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Production of Various Chemicals from Nyamplung Oil with Catalytic Cracking Process

by Agus Budianto

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Production of Various Chemicals from Nyamplung Oil with Catalytic Cracking Process

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Abstract

Objectives: Obtained data about chemicals that formed at nyamplung oil cracking, also studied the effect of temperature on product composition.

Methods/Statistical analysis: The method of analysis used is gas-chromatography and mass spectrometry (GCMS). The resulting product is analyzed and studied in the temperature influence of Nyamplung oil process with Zn-HZSM-5 / γ Alumina catalyst. Furthermore, the compounds obtained are grouped. The chemicals produced are grouped as biogasoline, biokerosene, biodiesel and other materials based on the amount of carbon and functional groups on the compound.

Findings: The result of the research shows that oil of Nyamplung can be cracked to produce chemicals of alkanes, alkenes, carboxylic acids, benzene and its derivatives and aldehide. The chemicals are also grouped into 3 kinds of biofuel namely biodiesel, biogasoline and biokeresene. Biokerosene composition is higher than biogasoline and biokerosene in nyamplung oil cracking product.

Application/Improvements: The highest composition of chemicals from Nyamplung oil cracking is oleic acid with a content of 41.19% wt

***Keywords*:** Catalytic, Chemical, Nyamplung oil, Oleic acid, Production

Introduction

Nyamplung plant (Calophyllum Inophyllum L) is a suitable plant to grow in Indonesia. It usually grows in coastal areas and develops naturally well. This plant produces Nyamplung fruit. Nyamplung fruit contains Nyamplung oil, an easy method used to produce nyamplung oil from nyamplung fruit is by press method. [1]. Nyamplung fruit can produce Nyamplung oil with high yield up to 73%. Nyamplung plants are known as very interesting plant. Land available in various islands and beaches in Indonesia are very suitable for the cultivation of Nyamplung plants. The development of the Nyamplung plantation plant can be planned from now and based on the calculation in 2025 Indonesia needs 254,000 hectares of Nyamplung plantation. Appropriate calculations and perfect planning can absorb the workforce available in Indonesia. It is estimated that at least need more than 254 thousand new workforce in this sector. [2].

Nyamplung oil is already used by the fishermen of Madura island as fuel for fishing boats, however the motor engine easily got heated, often lost power and quickly damaged [3]. The Nyamplung oil is also used as fuel torch and lights in the Village. Nyamplung oil used as motor engine fuel still requires trans esterification process [4] or cracking process [5].[6]. The process undertaken essentially is to reduce the viscosity of Nyamplung oil to meet the fuel specifications.. In Indonesia, biofuel is usually used simultaneously or mixed with Pertamina diesel oil.

This paper discuss the utilization of Nyamplung oil to become liquid organic fuel. The process used is cracking with the aid of zeolite type catalyst HZSM-5. The resulting product is liquid hydrocarbon. The amount of carbon in the hydrocarbon is 5 -18. This product has in common with a mixture of kerosene, diesel and gasoline available on the market. [5]. Dewajani et al conducted a study aimed at using NI-HZSM-5 catalyst. The focus of this research is to obtain a catalyst that produces maximum organic liquid product.. The rise of nickel content in the catalyst improves the selectivity of paraffins. The nickel-added HZSM-5 increases the selectivity of liquid products by up to 75%. [6]

There was research about the modification of Nyamplung oil into biodiesel or biofuel but it still need further research to get cheaper and more effective catalyst, low operation temperatures, and and the high selectivity of the desired product. Combined catalyst Zn-HZSM-5 and γ Alumina with composition (1: 1) and (1: 2) have been used for cracking Nyamplung oil. The main product desired was liquid biofuels. The results show that Zn-HZSM-5 / γ Alumina (1 : 2) produces biodiesel product with the highest selectivity of 73.86%. In the cracking process, the cracking reaction temperature conditions produce different product compositions [3]. The catalyst liquefaction effort for the cracking process of plant oil including Nyamplung has been done by several researchers. Some researchers are interested in adjusting the HZSM-5 catalyst by impregnating certain metals. As is done by Agus Budianto et al who adds metal Palladium and Platinum metal to catalyst HZSM-5. This catalyst was tested on CPO and gave improved yield of liquid product [7]. Temperature rise and change of catalyst composition are attractive for exploitation of new chemicals and better fuels.

