able to convert 34.96 wt% of oil palm to gasoline [8], while the Al_2O_3 impregnated Co catalyst tranformed 100% palm oil to paraffin in the diesel component range [9].

Palm oil has high exposure in the community which,if the palm oil is used as biogasoline, there is a subtantial chance that it will disturb the current condition. The methyl ester of Palm Oil Mill Effluent (POME) has been done by esterification followed by transesterification[10], [11]. The methyl ester is then developed into liquid hydrocarbons through catalytic cracking [12], [13], [14]. The quality test results of catalytic cracking,that the viscosity is still greater than the gasoline's. The major difficulty encountered in converting methyl esters from POME a caused by Free Fatty Acid is very high (reaching ≥ 40%), and it takes a long time to converting (ie, 4 hours at the esterification stage and 2 hours at the transesterification stage). CPO was succeeded converting to methyl ester, by

ISSN : 2476-9533
Volume 3, October 2017

reacting methanol and CPO (6.44: 1) using ultrasonic irradiation aid at a frequency of 40 KHz, 400W, at 38.44 ° C and 25.29 minutes yield 97.85% [15].

In this study, POME was converted to methyl ester by ultrasonic irradiation method to shorten esterification reaction time just 20 minutes only and also transesterification reaction. The resulting methyl ester is further reacted to the catalytic cracking reaction to produce biogasoline (biokerosene or biosolar) fuel with a Ni / HZa and Cr / HZa catalyst, which is a zeolite catalyst impregnated with Ni, and Cr.

2. Material and Method

2.1. Preparationof POME

A total of 350 g of POME is inserted into a beaker, heated over a hot plate, then the mixture is filtered, the filter oil is heated at 105 ° C, and degumming the oil, from phosphatides, proteins, residues, water, and resins, with added H3PO4 % of 1-3% of the amount of POME. After degumming, the POME is poured into Erlenmeyer and then added 10% active zeolite from POME weight, and then stirred while heated to 110 - 120 °C for 1 hour to bleaching of the POME, and then FFA of the POME was determined. If FFA $\leq$ 2% can be esterified with an alkali catalyst, and if FFA $\geq$ 2% is necessary first esterification stage using acid catalyst (H_2SO_4)

2.2. Preparation Catalyst

2.2.1. Preparation of HZa catalyst. Natural zeolites were washed with distilled water. Zeolites were dried in an oven at 110°C, and It was sieved with a 125µm mesh, the natural zeolite (Za) obtained was fed into the beaker and then added HCl 2 M solution (1: 2), stirred with a magnetic stirrer for 4 hours without heating. It was then filtered and washed with distilled water, zeolite is dried in an oven at 110 °C (HZa)

2.2.2. Preparation of Ni / HZa and Cr / Hz catalyst. The Ni impregnation on HZa was done by mixing the HZa powder into a 0.1 M NiCl2.9H2O solution (1: 5 b / v), then refluxing at 85 ° C. for 3 hours, then filtered and heated to 120 ° C for 12 hours, obtained Ni / HZa bifunctional catalyst. Activation of Ni / HZa catalyst was performed by calcination in the muffle furnace at 500°C for 4 hours. The same step was performed to obtain a Cr / HZa bifunctional catalyst by replacing 0.1 M NiCl2.9H2O with 0.1 M Cr (NO3) 2 .6H2O.

2.3. Synthesis of Methyl Ester with Ultrasonic Irradiation

Esterification is operated by reacting methanol and POME (6: 1) in a round bottom flask with concentrated H_2SO_4 as a catalyst (1% by weight of POME). This mixture is in ultrasonic irradiation for 30 minutes at 45 kHz and 60 ° C, the result of the process is inserted in separating funnel and left overnight. After the results were separated, then determined FFA. If FFA $\geq$ 2% it is necessary to re-esterification. The final result of the esterification process was added methoxy (0.4 g NaOH: 40 ml methanol), then is an ultrasonic irradiation for 25 min at 60°C. The mixture was inserted in a separating funnel and held for one night. Methyl ester is washed with warm water.

