

Biogasoline from Palm Oil by Simultaneous Cracking and Hydrogenation Reaction over NiMo/zeolite Catalyst

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Abstract: The process of synthesizing biogasoline from palm oil through simultaneous catalytic cracking and hydrogenation reaction was conducted using a liquid phase batch reactor at atmospheric pressure with the presence of hydrogen gas. The reaction temperatures were 300°C and 320°C, while the reaction time were 1, 1.5 and 2 h for each temperature. A common simultaneous cracking and hydrogenation catalyst NiMo/zeolite (klinoptilolite type) was used with the catalyst/reactant weight ratio 1:75. The support of the catalyst was prepared by an ion exchange method using NH_4NO_3 aqueous solution. While the metals were impregnated using $\text{Ni}(\text{NO}_3)_2$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solutions as the metal sources, respectively. The decreasing density and boiling point of palm oil before and after reaction began have proven that a part of the triglyceride molecules in the palm oil were cracked to become smaller molecules. Further analysis using FTIR (Fourier Transform Infrared) spectra of palm oil before and after reaction had also shown that some hydrogenation reactions also took place after the palm oil cracking reaction was occurred. It's meaning that simultaneous cracking and hydrogenation reaction in this research was successfully going on. From the result of GC-MS (Gas Chromatography and Mass Spectrometry) analysis, the hydrocarbon contents of the biogasoline were known consisting mostly C8 to C15.

Key words: Biogasoline • Catalytic hydrocracking • Palm oil

INTRODUCTION

The possibilities of producing fuels from renewable resources such as biomass are recently one the major issues in global research activities [1-3]. These kinds of technologies are more environmentally-friendly and effectively contributed to sustainability development [4]. Vegetable oils have been the main subject of these researches [2], that mostly consisting triglyceride-a hydrocarbon molecule formed when a propane molecule is bonded with three fatty acids at each of the carbon atoms. This molecule has a quite similar structure with the hydrocarbons in crude oil. Furthermore, it is a very potential alternative as fossil oil substitutes in producing hydrocarbon fuels. Among the vegetable oils, palm oil is known to be one of the most potential alternatives because of its high amount of production, especially in tropical country like Indonesia and Malaysia [4].

Some researches have been done to produce liquid fuels from palm oil. Twaiq, have proved that catalytic

cracking of palm oil using HZSM-5 catalyst at 350°C could produce light products such as methane, ethane, gasoline, kerosene, diesel oil and BTX (benzene, toluene, xylene) [2]. He also proved that liquid fuels can also be produced from palm oil-based fatty acid mixture which is the waste from palm oil industry and also from used cooking oil [5, 6].

Other attempts, different researchers, using different methods and also using different catalysts have also been done to convert palm oil for producing liquid fuels efficiently [1-9]. However, an attempt to produce gasoline from palm oil through simultaneous cracking and hydrogenation reaction, which were commonly done on crude oil refinery, had not been treated.

The research was purposed to study the possibility of simultaneous cracking-hydrogenation reaction application in the process of liquid fuel production from palm oil, using simultaneous cracking-hydrogenation catalyst in a different reaction condition. The method was developed based on best practices in refined crude oil

processing where thermal cracking reaction is commonly done in gas phase reactor at high pressure condition.

In this research, thermal cracking reaction was proposed taking in liquid phase reactor with the reaction temperature below the initial boiling point of palm oil and in atmospheric pressure.

MATERIALS AND METHODS

Preparation of Catalysts: The catalyst used for this experiment was a dual function catalyst NiMo/zeolite which is common in a simultaneous cracking and hydrogenation reaction unit in refined crude oil. Zeolite, clinoptilolite type, was supported in the form of H-zeolite, is an acidic mineral that can promote cracking reaction, while nickel (Ni) and molybdenum (Mo) metals are needed to promote hydrogenation after the cracking. H-zeolite was prepared from Indonesian natural zeolite-mostly consisted of clinoptilolite type, by ion exchange method using ammonium nitrate solution (1 N) as the source of proton. After the ion exchange, the support was dried at 120°C and then calcified at 520°C for 5 h. Nickel and molybdenum granular were impregnated to the H-zeolite by adding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ aqueous solutions, to obtain nickel loading not less than 3.5% and molybdenum loading 5 times as same as the nickel loading. After each impregnation, the catalyst was dried at 90°C and after the last drying the catalyst was calcified at 300°C for 3 h.

Simultaneous Cracking and Hydrogenation of Palm Oil:

The simultaneous cracking and hydrogenation of palm oil was carried out in a liquid phase batch reactor (tubular,

10 mm OD and 50 mm height, pyrex glass made) with stirrer and heating jacket, in atmospheric pressure, with the presence of hydrogen gas. The reactor was also equipped with a reflux tunnel in order not to make it over-pressured without losing any light hydrocarbon products formed in the reaction. Reaction conditions were: reaction temperature = 300°C and 320°C; catalyst/reactant weight ratio = 1/75; reaction time = 1.0 h, 1.5 h and 2.0 h.