This research was developed to obtain the effect of process temperature and change of Zn-HZSM-5 / γ Alumina catalyst composition on the formation of new chemicals from Nyamplung oil.

2. Materials and Methods

2.1 Materials and Resin Characteristics

The raw material of cracking process with catalyst is Nyamplung oil from Madura. Nyamplung oil used is not purified and is not bleached. Nyamplung oil used is natural oil and its composition has been reported by Agus budianto [3]. Catalyst used modified HZSM-5 catalyst with addition of Zn metal and addition of catalyst γ Alumina with composition (1: 3). Other materials are nitrogen gas and hydrogen gas.

2.2 Tools and Installation Management

The preparation of catalyst in this study is using methods developed by Agus Budianto [3]. The catalyst is prepared by heating it in a special heater at a temperature of 150 ºC. The prepared catalyst is placed in a reactor which also functions as an evaporator, as shown in Figure 1. The Nyamplung oil that is already available in the reactor is heated at 350 ºC. The Nyamplung oil vapor passes through catalyst and cracking process occurs. The mixture of Nyamplung oil vapor and the cracking product flow into the condenser. The condensed liquid product is accommodated and subsequently analyzed its composition using GCMS.

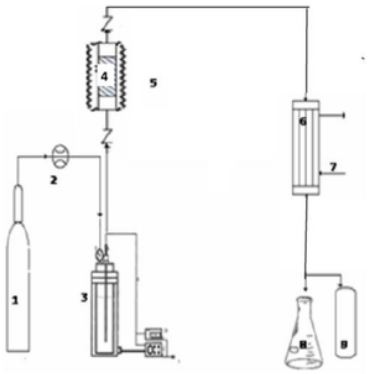

Figure 1. Equipment used to transform Nyamplung oil into various chemicals.

Explanation:
1. Nitrogen
2. Flow meter
3. Evaporator
4. Catalyst
5. Fixed bed reactor
6. Condensor
7. Cooling water

2.3 Research Procedure

The experiment began by incorporating Nyamplung oil into the available evaporator. Furthermore the catalyst was also incorporated in the fixed bed of the reactor. The evaporator was heated to 250 ºC and the reactor was heated to 300 ºC. The boiling Nyamplung oil on the evaporator will evaporate and flow into the fixed bed reactor. In the reactor, the Nyamplung vapor oil will undergo a process of cracking with the help of catalysts to form various chemical mixtures. The product out of the reactor was passed into the condenser forming a liquid and gas phase. Organic liquid products are collected in a tube and then analyzed using GCMS.

3. Result and Discussion

Physical Analysis

Physical analysis of liquid products was done by measuring the density. The result of density measurement of organic liquid product from Nyamplung oil was presented in Table 1.

Table 1. The density of organic liquid product (OLP) in the process of Nyamplung oil cracking using catalyst of Zn-HZSM5/ γ Alumina (1:3)

Cracking Temperature ºC	Density, Kg. m^{-3}
300	930
350	900

400	840
450	800

Figure 2. The organic liquid product (OLP) of Nyamplung oil cracking using a combined catalyst of Zn-HZSM5 and γ Alumina with composition (1: 3) at (a) Temperature 300 ºC ; (b) Temperature 350 ºC

The organic liquid product has density 800-900 kg.m^{-3}. Compared with the regular diesel quality standard EN 590 which requires density of biodiesel of 860-900 kg.m^{-3}, density The organic liquid product of nyamplung oil treatment by cracking process with Zn-HZSM-5 and γ Alumina combined catalyst at 350 ºC temperature has fulfilled the specification. OLP produced from nyamplung oil at other temperatures still requires an advanced process. Physical observation of the product can be seen in Figure 2. This figure shows that liquid organic products are blackish brown. Figure 2. Shows that direct physical observation cannot be distinguished between organic liquid products at temperatures of 300 and 350 C. To obtain clear biofuels still require further separation and filtration processes.