2.4. Catalytic Cracking Methyl Ester with Ni/HZa and Cr/HZa Catalysts

The catalytic cracking reaction of the methyl ester is carried out using a set of reflux devices. The methyl ester was introduced into a three-neck flask, and a Ni / HZa catalyst (5%) was added, then heated to a temperature of 380°C for 2 hours, after refluxed and then was distilled to separate the biofuel product. The biofuels were analyzed by using GC-MS, and were characterized by density test, viscosity test, fogging test and the acid number test. The same was done for catalytic cracking reactions using Cr / HZa catalysts.

ISSN : 2476-9533
Volume 3, October 2017

3. Results and Discussion

The catalytic activity of natural zeolite can be increased by activation and impregnation of the active metal on the surface of natural zeolite, as it will form two active sites, namely acid sites and catalytically active metal sites. This catalyst is called a bi-functional catalyst, which have two types of active sites, i.e. acid sites that serve for cracking and metal sites that act for dehydrogenation. In this study the active metals that are impregnated in zeolites were Ni and Cr. The presence of Cr and Ni metals introduced into the zeolite will increase the acidity of the catalyst or Lewis acid site. In addition, active metal exposure may also increase the Si / Al ratio and the specific surface area (SSA) of the catalyst [16]. The impregnation of the active metal on the zeolite surface can increase the SSA [17].

The trans-esterification stage begins by giving treatment to POME including filtering, heating, degumming, and bleaching. Free fatty acids (FFA) of POME 43,76%, to avoid soap formation, conversion of POME to methyl ester is done two stages, esterification and trans-esterification Esterification is intended to convert FFA to methyl ester with a strong acid catalyst (H_2SO_4). The esterification of this study was performed by ultrasonic irradiation method for 20 minutes. The use of ultrasonic irradiation at this stage can increase the formation, growth and rupture of cavitation, the phenomenon of bubbles forming from the liquid stream, in areas where the liquid pressure falls below the vapor pressure. As a result of the phenomenon is the reaction goes faster [18]. Esterification was done three times. FFA oil decreased to 1.3%. Furthermore, trans-esterification was carried out by reacting the esterification process with a NaOH acting as an alkoxide which is a strong nucleophile and methanol. The ratio of the mole ratio of methanol and oil used in the study was 6: 1, whereas the catalyst used was 1% of the weight of the oil, needed excessive methanol, intended so that the soap does not form solids, but soluble in methanol. In this study the trans-esterification reaction was performed with the aid of ulatrasonic irradiation for 20 minutes.

The trans-esterification reaction begins with the formation of soap as a result of a triglyceride reaction with a NaOH, with ultrasonic irradiation, the formation of soap can take place more quickly because of the formation of small droplets of the NaOH catalyst (dissolved in methanol) undergoing cavitation such as methanol. The droplet may expand the surface area for the occurrence of saponification reactions between triglycerides and NaOH catalysts. This formed soap acts as a transfer phase and increases the mixing of oil with methanol, so that the reaction of methyl ester formation can take place more quickly. The yield of methyl ester from POME conversion result was 71,6%.

The components of methyl ester as a result of POME conversion based on GC-MS analysis are presented in **Table 1**.

Table 1. Components of Methyl Ester as a Conversion Result of POME

No	Components	Molecular formula	Molecular weight(g/mol)	(%)
1	Myristic acid methyl ester	$C_{15}H_{30}O_2$	242	1,1
2	Palmitate acid methyl ester	$C_{17}H_{34}O_2$	270	52,4
3	Oleate acid methyl ester	$C_{19}H_{36}O_2$	296	41,1
4	Stearic acid methyl ester	$C_{19}H_{38}O_2$	298	5,4

ISSN : 2476-9533
Volume 3, October 2017

Characterization of methyl ester of POME conversion results is presented in Table 2.

