Effect of Temperature and Catalyst to Feed Ratio on Production Biofuel from Fatty Acid of Palm Oil Industrial Sludge Hydrocracking

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ABSTRACT

... recovered from CPO waste sludge ... hydrocracking process using Ni/Mo ZrO_2 ...morillonite. Hydrocracking was conducted ... reactor and variation was made on ... process and catalyst to feed weight ratio. ... analyzed using gas chromatography. It ... increasing temperature and ratio caused ... fatty acid conversion through ... The highest conversion was 90% ... °C dan 0.25 ratio. The oil produced ... gasoline. kerosene and diesel fraction each ... 5% (w/w) respectively.

...cracking, catalyst, fatty acid, biogasoline

INTRODUCTION

... palm oil processing produce high amount of ... of liquid and sludge. This waste contains ... emulsion which disposed during process. ... is hard to separated into its constituent ... sedimentation in addition of long time. ... industrial crude palm oil (CPO) waste ... not only to gain lipid but also to reduce ... damage.

... process from industrial CPO waste sludge ... focus on recovering lipid only, advance ... conducted to reuse and convert it into fuel. ... of the recovery product are fatty acids ... According to previous researchers, ... containing this compounds can be treated ... Pd C [1], Alumina, Al-MCM-41 and ... Zeolite. silica-alumina [3] and Co/Mo ... Montmorillonite [4] to produce fuel ... gasoline and diesel fraction. Catalyst role is ... in catalytic conversion of recovered ... it will influence reaction mechanism as ... composition resulted. Catalyst properties ... area, porosity and metal impregnated ... influenced its catalytic performance.

... recovered oil involves several catalyst ... reaction i.e cracking, hydrogenation, ... decarbonylation, aromatization etc ... which take event between them. Among reactions which would proceed depend on the choice of catalyst and reaction condition. In case of reaction conditions, some variables can be consider to influence namely temperature and catalyst to oil feed ratios.

METHODS

A. Materials

Natural clay of type Na-Montmorillonite provided by P.T. Tunas Inti Makmur Semarang, water used were demineralized, whilst NaCl, $AgNO_3$, Zirconium Oxychloride, $Ni(NO_3)_2$ and ammonia provided by Merck. Hydrogen gas produced by P.T. BOC Indonesia.

B. Design and Characterization of Ni/Mo ZrO2 Pillared Montmorillonite Catalyst

The first step of making catalyst involve pillarization of Montmorillonite using ZrO_2 followed by impregnating Ni and Mo metal. Na-Montmorillonite provided by P.T. Tunas Inti Makmur has composition SiO_2 62.36%, Al_2O_3 16.26%, Fe_2O_3 4.83%, CaO 4.82%, Na_2O 4.53% and Lost of Ignition (LOI) 7.19%.

Monmorillonite was grinded using porcelain mortar followed by sieve shaker of 100 mesh size. Fined Montmorillonite was washed by aquadest, filtered and dried oven. 150 g dried Montmorillonite were submerged into saturated NaCl 500 mL and stirred for 24 hours. Saturation by NaCl was conducted to exchange cations within Montmorillonite layers. Inhomogeneity of cations within Montmorillonite layers would caused imperfect pillarization result. After being saturated for 24 hours, Montmorillonite was washed using demineralyzed water to remove Chloride ions from its surface. Washing and filtration were carried out until filtrate were clean and clear and showed no precipitation when tested using $AgNO_3$. Being cleaned from Chloride ions, Montmorillonite was dried oven at 110-120°C and marked as Na-Montmorillonite (M).

Na-Monmorillonite 100 g amount were dispersed into demineralyzed water and stirred using magnetic stirrer for 5 hours. Zirconium oxychloride 0.1 M was poured into dispersion little by little up to 250 mL volume. These would provide intercalation process of Zirconium oxychloride into Na-Montmorillonite layers. Intercalation result was washed by demineralyzed water several times to remove Chloride ions followed by dried oven at 110-

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120°C and grinded using porcelain mortar to achieve 100 mesh size. Fined Na-Montmorillonite intercalated by Zirconium oxychloride were calcined at 350°C in N_2 atmosphere for 3 hours and then oxidized using O_2 gas at same temperature and time length. The resulting product was marked as ZrO_2 pillared Montmorillonite (MZ).

