Conference Paper

Production of Biodiesel from Palm Oil Oil Using Nizn /Al2o3 Catalyst As Biomass Alternative Energy

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Abstract

Fossil energy is a limited source of primary energy, various efforts have been made to find alternative fuels that are renewable. Vegetable oil is one of the plants that can be a source of energy, but must be converted into other forms, namely alkyl esters (biodiesel). Biodiesel is a diesel fuel substitute that can be used as a raw material for making or mixing in transportation fuels. In this study, biodiesel will be produced using an esterification-transesterification process with NiZn/Al_2O_3catalyst. Process variables include: temperatures of 90,120,150 and 180oC. the ratio of feed methanol: palm oil at a ratio of 1: 15. The concentration of NiZn/Al2o3 catalyst was varied at 1, 1.5, 2, and 2.5%. NiZn/Al2O3 catalyst was synthesized using wet impregnation method with loading of nickel and Zink at 5% wt. The catalyst will be analyzed using XRD and SEM analysis. Nickel and Zink metals in the NiZn/Al_2O_3 catalyst catalyst have been dispersed on the surface of Al_2O_3. Al_2O_3 calcination before the impregnation process produced NiZn /Al_2O_3 catalyst with a crystallinity of 62,99%. The results of this study concluded that the biodiesel produced increased with increasing catalyst concentration, temperature, reaction in the esterification-transesterification process where at a temperature of 90oC and catalyst concentration 0.015 g catalyst / gr feed and reaction time of 1.5 hours obtained biodiesel yield of 35.8%, at temperature of 90oC and at a temperature of 180oC and catalyst concentration of 0.01 g catalyst/gr feed obtained biodiesel yield of 48.3%. Biodiesel was analyzed by GCMS to measure the composition of methyl esters and test the properties of biodiesel according to ASTM standards.

Keywords: Biodiesel, Palm Oil, Esterification-Transesterification, NiZn/Al_2O_3

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1. Introduction

The energy crisis in Indonesia is caused by an increase in petroleum consumption in daily life. This increase was due to the increase in the number of vehicles and industrial companies. In addition, the amount of petroleum is decreasing. Other energy sources must be found and empowered to solve this problem. One type of petroleum product is diesel which is an important part because it is used in various sectors. Reducing the amount of solar production causes Indonesia to import it from other countries. Steps that can be taken to reduce diesel consumption are using biodiesel. Due to reduced petroleum production, Indonesia's export value has declined. To overcome these problems, there needs to be research to produce alternative energy, one of which is biodiesel.

Biodiesel is an alternative fuel for diesel engines produced from transesterification reactions between vegetable oils or animal fats that contain triglycerides with alcohols such as methanol and ethanol. This transesterification reaction requires strong base catalysts such as sodium hydroxide or potassium hydroxide to produce new chemical compounds called methyl esters (Gerpen, 2005).

One example of vegetable oil that can be used for making biodiesel includes palm oil. This material is considered more economical and efficient. But the drawback is the high content of free fatty acids (Free Fatty Acid, FFA) and the presence of other impurity compounds. High FFA levels can inhibit the reaction of biodiesel formation, because the COH used as a catalyst will react with FFA to form soap. Besides that the resulting soap will complicate the separation of biodiesel purification. Therefore, it is necessary to pretreatment against palm oil before being processed into biodiesel so that the FFA content can be reduced.

Table 1: CPO Production in Indonesia 2010-2014.

Years	Production(ton)	Escalation Production (%)	Consumption per Capita (kg)
2010	3.89	-	14.90
2011	4.20	7.38	15.00
2012	4.22	0.47	15.40
2013	4.77	11.53	16.00
2014	5.39	11.50	16.50

In Government Regulation (PP) number 5 of 2006, petroleum consumption must be reduced to 20% of national energy consumption (PP no. 5, 2006). One step that can be done is the conversion of diesel fuel to biodiesel. Biodiesel that will be developed in this research is B5 which consists of 5% biodiesel and 95% solar.