The composition of Nyamplung oil processing products

The product composition of the analysis results is shown in Table 2. Product composition (OLP) of nyamplung oil processed using cracking method with Zn-HZSM-5 and γ Alumina combined catalysts with composition (1: 3) at 300 ºC. Table 2 is a composition of Nyamplung oil cracking product. it is seen that the product contains 59 compounds consisting of alkanes, alkenes, and other substances such as organic acids, benzene and derivatives, styrene and aldehyd. This shows the use of a combined catalyst of Zn-HZSM-5 and γ Alumina (1: 3) in the Nyamplung oil treatment by cracking method at a temperature of 300 ºC has the potential to form a wide variety of liquid organic substances.

Table 2. The composition of the Nyamplung oil processing product using Zn-HZSM-5 and γ Alumina combined catalysts (1: 3) by cracking method at 300 ºC reaction temperature

Components	% wt	Components	% wt
1 Hexadecene	1.48	5 Nonadecene	0.21

3 Hexadecene	1.1	1 Methoxyphenil	0.27
2 Tridecene	0.09	2 Butenoic Acid	0.13
5 Octadecene	0.18	2 Hexenoic Acid	0.3
6 Tridecene	0.13	2 Naphtalenone	0.2
7 Hexadecene	0.29	2 Propenoic Acid	0.69
8 Heptadecene	4.5	9 Octadecenonic Acid	0.27
9 Octadecyne	0.14	Benlzaldehyde	0.24
Cyclopentadecanone	9.88	Benzene	0.13
Heptadecene	1.83	Benzene Ethyl	0.14
Pentadecane	2.15	Benzene Methyl	0.09
Tridecane	0.53	Benzene Pentyl	0.13
1 Hexadecene	1.48	Benzenemethanamine	0.11
Hexadecane	3.76	Decanoic Acid	0.87
1 Octene	0.06	Heptanoic Acid	0.27
1.3 Cyclopentadiene	0.28	Hexadecanoid Acid	0.22
1.3 Heptadiene	3.02	Hexanoid Acid	19.24
1.5 Hexadiene	0.23	Octadecanoic Acid	12.19
2 Octene	0.07	Octanoic Acid	0.25
2.6 Octadiene	0.1	Oleic Acid	17.41
6 Heptene	0.11	Oxacyclotetradecane	13.05
Nonane	0.09	Phenol	0.36
Cyclohexane	1.05	Styrene	0.41
Octane	0.05	Trans Cinnamic Acid	1.04
Tricyclo Hexane	0.24	1 Methoxyphenil	0.27
1 Undecene	0.14	1.9 Tetradecadiene	0.1
2 Dodecene	0.11	10.12 Hexadecadienal	0.1
5 Undecene	0.53	2 Pentadecanone	0.17
Nonadecane	0.14	10.12 Hexadecadienal	0.1

Cyclotetracosane	0.16

The process of Nyamplung oil cracking using Zn-HZSM-5 and γ Alumina (1: 3) combined catalysts at 350 ºC gives organic liquid product. The composition of the organic liquid product can be seen in Table 3. The table shows that the composition of liquid organic products is less and more specific than at 300 ºC. The main composition is Hexadecanoic acid with 29.08% wt content followed by tetra decane and heptadecane. This organic liquid product also contains esters and olefins. These results also have similarities with Nyamplung oil cracking using Ni / ZSM-5 with its liquid organic product. Research results of Dewajani et al showed that liquid organic products contain alkanes, alkenes, cyclic, aromatic alcohol and acid. The difference is the presence of alcohol [5]. Interestingly, the use of Zn-HZSM-5 and γ Alumina (1 : 3) combined catalysts was the formation of C14 and C17 alkanes with a combined content of nearly 33.8%. If the liquid product is still acidic, biofuel still needs to be neutralized, but if the acid product or ester is desired, it can be continued with separation or esterification process..

