

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

By hatta dahlan



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Co-Organized by

- Research and Development Institute, Thaksin University, THAILAND
- Université de Moncton, CANADA
- University of Maryland, USA
- National Research Council of Thailand (NRCT), THAILAND
- Faculty of Science, Thaksin University, THAILAND
- Research Center in Energy and Environment, Thaksin University, THAILAND

1
Message from the President of Thaksin University

On behalf of Thaksin University, it is an honor, and a pleasure, to welcome all participants to the 2013 International Conference on Alternative Energy in Developing Countries and Emerging Economies held in Bangkok, Thailand.

Climate change is a serious issue that threatens economic and social development in all countries. While the World has historically relied greatly on fossil fuels as a primary source of energy, humanity is rapidly realizing that we collectively need to find and adopt new patterns of energy production and consumption, new methods of transportation, and different types of land use and waste management to reduce the impacts of climate change.

The 2013 AEDCEE Conference will bring together leaders in the alternative energy industry, academic experts, research sectors and governments to meet, interact, exchange ideas and discuss the state of the art of advanced technology, research and development related to alternative energy sources. Solutions will also be offered in order to respond to the growing demand from developing countries who aspire to achieve environmentally sustainable economic growth.

I would like to express my deepest gratitude and sincere thanks to the Research and Development Institute and the Research Center in Energy and Environment of Thaksin University, along with our international partners, the Université de Moncton (Canada) and the University of Maryland (USA), who have contributed in one way or another to the success of the Conference. I also want to express my deepest appreciation to the sponsors of the Conference, who believe in our people and in Thaksin University.

It is by working collectively and cooperatively that we will move towards the sustainable development of our nations. I trust this Conference will help to take us closer to our goals of implementing alternative energy sources for developing countries and emerging economies.

While in Thailand, may you also take the opportunity to visit our great country and see, first-hand, why we are called the *Land of Smiles*.

Cordially,

Associate Professor Dr. Somkiat Saithanoo
President, Thaksin University

1

Message from Co-Organizer (Université de Moncton)

The 2013 AEDCEE Conference follows a most successful first edition held in 2011 in Hat Yai, Thailand. The interest in this Conference confirms a growing trend towards renewable and alternative energy in developing countries and in emerging economies.

Energy security is an important determinant in the economic development of jurisdictions and the quality of life of people. Over the past two centuries, countries from the North had the privilege to develop using abundant fossil fuel based energy, and more recently, nuclear energy. During this period, carbon emissions were not an issue, and nuclear waste was considered, and is still unfortunately considered in many jurisdictions, a problem that we leave to future generations to solve.

In the context of climate change and growing concerns regarding nuclear energy, developing countries and emerging economies do not have the same privilege. While this is a challenge, it is also an opportunity.

Indeed, as mentioned by Kandeh Yumkella, Chair of the UN-Energy, “Developing countries, many of them growing rapidly and at a large scale, have the opportunity to leapfrog conventional energy options and move directly to cleaner energy alternatives that will enhance economic and social development”. The rapid development of alternative energy options based on renewable energy sources offers developing countries and emerging economies the possibility to access indigenous energy sources for their economic and social development.

The objective of the AEDCEE Conference series is to offer opportunities to disseminate knowledge, and exchange information and best practices, for an efficient development of alternative energy for countries in the South. The strong response from the academic, industry and government communities is an encouraging sign that alternative energy and renewable energy are viable energy options for jurisdictions.

Thaksin University is emerging as a leader for alternative and renewable energy in Thailand and South East Asia. It is with honour that the Université de Moncton, Canada, is participating in the organisation of the 2013 AEDCEE Conference and on its Scientific Committee.

We wish all participants a good and productive conference, fruitful discussions and new friendships.

Yves Gagnon P.Eng., D.Sc.,
Professor and K.C. Irving Chair in Sustainable Development
Université de Moncton, Canada

1
Message from the Co-Chairs

Following a most success first edition in 2011, we are proud to organize and host the 2013 International Conference on Alternative Energy in Developing Countries and Emerging Economies (2013 AEDCEE).