The biodiesel production process uses NiZn/Al_2O_3 catalyst in which this catalyst uses NiZn metal indicating that Zn metal has high hydrogenation ability when combined with Ni metal. The esterification-transesterification process at temperatures below 300oC produces 60-80% yield of diesel (Kumar et al, 2010). However, the higher the temperature used in the esterification process - transesterification, the fraction of diesel will decrease and the lighter hydrocarbon fractions such as kerosene and naphtha will increase (Verma et al, 2015). The process used in biodiesel production is

2. Research Method

2.1. Material

Aluminium potassium sulfate dodecahydrate ($KAl(SO_4)_2.12H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$, Merck), aluminium hydroxide ($Al(OH)_3.xH_2O$, Merck), alumina (Al_2O_3, PT. Inalum), commercial gamma-alumina (γ-Al_2O_3), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Merck), ammonium heptamolybdate tetrahydrate $ZnSO_4.7H_2O$, Merck, Palm Oil

2.2. Tools

In this study the tool used was a hot plate and magnetic stirrer which was connected to the cooling back and three neck flasks which were installed with stabs and clamps to maintain the biodiesel production process.

2.3. Catalyst preparation

1. Al_2O_3 dried in the furnace at 300°C for 1 hour.
2. $Ni(NO_3)_2.6H_2O$ as much as 2,476 grams, 6,439 grams $ZnSO_4.7H_2O$ total, as many as 0.64 ml H_3PO_4 were dissolved in 25 ml of distilled water and 10 grams Al_2O_3 mixed into a solution.
3. The solution was impregnated while heated at a temperature of 60°C for 12 hours.
4. The impregnated solution is filtered with filter paper to get the sediment.
5. The precipitate is dried in an oven at 120°C for 24 hours.
6. The dry precipitate from the oven is derived in the furnace at 600°C for 5 hours.
7. Characterization of Catalysts

Catalysts are characterized using XRD and SEM analysis.

2.4. Esterification and transesterification methods

When comparing biodiesel with diesel, the thing that needs to be considered is the level of fuel emissions. Biodiesel produces smaller levels of hydrocarbon emissions, around 30% compared to diesel; CO emissions are also lower, around 18%, particulate molecule emissions 17% lower; while for NOx emissions is around 10%; so that overall, biodiesel emission levels are lower compared to diesel, so its use is more environmentally friendly. (Firdaus, 2009)

The process of making biodiesel from used crude palm oil will pass through the following stages (Firdaus, 2009):

1. the process of refining used crude palm oil from impurities and water content
2. esterification of free fatty acids contained in crude palm oil,
3. trans-esterification of triglyceride molecules into methyl esters, and
4. separation and purification

$CH_2 – O – CO – R'$ | CH_2OH | $CH_3 – O – CO – R'$

$CH – O – CO – R''$ + 3 CH_3OH $\xrightarrow{\text{Catalyst}}$ $CHOH$ + $CH_3 – O – CO – R''$

$CH_2 – O – CO – R'''$ | CH_2OH | $CH_3 – O – CO – R'''$

Triglyceride Methanol Glycerol Methyl Ester – Biodiesel

Figure 1: Biodiesel Production Stage.

The esterification and transesterification methods are used to convert crude palm oil into biodiesel. Esterification uses acid catalysts, such as ($NiZn/Al_2O_3$). The steps in esterification and transesterification are shown in Figure 1.

Preparation of raw materials and catalysts

Catalysts XRD and SEM

Esterification and Transesterification Process

At catalyst concentration 0,01gr/gr,0,015gr/gr,0,02gr/gr dan 0,025gr/gr at temperature 90ºC

at temperature
90ºC,120ºC,150ºC, 180ºC at 0,01gr/gr

GCMS analysis to see biodiesel results

3. Results and Discussion

3.1. Raw material analysis

GCMS analysis results from crude palm oil raw material showed that the composition of dirty oil in the form of fatty acids consisting mostly of palmitic acid ($C_{16}H_{32}O_2$) and oleic acid ($C_{18}H_{34}O_2$) The methyl esters obtained were in accordance with the fatty acid content found in the base material coconut crude palm oil and palm oil used for biodiesel synthesis, such as oleic acid, palmitic acid, stearic acid and arachidat acid (Goering, et al., 1982 in Wind, AP, 2010), ricinoleic acid derived from palm oil. The risinoleic ester, including a unique ester, has an OH group and a double chain, has the highest lubricity value among other esters.

Table 2: Raw Material GMCS Analysis.