Table 3. The composition of the Nyamplung oil processing product using Zn-HZSM-5 and γ Alumina combined catalysts (1: 3) by cracking method at 350 ºC reaction temperature

Components	**% wt**
Tetradecane	20.3
Heptadecane	13.57
Hexadecanioc acid	29.08
9 – Octadecenoic Acid	11.64
Octadecenoic Acid	5.9
Olefin / Alkenes :	
1-Pentadecene	6.17
8- Heptadecane	4.71
Ester :	
Ethyl Oleat	

The composition of the Nyamplung oil treatment product using the cracking method with the aid of a combined catalyst of Zn-HZSM-5 and γ Alumina (1: 3) at 400ºC temperature can be seen in Table 4. The table shows that the composition of liquid organic products is alkanes, alkenes, carboxylic acids and esters. There are only 8 chemicals detected. This shows that mulsi catalysts work to direct chemical reactions toward specific

products. The resulting alkanes appear to have chains of C14 and C17, shorter than at 350°C. The main composition is Hexadecanoic acid with a content of 29.08% wt followed by oleic acid and pentadecane. This organic liquid product also contains esters and olefins.

Table 4. The composition of the Nyamplung oil processing product using Zn-HZSM-5 and γ Alumina combined catalysts (1: 3) by cracking method at 400 °C reaction temperature

Components	**% wt**
Heptadecane	7.67
Pentadecane	11.07
Hexadecanoic acid	4.20
n - Hexadecanoic acid	18.91
9 Octadecenoic Acid	7.42
Octadecanoic Acid	2.56
Oleic acid	13.7
Octanoic acid	2.56
n-Decanoic acid	8.19
1-Pentadecene	5.75
8- Heptadecane	5.62
2- Undecene	2.89
1-Cyclohexene	4.77
Ethyl Oleat	4.69

The composition of the Nyamplung oil treatment product using the cracking method with the aid of a combined catalyst of Zn-HZSM-5 and γ Alumina (1: 3) at 450 °C temperature can be seen in Table 5. The table shows that the composition of liquid organic products such as Toluene, napthalene, alkane, alkene, carboxylic acid , aldehyd and esters. This product is very interesting because it contains preservative. Alkanes appear to have shorter C chains than at 350 °C. The main composition is Oleic acid acid with 41.19% wt content followed by n-hexadecanioc acid and Octadecanoic acid. This organic liquid product also contains aldehyd and Toluene.

Table 5. The composition of the Nyamplung oil processing product using Zn-HZSM-5 and γ Alumina combined catalysts (1: 3) by cracking method at 450 °C reaction temperature

Components	% Wt
Toluene	0.09
1-Octene	0.05
Octane	0.05
2-Octene	0.06
1,3-Cyclopentadiene	0.2
Cyclohexene	1.02
1,5-Heptadiene	0.51
Ethanone	0.2
7-Cyclooctatetraene	0.36
Heptadiene	0.16
Benzaldehyde	0.13
5-Undecene	1.33
Naphthalene	0.05
Tridecane	1.09
Decanoic acid	0.13
Trans-cinnamic acid	0.13
Pentadecane	1.08
3-Hexadecene	0.36
Cyclohexadecane	0.11
Hexadecane	1.33
8-Heptadecene	1.34
Heptadecane	0.87
Cis-9-hexadecenal	0.41
1-octadecene	1.96
Pentadecanoic acid	0.26
n-hexadecanioc acid	19.77
Cyclopentadecanone	1.87

9-octadecenoic	3.36
Heptadecanoic acid	1.16
Oleic acid	41.19
Octadecanoic acid	19.41

Analysis of biofuel produced percentage against catalyst temperature

Liquid organic chemicals from the nyamplung oil cracking process which belongs to alkanes and alkenes are classified as biofuel. biofuel components are based on the number of C hydrocarbon atoms. For the C6-C11 number of atoms, including the biogasoline group, C12-C15 is classified as biokeresene, while C16-Cn is classified as biodiesel. Biofuel group data for organic liquids from nyamplung oil cracking using a combined catalyst at various temperatures can be seen in Table 6. This table shows that the number of biofuel components is strongly influenced by cracking temperatures. The results of grouping biofuel components in table 6 are shown in Figure 3.