We hope this event will enable participants from developing as well as developed countries to meet and exchange their knowledge and valuable experiences in dealing with alternative energy and energy efficiency technologies. We also wish the Conference will result in producing recommendations and inputs for establishing workable strategies and action plans on these issues.

The 2013 AEDCEE Conference is hosting seasoned authors who contribute scientific and technical high quality papers on the topic of the Conference. We hope the Conference will serve as a guideline for our endeavor regarding alternative energy development and deployment that will lead to a better environment for future generations, the children of our children.

Likewise, we do hope you will enjoy the Thai hospitality and food. We would like to thank the official sponsors of the Conference, the National Research Council of Thailand (NRCT), Provincial Electricity Authority (PEA), Electricity Generating Authority of Thailand (EGAT), the National Science and Technology Development Agency (NSTDA), the Research and Development Institute-Thaksin University, the Faculty of Science-Thaksin University, the Research Center in Energy and Environment-Thaksin University, the Université de Moncton (Canada), the University of Maryland (USA) and the private sector.

On behalf of Thaksin University, our partners and our sponsors, we are deeply grateful again for your participation in the 2013 AEDCEE Conference, and for presenting your great and outstanding research work.

Thank you and Sawasdee,

Asst. Prof. Dr. Pornpun Khemakunasai
Director, Research and Development Institute
Science
Thaksin University

Dr. Sarapee Chairat
Dean, Faculty of
Thaksin University

Asst. Prof. Dr. Jompob Waewsak
Director, Research Center in Energy and Environment
Thaksin University

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

Fatty acid which recovered from CPO waste sludge was treated by hydrocracking process using Ni/Mo ZrO₂ pillared Montmorillonite. Hydrocracking was conducted in fixed bed reactor and variation was made on temperature process and catalyst to feed weight ratio. Resulting oil was analyzed using gas chromatography. It appeared that increasing temperature and ratio caused increasing in fatty acid conversion through hydrocracking. The highest conversion was 90% achieved at 475°C dan 0.25 ratio. The oil produced comprised of gasoline, kerosene and diesel fraction each of 36%, 15% and 5% (w/w) respectively.

Keywords: hydrocracking, catalyst, fatty acid, biogasoline

INTRODUCTION

Industrial palm oil processing produce high amount of wastes comprise of liquid and sludge. This waste contains lipid in form of emulsion which disposed during process. The emulsion is hard to separated into its constituent through simple sedimentation in addition of long time. Oil recovery from industrial crude palm oil (CPO) waste sludge aimed not only to gain lipid but also to reduce environmental damage.

Oil recovery process from industrial CPO waste sludge should not focus on recovering lipid only, advance process can be conducted to reuse and convert it into fuel. Main components of the recovery product are fatty acids and triglyceride. According to previous researchers, vegetables oil containing this compounds can be treated catalytically using Pd/C [1], Alumina, Al-MCM-41 and HZSM-5 [2], faujasite, silica-alumina [3] and Co/Mo TiO₂-pillared Montmorillonite [4] to produce fuel consists of gasoline and diesel fraction. Catalyst role is very important in catalytic conversion of recovered vegetable oil. It will influence reaction mechanism as well as product composition resulted. Catalyst properties such as surface area, porosity and metal impregnated obviously determined its catalytic performance.

Conversion of recovered oil involves several catalyst assisted reaction i.e cracking, hydrogenation, decarboxylation, decarbonylation, aromatization etc which compete to 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, AgNO₃, Zirconium Oxychloride, Ni(NO₃)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 ZrO₂ followed by impregnating Ni and Mo metal. Na-Montmorillonite provided by P.T. Tunas Inti Makmur has composition SiO₂ 62.36%, Al₂O₃ 16.26%, Fe₂O₃ 4.83%, CaO 4.82%, Na₂O 4.53% and Lost of Ignition (LOI) 7.19%.