No	Name of compound	Component	Composition (%)
1	Sebacic Acid	$C_{10}H_{18}O_4$	2,05
2	Palmitoleat Acid	$C_{16}H_{30}O_2$	2,36
3	Palmitat Acid	$C_{16}H_{32}O_2$	54,77
4	Linoleat Acid	$C_{18}H_{32}O_2$	2,63
5	Oleat Acid	$C_{18}H_{34}O_2$	23,23
6	Risinoleat Acid	$C_{18}H_{34}O_3$	1,58
7	Stearat Acid	$C_{18}H_{36}O_2$	5,04
8	Hidroksistearat Acid	$C_{18}H_{36}O_3$	2,96
9	Oktadekanoik Acid	$C_{18}H_{36}O_4$	2,35
10	Dioctyl Fumarate	$C_{19}H_{34}O_4$	3,04

3.2. Results of XRD and SEM analysis

To determine the effect of the impregnation process on the NiZn/ Al_2O_3 catalyst produced, XRD analysis was carried out. NiZn/Al_2O_3 catalyst was synthesized using wet impregnation method with loading of nickel and zinc used was 5% wt Al_2O_3.

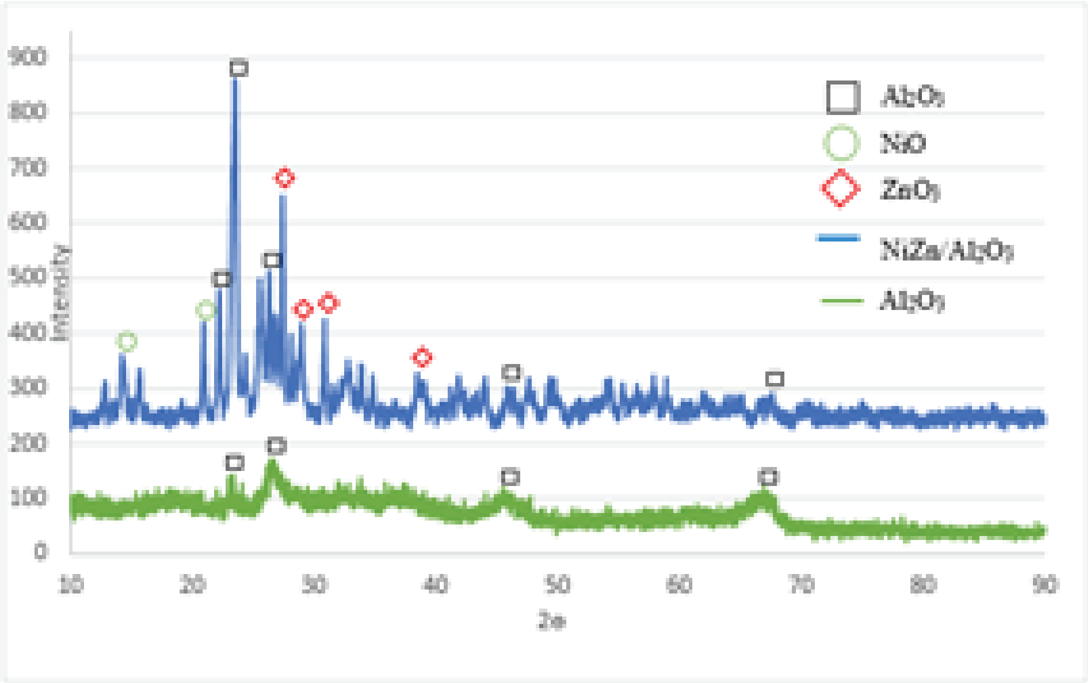

Figure 2: Diffractogram of Al2O3 raw material and Ni / Al2O3 catalyst.

Showing the results of the XRD analysis in the form of a diffractogram of the raw material Al2O3 (Green) and the catalyst NiZn/Al_2O_3 (Blue) where the position of the peak intensity point is observed at 2θ. The appearance of NiO diffraction pattern at 14.44o; 21.03o and ZnO_3 at the point of 27.50o; 28.99o; 30,94o; 38.55o shows that NiO and ZnO_3 crystals have been embedded on the surface of Al_2O_3. Al_2O_3 raw material has a crystallinity of 53.19% while NiZn/Al_2O_3catalyst has a crystallinity of 62.99%. The intensity of the cusp shows the crystallinity of the catalyst. At the point of Al_2O_3 intensity (22.31o and 26.47o) there is an increase in the peak point intensity which shows that the crystallinity of Al_2O_3 has increased (Liu et al, 2016).