Table2. Methyl Ester Characteristics of POME Conversion Results

Parameter	Unit	Methyl Ester	SNI Methyl Ester
The acid number	mg KOH/g oil	1.12	Maks 0,8
Water content	%weight	0.74	Maks 0,05
Density	g/cm^3	0.85	0,85-0,89
Kinematic viscosity 40^0C	cSt	1.69	2,3 - 6,0
Pour point	^0C	8.50	Maks 18^oC
Clouding Point	^0C	8.84	Maks 18^oC

According to Table 2., the methyl ester parameters have met the SNI, only the acid number and water content are still high enough. The high number of acids can lead to corrosive properties and high water levels allow for hydrolysis reactions that can cause elevated FFA levels [19].

Catalytic cracking is a method of breaking of compounds with long carbon chains into compounds with simpler carbon-chains through the aid of catalysts which can improve the quality and quantity of products, and take place at low temperature and pressure [20]. The reaction step of catalytic cracking of methyl esters is estimated through 3 step of initiation step which is reaction between alcohol with catalyst to form carbonium ion and stabilized radical. Step propagation is the reaction between carbonium ions and stabilized radicals with methyl esters, while the termination step is the re-forming of the catalyst.

The process of catalytic cracking of methyl ester in this study was carried out by heating for 3 hours at 380°C, methyl ester with 5% catalyst (Ni / HZa and Cr / HZa). Results of catalytic cracking of methyl esters were analyzed using GCMS. The component is presented in **Table 3 and 4.**.

Table 3. Biofuel component as a result of catalytic cracking Methyl Ester with Ni / HZa catalyst

Component	Number of Carbon Chains	%
Gasoline	C5 - C10	-
Kerosene	C11 - C12	-
Gas oil	C13 - C17	2.44
Heavy gas oil	C18 - C25	-
Short chain methyl esters	$C_{11-15}H_yO_z$	14.41
Long chain methyl esters	$C_{16-19}H_yO_z$	83.15

Table 4. Biofuel component as a result of catalytic cracking methyl ester with Cr / HZa catalyst

Component	Number of Carbon Chains	%
Gasoline	C5 - C10	-
Kerosene	C11 - C12	-
Gas oil	C13 - C17	5.44
Heavy gas oil	C18 - C25	-
Short-chain methyl esters	$C_{11-15}H_yO_z$	15.19
Long-chain methyl esters	$C_{16-19}H_yO_z$	79.37

Analysis with GCMS showed that hydrocarbon compounds were produced in the catalytic cracking reaction of methyl ester with Ni / HZa catalyst, and Cr / HZa, able to produce equivalent hydrocarbon gas oil respectively by 2, 44%, and 5.44%. The Ni / HZa, and Cr / HZa catalysts were able to convert long-chain methyl esters to methyl esters with shorter-chain respectively by 14.41%, and 15.19%. Cr / HZa catalysts have a better ability to produce hydrocarbon fractions and produce methyl esters with shorter carbon chains

ISSN : 2476-9533
Volume 3, October 2017

The physical characteristics of biofuel from catalytic cracking methyl ester reaction using Ni / HZa catalyst, and Cr / HZa are presented in **Table 5**

Table 5. Biofuel Characteristics of Catalytic Cracking Methyl Ester Reaction Results

Parameter	Unit	Sample				
		Methyl Ester	Biofuel from catalytic cracking results with catalyst		Gasoline	Kerosene
			Ni/HZa	*Cr/HZa*		
Kinematic viscosity 40^0C	cSt	1,683	1,391	1,322	0,456	1,058
Density	g/cm^3	0,849	0,799	0,795	0,772	0,795
Pour point	^{0}C	5,67	0	0	0	0
Clouding Point	^{0}C	1,67	1,67	1	1	1
Water content	% weight	0,739	0,932	2,102	0,26	0,46
The acid number	mg KOH/g oil	1,122	1,86	1,68	0,748	0,935