MZ resulted from previous procedure was soaked in Ni and Mo solution for 24 hours followed by air dried. Drying process was continued by oven dry at 110-120°C for 3 hours and then the mixture were calcined by flowing N_2 at 350°C for 3 hours followed by oxydation at the same temperature for 2 hours. The next steps of process were reduction using H_2 at 350°C for 2 hours and resulting catalyst was marked as Ni/Mo-ZrO_2 pillared Montmorillonite (NMMZ). NMMZ is ready for next steps including characterization, activity test and used as hydrocracking catalyst of lipid recovered from waste sludge of CPO industry.

C. *Synthesis Hydrocracking of Oil Recovered from Waste Sludge of CPO Industry*

Hydrocracking reactor used in this experiment designed in fixbed system having inner diameter 2.5 cm, length 40 cm and volume 196.43 cm^3 (Hasanudin 2013). 12 g of catalyst was placed in reactor and H_2 gas was allowed to flow at 2 mL/sec rate after then hydrocracking process started at desired temperature for 15 minutes. Flowing gas was maintained in order to ensure no more air trapped in reactor.Hydrocracking of lipid recovered from waste sludge was carried out by heating it in preheater reactor at 80-90°C to form liquid phase of lipid. Liquified lipid was pumped into gas former reactor using peristaltic pump. Pump flow was arranged in desired flowing rate which then gas was formed and streamed into reactor using H_2 as carrier gas at 1.0 mL/sec.

The resulting products came out from upper part of reactor and flow into condensor or water cooling system. Light oil produced, unreacted lipid and water would liquified in the condensor and collected in an erlenmeyer. Uncondensed gas was arranged to enter gas collector whereas coke deposited on catalyst were collected and counted using gravimetry method. Acetone was used to washed reactor everytime hydrocracking process completed.

Light oil produced from the process was vacuum distilled at 200°C to obtain gasoline, kerosene and diesel distillate. Light oil remains in distillation flask can be consider as remnants of reactant which not undergo hydrocracking process. The distillates obtained were analyzed using gas chromatography to determine its composition and to measure success of hydrocracking carried out. NMMZ catalyst were used in several hydrocracking process held at different temperature i.e 400, 425, 450, 475 and 500°C and catalyst to feed ratios of 0.08; 0.10; 0.15; 0.20 and 0.25 (w/w).Result and Discussion

A. *Preparation and Characterization Result of Ni/Mo-ZrO2 Pillared Monmorillonite*

The NMMZ catalyst was made through impregnation method of Ni from $Ni(NO_3)_2.6H_2O$ as [illegible] from $(NH_4)_6Mo_7O_{24}.4H_2O$ as precursor [illegible] MZ. Initial characterization was done [illegible] EDX and the resulting image was [illegible] Comparation between SEM image of [illegible] catalyst show that NMMZ contains more [illegible] i.e. Ni and Mo metals sticked onto [illegible] sticking of Ni and Mo metals on MZ [illegible] altered surface tophology of Montmorillonite

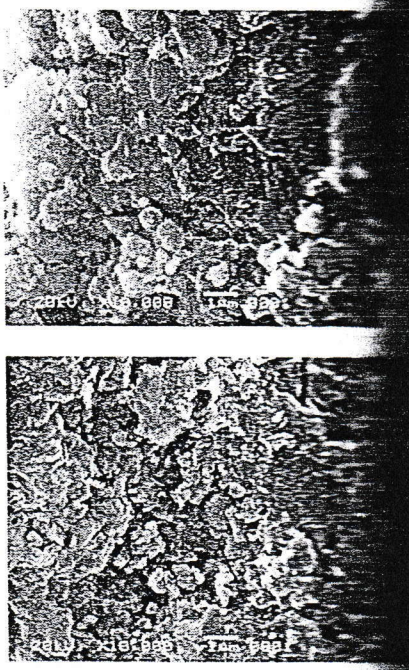


Fig. 1. SEM images of MZ and NMMZ

Metals content of NMMZ catalyst [illegible] EDX methods shows on table I. Ni [illegible] according to table are 4.98% and [illegible] Conversion into mole/g catalyst give [illegible] mole/g catalyst for Ni and 0.014 mole g [illegible]