SEM characterization aims to determine the morphology of Al_2O_3 raw material and NiZn/Al_2O_3catalyst. Morphology plays an important role in catalyst activity and selectivity. SEM analysis of NiZn/Al_2O_3 catalysts

Shows the results of SEM analysis of the raw materials Al_2O_3 (a) and (c) then the catalyst NiZn/Al_2O_3 (b) and (d). From the results of SEM analysis, it is known that Al_2O_3 has been covered by NiO and ZnO_3 particles which means that the impregnation process

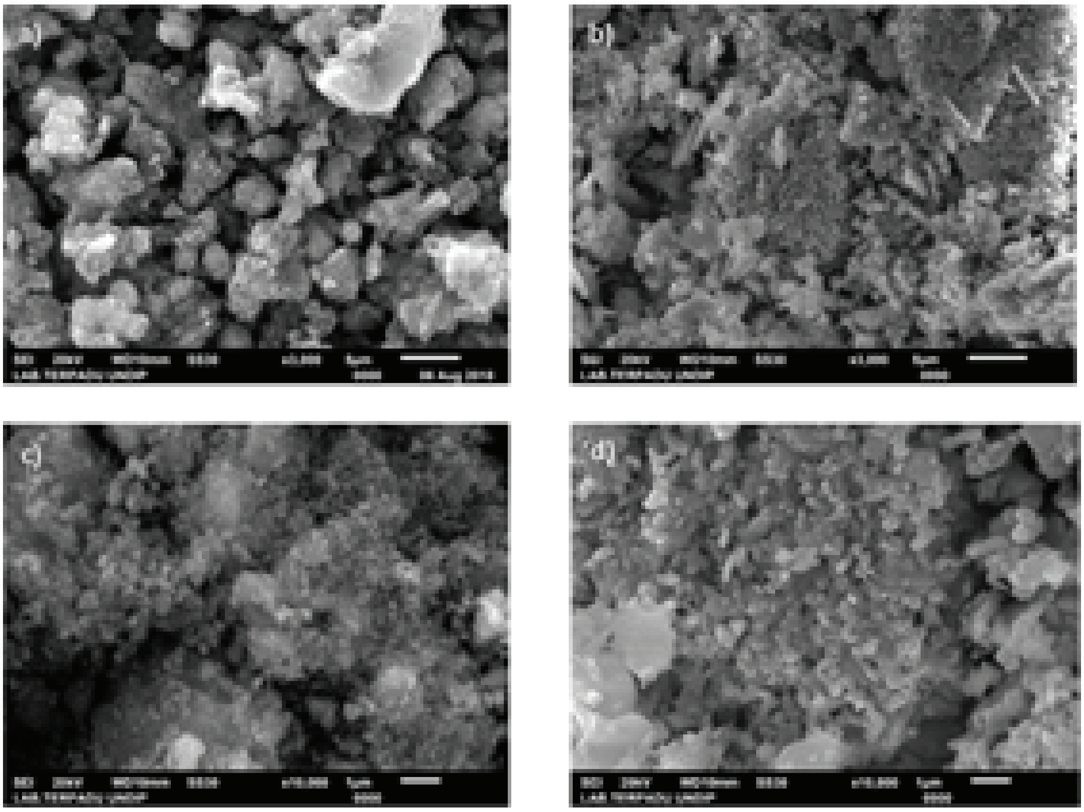

Figure 3: Results of SEM Analysis a) Al_2O_3 3.000x, b) NiZn/Al_2O_3 3.000x, c) Al2O3 10,000x, d) NiZn/Al_2O_3 10,000x magnification.

carried out has had an impact on the morphology of the catalyst where NiO and ZnO_3 have been dispersed on the surface of Al_2O_3.

3.3. Effect of catalyst concentration

The esterification-transesterification process was carried out at a temperature of 90oC for 1.5 hours, and the catalyst concentration used was 0.01; 0.015; 0.02; 0.025; gram catalyst / gram feed. Based on the results of the study, a calculation was made regarding the yield of biodiesel products on each catalyst concentration used to determine the effect of the catalyst concentration used on the yield of liquid products (biodiesel).