Based on Table 5., it is known that biofuel density is 0.799 g / mL (with Ni / HZa catalyst) and 0.795 g / mL (with Cr / HZa catalyst) has approached kerosene density (0.792 g / mL), and the viscosity of biofuel resulted is 1,392 cSt (using Ni / HZa catalyst) and 1,322 cSt (using Cr-HZa)that is smaller than methyl ester viscosity (1,683 cSt), but the viscosity of both biofuels has not equal to kerosene viscosity (1,045 cSt) and gasoline (0.449 cSt), so it can not be used as fuel equivalent kerosene or gasoline with 100% biofuel composition. The decrease in the viscosity of both biofuels can be done by blending biofuel with kerosene or gasoline. On the Table 5. the fog and pour points of both biofuel catalytic cracking of methyl ester using Ni / HZa and Cr / HZa catalysts are similar and almost to the point of fog and pour point of gasoline and kerosene, so that the biofuel can be used in areas with cold climates. The decrease in the viscosity of both biofuels can be done by blending biofuel with kerosene or gasoline. Biofuel acid levels are still high, even higher when compared with methyl esters. This may be possible because the catalyst used is a homogeneous catalyst of sulfuric acid which is difficult to separate apart during the separation process.

The water content of biofuel is still quite high, but the moisture content of methyl ester and biofuel resulted from cracking catalytic methyl ester with Ni / HZ catalyst is near kerosene water content

4. Conclusion

Methyl esters of POME can be synthesized with the help of ultrasonic irradiation, with a yield of 71.6%. The use of Ni / HZa and Cr / HZa catalysts in catalytic cracking methyl ester reaction resulted in 68,191% and 63,867% respectively of biofuels. The use of Ni / HZa catalyst capable of cracking methyl ester into gas oil is 2,44%, and short-chain methyl ester is 14,41%. The use of Cr / HZa catalyst capable of cracking methyl esters into gas oil of 5.44%, and short-chain methyl ester of 15.19%. Characteristics of biofuel result using Ni / HZa catalyst is density 0,799 g / mL; kinematic viscosity 1,391 cSt; fog point 1.67°C; pour point 0°C; acid number 1.86 mg KOH / g of oil; water content 0.932%, and using Cr / HZa catalyst is density 0,795 g / mL; kinematic viscosity 1,322 cSt; fog point 1°C; pour point 0°C; acid number 1.68 mg KOH / g of oil; water content of 2.102%

ISSN : 2476-9533
Volume 3, October 2017

Acknowledgment
Thanks to:
1. Directorate General of Research and Development, Ministry of Research, Technology and Higher Education who had approved funding in Research MP3EI 2017 (Contract Nomer : 061/SP2H/LT/DRPM/IV/2017, April 6, 2017)
2. My beloved daughter Noorlaksmita Yonas R. for enhancing the article.