Montmorillonite 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 demineralized 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 AgNO₃. 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 demineralized 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 demineralized 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 N₂ atmosphere for 3 hours and then oxidized using O₂ gas at same temperature and time length. The resulting product was marked as ZrO₂ 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 N₂ at 350°C for 3 hours followed by oxydation at the same temperature for 2 hours. The next steps of process were reduction using H₂ at 350°C for 2 hours and resulting catalyst was marked as Ni/Mo-ZrO₂ 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 cm³ (Hasanudin 2013). 12 g of catalyst was placed in reactor and H₂ 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 H₂ 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 Montmorillonite

The NMMZ catalyst was made through impregnation

method of Ni from Ni(NO₃)₂·6H₂O as precursor and Mo from (NH₄)₆Mo₇O₂₄·4H₂O as precursor into host material MZ. Initial characterization was done by using SEM EDX and the resulting image was shown at picture 1. Comparison between SEM image of MZ and NMMZ catalyst show that NMMZ contains more small particles i.e. Ni and Mo metals stucked onto MZ surface. The sticking of Ni and Mo metals on MZ surface did not altered surface topology of Montmorillonite.

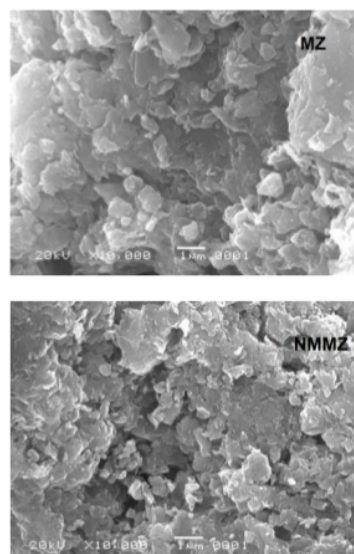


Fig. 1. SEM images of MZ and NMMZ catalysts.

Metals content of NMMZ catalyst according to SEM EDX methods shows on table I. Ni and Mo content according to table are 4.98% and 1.32% (w/w). Conversion into mole/g catalyst give result of 0.085 mole/g catalyst for Ni and 0.014 mole/g catalyst for Mo.

TABLE I
METALS CONTENT OF NMMZ CATALYST

No.	Metal	Content (%)
1	Si	27.93
2	Al	8.51
3	Fe	2.89
4	Ni	4.98
5	Zr	8.98
6	Mo	1.32

TABLE II
SURFACE PARAMETERS OF MZ AND NMMZ

Parameters	Unit	Value	
		MZ	NMMZ
Specific surface area	M ² /g	121.76	93.44
Pore volume	mL/g	0.16	0.14
Average pore radii	Å	25.60	30.24

Results for specific surface area, pore volume and average pore radii determination were showed on table II. Specific surface area of NMMZ according to table is lower then MZ although it still has higher value compare

1 to specific surface area of M. Decreasing specific surface area on NMMZ obviously due to Ni and Mo impregnated onto Montmorillonite surface each has content 0.085 mol/g and 0.014 mol/g respectively. If we multiply with Avogadro number to calculate number of particles present then we will have 4.20×10^{20} Ni particles and 6.92×10^{19} Mo particles covering every 1.00 m^2 of MZ surface.

B. Effect of Temperature on Hydrocracking Products

Lipid recovered from waste sludge of CPO industry was hydrocracked for 0.08 hours at catalyst to feed ratio 0.2 and hydrocracking temperature were varied from 400, 425, 450, 475 up to 500°C. Hydrocracking resulted several products including gas, oil (gasoline, kerosene and diesel) polar products (water and water soluble products) and coke. The effect of temperature on Hydrocracking was determined by counting conversion and yield percentage of products obtained. The calculation results were shown on Fig. 2.

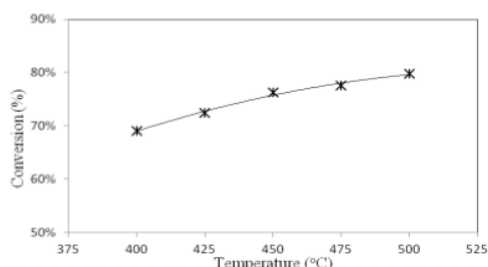


Fig. 2. Effect of temperature on hydrocracking of lipid recovered from waste sludge of CPO industry.