Table 6. Percentage of the content of organic liquid product that is grouped into biodiesel, biogasoline, biokerosene and others in various temperature using Zn-HZSM-5 and γ Alumina (1:3) catalysts

Fraction	Compound	% wt			
		300 °C	350 °C	400 °C	450 °C
Biodiesel	3-Hexadecene	1.1			0.36
	7-Hexadecane	0.29			
	1- Hexadecane	2.96			
	Hexadecane	3.76			1.33
	Cyclohexadecane				0.11
	8- Heptadecane	4.5	4.71	5.62	1.34
	1-octadecene				1.96
	5- octadecene	0.18			
	9- octadecene	0.14			
	Tricyclohexene	0.24			
Biokerosene	Tridecane	0.53			1.09
	2- Tridecane	0.09			
	6- Tridecane	0.15			
	Tetradecane		20.3		
	Heptadecane	1.83	13.57	7.67	
	Pentadecane	2.15		11.07	1.08
	1-Pentadecene		6.17	5.75	
	Undecene				

	1-Undecene			2.89	
	5-Undecene	0.53			1.33
	2-Dodecene	0.11			
	Cyclohexene	1.05	4.77		1.02
	Octene	0.05			0.05
	Cyclopentadecanone				1.87
	1.3-cyclopentadiene	0.28			0.2
	1.3 Heptadien	3.02			0.57
Biogasoline	1.5 Hexadiene	0.23			
	2-Octene	0.07			0.06
	Toluene				0.07
	2.1 Octadiene	0.1			
	6-heptene	0.11			
	Nonane	0.03			
	1-octene	0.06			0.05
	Heptadien				0.16
	Cyclooctratetraene				0.36
The Total of Biofuel Components:		23.56	49.52	33.00	12.65

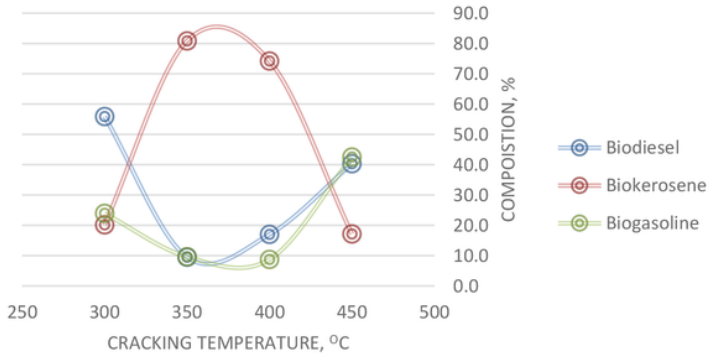

Figure 3. The composition of biogasoline, biodiesel and biokerosene in Nyamplung oil processing products using cracking method with the aid of Zn-HZSM-5 and γ Alumina (1: 3) combined catalysts at various temperatures

The composition of Nyamplung's liquid oil treatment products using the cracking method at various temperatures is analyzed and grouped. Chemicals contained in liquid products are grouped in biofuels. The grouping is divided into 3, namely bio-gasoline, bio-diesel and bio-kerosene. Based on this grouping then Nyamplung oil processing product using cracking method with the aid of catalyst can be seen in Figure 3. This figure shows that biokeresene is the component with the highest content in this composition, where the highest biokerosene content of 80.9% occurs in temperature 350 ºC. The highest biodiesel composition of 55.89% occurred at 300 ºC. The results of this study were better than biofuels using Zn-HZSM5/γ Alumina (1:2) catalyst which resulted in biodiesel concentration of only 27.2% wt [3]. The effect of temperature on the composition of biodiesel in this study has a different tendency to the composition of biodiesel from candlenut oil. The highest levels of biodiesel that can be achieved by the processing of candlenut oil with this catalyzed cracking process occurs at a temperature of 350 ºC [8].

4. Conclusion

Nyamplung oil processing product using cracking method with the aid of Zn-HZSM-5 and γ Alumina (1: 3) combined catalyst produces various chemicals of alkanes, olefins, benzene and derivatives, carboxylic acid and aldehyde. Nyamplung oil treatment using cracking method with the aid of Zn-HZSM-5 and γ Alumina (1: 3) combined catalyst to produce the product with the highest composition is oleic acid with content 41.19% wt. Grouping of chemicals based on biofuels and others shows that the composition of liquid organic products dominated by biodiesel. The highest biodiesel composition of 55,89% occurred at 300 ºC.

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