The catalyst used in the esterification-transesterification process is NiZn/Al_2O_3 where the active side of the catalyst in the form of nickel and zinc metal which has a large reactivity serves to facilitate the formation of intermediate compounds on the catalyst surface (Anand et al, 2012) and provide high hydrogenation and cracking capabilities. (Srifa et al, 2010). The greater the concentration of catalyst used, the greater the number of active catalysts used as a place for hydrogenation and cracking. In this case, the best

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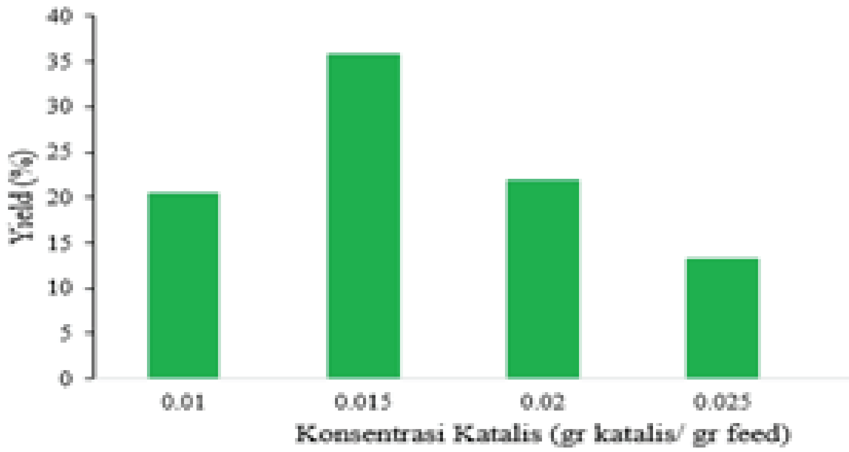

Figure 4: catalyst concentration on biodiesel yield.

catalyst concentration used in the esterfication-transesterification process in making the diesel fraction is 0.015gr / gr (C16-C19).

3.4. Temperature influence

In the esterification-transesterification process is the effect of the reaction temperature on the yield of biodiesel produced. The process was carried out for 1.5 hours with a catalyst concentration of 0.01 gram catalyst / gram feed, at temperatures of 90, 120, 150, and 180oC. Based on the results of the study, calculations were carried out on the yield of liquid products (biodiesel) for each catalyst concentration used to determine the effect of the reaction temperature used on the yield of liquid products (biodiesel).

3.5. Biodiesel content of GCMS analysis results

Based on the GCMS analysis results showed that in table 3 the main components contained in the biodiesel sample were methyl 9-octadecanoate (49.45%), methyl hexadecanoate (20.79%), and methyl 9,12-oktaekanoate (18.87%). From these data it can be stated that the biodiesel compound is truly true, namely methyl ester. Analysis with GCMS shows that there are no free fatty acids contained in biodiesel. This shows that the adsorption process is capable of producing biodiesel in the form of methyl esters.

4. Conclusion

NiZn/Al_2O_3 catalyst synthesized using wet impregnation method with pretreatment in the form of Al_2O_3 calcination produced a catalyst with a crystallinity of 62.99% which can be

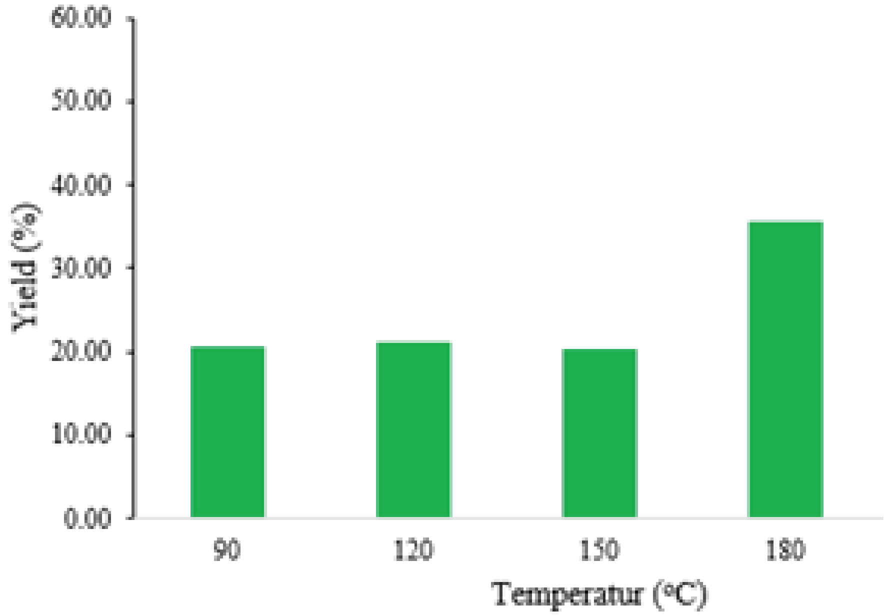

Figure 5: Temperature of biodiesel yield.