1 Conversion of recovered lipid is about 69.00% to 80.00% at temperature range from 400 to 500°C, the conversion increase as temperature increase. The increase of conversion is not always followed by increase of oil product. The oil product obtained relatively constant up to 450°C hydrocracking temperature (Fig. 3). In contrast with gaseous product, result showed that it still increase along with increase on temperature while coke produced was decreased.

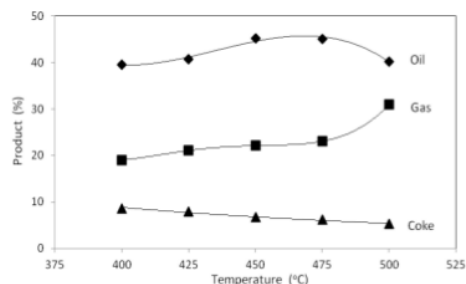


Fig. 3. Effect of hydrocracking temperature on product distribution.

1 These could happen due to at higher temperature activation energy of reaction is easy to accomplish and it caused more easy of hydrocracking process

1 too occurred.

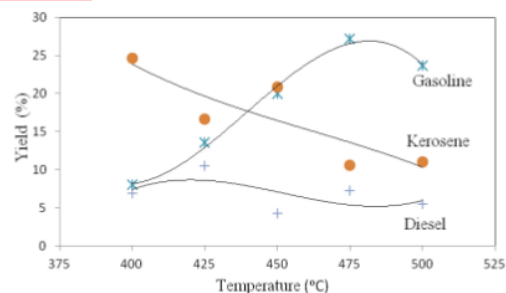


Fig. 4. Effect of hydrocracking temperature on gasoline, kerosene and diesel produced.

Gasoline formed on hydrocracking of recovered lipid tend to increase along with increase of temperature (Fig. 4). Length of Carbon chain in gasoline smaller than 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.

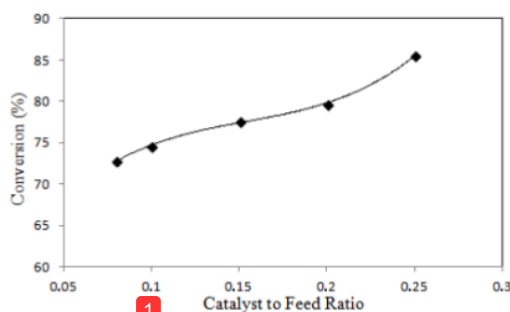


Fig. 5. Effect of catalyst to feed ratio on conversion of recovered lipid hydrocracking.

1 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.

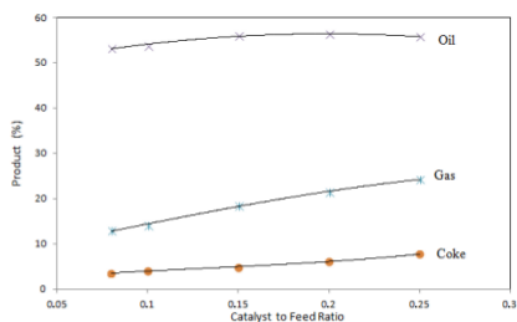


Fig. 6. Effect of catalyst to feed ratios on product distribution.

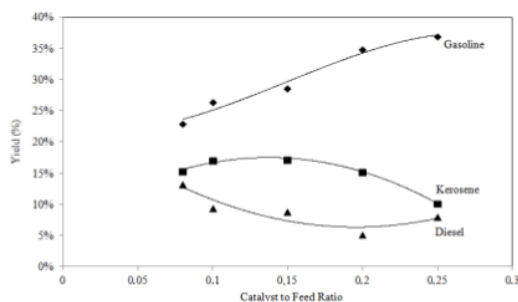


Fig. 7. Effect of catalyst to feed ratios on gasoline, kerosene and diesel produced.

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 catalyst 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.

ACKNOWLEDGMENT

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