TABLE I
METALS CONTENT OF NMMZ CATALYST

No.	Metal	Content
1	Si	[illegible]
2	Al	[illegible]
3	Fe	[illegible]
4	Ni	[illegible]
5	Zr	[illegible]
6	Mo	[illegible]

TABLE II.
SURFACE PARAMETERS OF MZ AND [illegible]

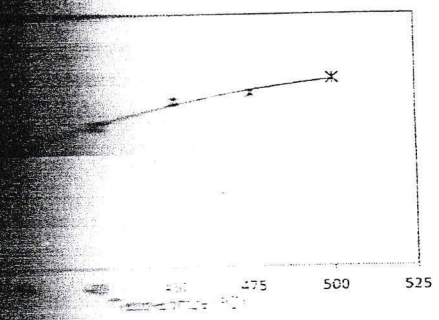
Parameters	Unit	
		MZ
Specific surface area	M2/g	121.7[illegible]
Pore volume	mL/g	0.1[illegible]
Average pore radii	Å	25.6[illegible]

Results for specific surface area [illegible] average pore radii determination were [illegible] Specific surface area of NMMZ [illegible] lower then MZ althought it still has [illegible]

of M. Decreasing specific surface
due to Ni and Mo impregnated
surface each has content 0.085
respectively. If we multiply with
to calculate number of particles
have 4.20 x 10^{20} Ni particles and
covering every 1.00 m^2 of MZ

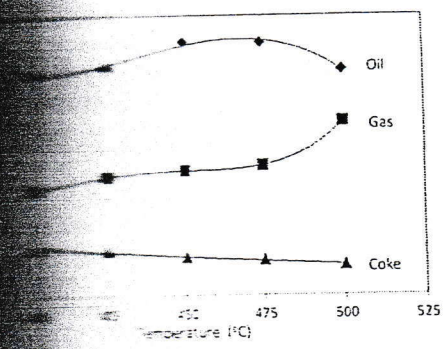
Hydrocracking Products

waste sludge of CPO industry
hours at catalyst to feed ratio
temperature were varied from 400,
500°C. Hydrocracking resulted
gas, oil (gasoline, kerosene
water and water soluble
The effect of temperature on
measured by counting conversion
of products obtained. The
on Fig. 2.



hydrocracking of lipid recovered from
of CPO industry.

lipid is about 69.00% to
range from 400 to 500°C, the
temperature increase. The increase
followed by increase of oil
obtained relatively constant up
temperature (Fig. 3). In contrast
result showed that it still increase
temperature while coke produced



temperature on product distribution.

due to at higher temperature
reaction is easy to accomplish and it
of hydrocracking process
tooccured.

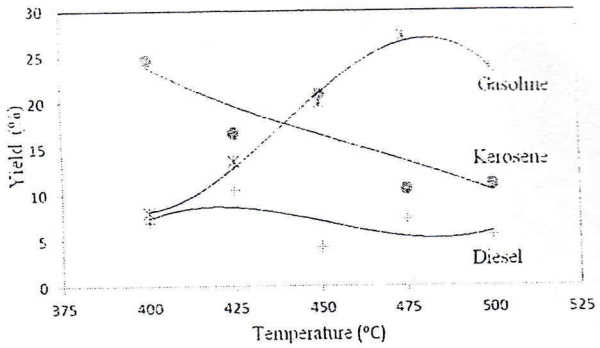


Fig. 4. Effect of hydrocracking temperature on gasoline, kerosene and diesel produced.

Gasoline formed on hydrocracking of recovered lipid tend to increase along with increase of temperature (Fig. 4). Length of Carbon chain in gasoline smaller then kerosene and diesel. The highest length of Carbon chain belong to diesel which formed in the reaction product mixtures. At temperature around 400°C gasoline produced still lower compare to kerosene and diesel, it showed as dominant product started up to 450°C. At 475°C gasoline formed showed constant value.