Table 3: Analysis of Biodiesel Content with GCMS.

Top	area(%)	Compound name	Molecular formula
1	0.19	Methyl dodecanoate	C13 H26O2
2	1.36	Methyl tetradekanoate	C15H30O2
3	0.96	Methyl 9-hexadecanoate	C17H32O2
4	20.79	Methyl hexadecanoate	C17H34O2
5	0.11	14- Methyl hexadecanoate	C18 H36O2
6	18.87	Methyl 9,12 octadecanoate	C19 H34 O2
7	48.3	Methyl 9-octadecanoate	C19 H36O2
8	7.68	Methyl octadecanoate	C19H38O2
9	0.19	Methyl 11-eikosenoat	C21H40O2
10	0.41	Methyl eikosenoate	C21 H42O2

used in the esterification-transesterification process to produce biodiesel production. At 0.015gr / gr catalyst concentration yields the highest yield of biodiesel with a percentage of 35.8% and for the best conditions at 180oC at 48.3%. Data from GCMS analysis also showed the content of methyl 9-octadecanoate containing 48.3% of the area, methyl hexadecanoate (20.79%), and methyl 9,12-octadecanoate (18.87%). thus using palm oil and NiZn/Al_2O_3 catalyst can be used to produce biodiesel as an alternative energy based on biomass.

Figure 6: Biodiesel.

References

[1] Anand M, Farooqui S A, Kumar R, Joshi R, Kumar R, Sibi MG, Singh H, Sinha A K. 2016. Optimizing renewable oil hydrocracking conditions for aviation bio-diesel production. Fuel Proc Tech. 151: 1-2

[2] Firdaus. 2009. "Sintesis and Analisi Kualitas Biodiesel dari Minyak Jelantah (Tesis)."Bandung. ITB

[3] Gerpen Vj. 2005. Biodiesel Processing And Production. Fuel Process Technol 86.1097-1107

[4] Kumar R, Rana B.S, Tiwari R, Verma D, Kumar R, Joshi R K. 2010. Hydroprocessing of jathropha oil and its mixtures with gas oil. Green Chem. 12 :2232-2239

[5] Laila, Lia dan L. Oktavia. 2017. Kaji Eksperimen Angka Asam dan Viskositas Biodiesel Berbahan Baku Minyak Kelapa Sawit dari PT Smart Tbk. Jurnal Teknologi Proses dan Inovasi Industri 2(1): 27-31.

[6] Liu H, Liu C, Yin C, Liu B, Li X, Li Y, Chai Y, Liu Y. 2016. Low temperature catalytic hydrogenation naphthalene to decalin over highly loaded NiMo, NiW and NiMoW catalyst. Cat Today. 8

[7] Meher LC, D.C.Sager,S.N. Naik. 2006. Technical Aspects of Biodiesel Production by Transesterification–A Review. Renewable and Sustainable Energy Reviews 10(1):248–268

[8] Raia, Rodrigo Zunta, L. S. da Silva, S. M. P. Marcucci, dan P. A. Arroyo. 2016. Biodiesel Production from Jatropha curcas L. Oil by Simultaneous Esterification and Transesterification using Sulphated Zirconia. Catalyst Today 289(1): 105-114

[9] Triyono W, Pulung A N, Sihombing J L. 2011. Hidrorengkah Minyak Laka Menjadi Fraksi Bahan Bakar Cair Menggunakan Katalis Zeolit Alam. Jurnal Penelitian Saintika.

[10] Verma D, Kumar R, Rana B S, Sinha A K. 2011. Aviation fuel production from lipids by a single-step route using hierarchical mesoporous zeolites. Energy Environ Sci. 4: 1667-1671.