References

[1] Meher, LC., Sagar, V. D, and Naik, S.N. 2006. *Techhnical aspect of biodiesel production by transesterification*- a review. Renew sust energy Rev; 10:248-68
[2] Hideki, Fukuda., Kondo, A., and Noda, H. 2001. Biodiesel fuel production, by transesterification of oil. J biosci Bio eng; 92(5): 405-16
[3] Vyas, A.P., Verma. J.L., and Subramanyam, N. 2010. A Review on FAME production Processes. Fuel Vol. 89: 1-9
[4] Jan, L., and Bemd, O., 2004. *The Influence Of Mass Transfer On Biodiesel Production*. Chem Eng Technol: 27 (1) : 1156 – 9
[5] Hanh, H. O., Nguyen, F., T., , Kenji, O., Maeda, Y., and Rokuro, N. 2007. *Effects of Molar Ratio, Cathalyst Concentration and Temperature on Transestherification of Triolein with Ethanol Under Ultrasonic Irradiation*. Jpn J Pet Inst 50 (4) : 1 95-9.
[6] Tani, H. , Hasegawa, T. Shimouchi, M. , Asami, K., and Fujimoto. K.2011. Selective catalytic decarboxy-cracking of triglyceride to middle-distillate hydrocarbon. Catalysis Today *164 . 410–414*
[7] Stavarache, Carmen, Vinatoru M, Maeda Y, and Bandow H.2007. *Ultrasonically Driven Continuous Process For Vegetable oil Transestherification*. Ultrason Sonochem 2007:14:413-7.
[8] Bahnur, T. S., and Saidina, N.A. 2006. CATALYTIC CRACKING OF PALM OIL TO GASOLINE OVER PRETREATED Cu-ZSM-5. *Jurnal Teknologi*, 44(F) Jun : 69–82
[9] Sotelo-Boyás, R., Trejo-Zárraga, F. and Hernández-Loyo, F. 2012. Hydroconversion of Triglyceridesinto Green Liquid Fuels. InTech Journal.
[10] Sundaryono, A., 2009. Pengembangan Limbah Cair Pabrik Minyak Kelapa Sawit (PMKS) Sebagai Sumber Energi Alternatif Biokerosene di Provinsi Bengkulu, Proseding Seminar Nasional FMIPA Yogyakarta, Yogyakarta
[11] Sundaryono, A. 2011. KARAKTERISTIK BIODIESEL dan *Blending* BIODIESEL dari *Oil Losses* LIMBAH CAIR PABRIK MINYAK KELAPA SAWIT. Jurnal Teknologi Industri Pertanian. Vol. 21. Bogor : IPB
[12] Sundaryono, A dan Budiyanto. 2010. Pembuatan Bahan Bakar Hidrokarbon Cair Melalui Reaksi *Cracking* Minyak Pada Limbah Cair Pengolahan Kelapa Sawit. Jurnal Teknologi Industri Pertanian. Vol. 20 (1). 14 – 19. Bogor : IPB
[13] Sundaryono, A., dan Handayani, D. 2012. Pengembangan limbah cair pabrik minyak kelapa sawit sebagai *biogasoline* melalui reaksi perengkahan katalitik dengan katalis berbasis zeolit di Provinsi Bengkulu, Laporan Penelitian Hibah Bersaing, Universitas Bengkulu.
[14] Sundaryono, A., Handayani, D., Budiman, Winda, S., 2015. Perengkahan katalitik metil ester dari aminyak limbah cair Pabrik Minyak Kelapa Sawit dengan katalis Cr/Mo/HZA dan Ni/Mo/HZA. Jurnal Teknologi Industri Pertanian Vol 25, No. 1, 78-84.
[15] Thaiyasiut, IWP and Pianthong, K. 2011. Ultrasonic Irradiation Assisted Synthesis of Biodiesel from Crude Palm Oil Using Response Surface Methodology. SWU Engineering Journal 6(1), 16-30
[16] Tarigan, S., 2009. Aktivitas Katalis Cr/Zeolit Dalam Reaksi Konversi Fenol dan Metil Isobutil Keton. UKA: Kabanjahe
[17] Setyawan. 2002. Pengaruh Perlakuan Asam, Hidrotermal dan Impregnasi Logam Kromium Pada Zeolit Alam dalam Preparasi Katalis. Jurnal ILMU DASAR, Vol. 3 No. 2, 2002: 103-109

ISSN : 2476-9533
Volume 3, October 2017

[18] Juliastuti, S. R., 2010. Penggunaan Teknologi Hydrothermal (Sub Kritis) Dan Ultrasonik Untuk Menghasilkan Syn Gas Dan Alkohol Dari Gliserol Sebagai Sumber Energi Alternatif Terbarukan. Tesis Institut Teknologi Surabaya
[19] Prihandana, R., 2006. Menghasilkan Biodiesel Murah : Mengatasi Polusi dan Kelangkaan BBM. Jakarta: Agro Media Pustaka
[20] Nurjannah. 2010. *Perengkahan Katalitik Minyak Sawit untuk Menghasilkan Biofuel*. Disertasi Jurusan Teknik Kimia Institut Sepuluh November Surabaya