C. Effect of Catalyst to Feed Ratio on Hydrocracking Products

Catalyst to feed ratio measured the amount of catalyst used per gram lipid which treated by hydrocracking. The higher ratio means the more amount catalyst used. Ratios were varied by 0.08; 0.1; 0.150; 0.200 and 0.250 at 475°C and contact time for 1 hour. The conversion resulted is shown on Fig. 5.

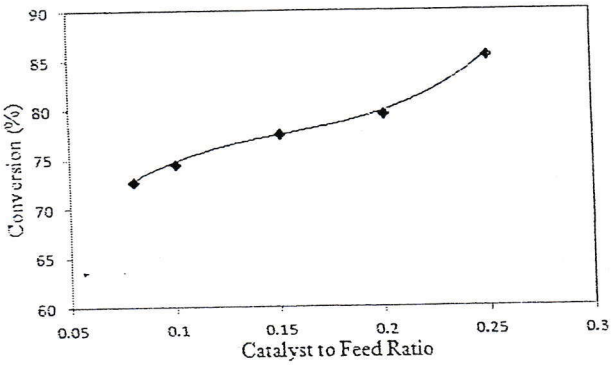


Fig. 5. Effect of catalyst to feed ratio on on conversion of recovered lipid hydrocracking.

Fig. 5 shows that conversion increase along with increase of ratio. Increase of conversion again did not followed by increase of oil product resulted. The oil product achieve relatively constant value until ratio 0.200, at ratio 0.250 oil product obtained slightly increased (Fig. 6). In contrast with gas product, increase of ratio caused increase in gas produced. These resulted because of the higher catalyst to feed ratio the higher total surface area provided for reaction to take place and it also increase reaction rate.

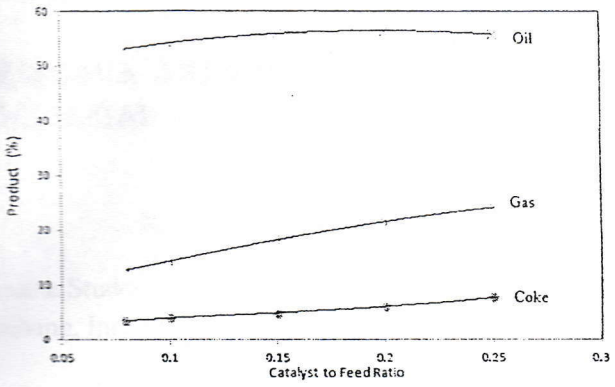


Fig. 6. Effect of catalyst to feed ratios on product distribution.

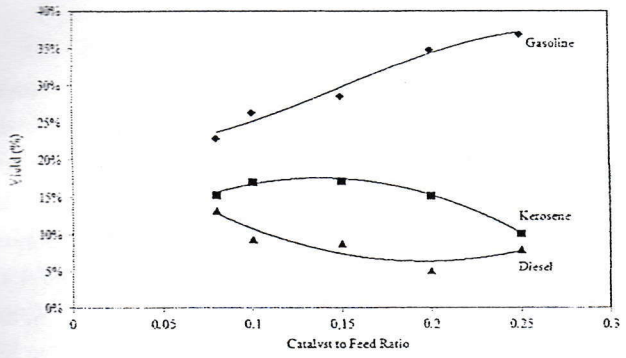


Fig. 7. Effect of catalyst to feed ratios on gasoline, kerosene and diesel produced.

Gasoline fraction of oil product resulted from hydrocracking process tend to increase as catalyst to feed ratio increase (Fig. 7) and it also shown as predominant product compare to kerosene and diesel. On the other hand, kerosene tend to decrease when catalyst to feed ratios increase. These resulted due to the highest catalyst ratios means the more total surface area available on catalayst and it caused more reactant cracked and form smaller compounds.

CONCLUSION

Catalyst prepared by impregnating Ni and Mo metals into pillared ZrO_2 Montmorillonite has ability to catalyzing hydrocracking of lipid recovered from waste sludge of CPO industry. Hydrocracking products comprise of gasoline, kerosene and diesel 36%, 15% and 5% respectively at temperature 475°C, contact time 0.1 h catalyst weight 12 g and catalyst to feed ratio 0.25.

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