The density and boiling point of the reaction products were measured to evaluate the reaction. The hydrocarbon content of the biogasoline products were also analyzed using FTIR (Fourier Transform Infrared Spectrometry; ATI Matson Genesis seri 931245S) and GC-MS (Gas Chromatography and Mass Spectrometry; HP Agilent GC 5890 seri 2+, MS 5972, packing DB 5 MS, analysis condition: 40-260°C).

To obtain the biogasoline, sample of the reactor product was distilled in an atmospheric distillation column. The distillations were done twice to get light hydrocarbons in high concentration.

The whole process of this experiment is illustrated in Fig. 1.

RESULTS AND DISCUSSION

Identification of catalytic cracking reaction: To evaluate the catalytic cracking reaction of triglyceride, the density and boiling point of reactor products were measured and compared to that's physical properties of the palm oil before reaction began. At room temperature density of palm oil before reaction began was 0.966 g/ml, while of the reactor products density with different reaction conditions at the same temperature were as shown in Table 1.

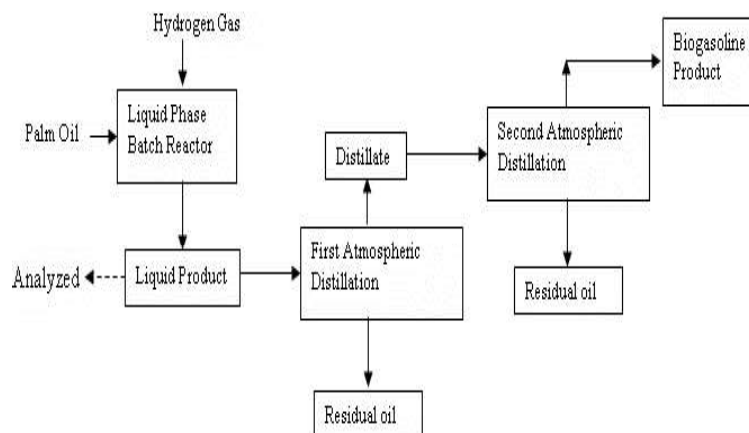


Fig. 1: Schematic illustration of the experimental step

As shown in Table 1, the density of all reactor products was smaller than palm oil density before reaction began. Therefore, it had been proven that light fraction or smaller molecule quantity in the products was increased during the reaction. In other words, the cracking of triglyceride molecules within the palm oil had really occurred.

In contrast to density decreasing phenomenon, the evaluation of cracking can also be done by comparing the boiling point and the recovery trend of reactor products with that's palm oil physical properties before the reaction. The comparison result is shown in Table 2.

Table 2 shows that the initial boiling points (IBP) of all reactor products are much lower than palm oil initial boiling point before the reaction began. This is also given another evidence that catalytic cracking products contain a good many of light hydrocarbon molecules than palm oil.

However, in the distillation process, the recovery temperature of the product especially for 10 and 20% recovery are mostly bigger than recovery temperature of palm oil. This might happen because the light fraction content in the products is not too much and the heavy molecules content such as triglyceride are still high. To get light fraction with higher purity (which was identified as biogasoline), distillate product from above first distillation is distilled once more. The IBP and recovery temperatures of this second distillation are shown in Table 3.

Identification of simultaneous cracking and hydrogenation reaction: It was shown at above explanation that the cracking of palm oil triglyceride, in this experiment, really existed. Anyway, the change in density and boiling point cannot prove that the cracking reactions were followed by hydrogenation. To evaluate possibility hydrogenation really occurred after the cracking, preliminary comparison FTIR spectra of one of the reactor products to FTIR spectra of palm oil before the reaction begin, was done. In here, product sample which was used, is [320°C; 1.5 h] product and it cause of this product tend high recovery percentage). The comparison is shown in Fig. 2.

The absorbance peak that will be evaluated here is the peak at 1375 cm^{-1} which is the peak of C—H bond in methyl ($-\text{CH}_3$) group [10]. Theoretically, if simultaneous cracking and hydrogenation reaction occurred, the amount of methyl group will increase. If only cracking reaction existed and the hydrogenation fails, the increased group will be $=\text{CH}_2$, not the $-\text{CH}_3$ group. The absorbance peak of C=O bond in the range of $1740\text{--}1745\text{ cm}^{-1}$ almostly same

Table 1: Density of reactor products

Reaction Temperature (°C)	Reaction time (h)	Density of reactor products (g/ml)	Density decrease percentage (%)
300	1.0	0.941 ± 0.0002	2.588
300	1.5	0.942 ± 0.0002	2.484
300	2.0	0.941 ± 0.0003	2.588
320	1.0	0.945 ± 0.0002	2.174
320	1.5	0.943 ± 0.0002	2.381
320	2.0	0.943 ± 0.0003	2.381

Table 2: Comparison of Initial Boiling Point (IBP) and recovery temperatures between palm oil and reactor products

Palm Oil	Reaction Temperature	Reactor products					
	(°C)	300	300	300	320	320	320
330 T _{recovery} (°C)	Reaction Time (h)	1.0	1.5	2.0	1.0	1.5	2.0
	IBP (°C)	165	200	160	170	168	163
	Recovery Percentage	T _{recovery} (°C)					
364	10%	382	375	385	376	379	365
371	20%	384	375	391	380	386	378
423	30%	390	378	396	385	395	380
430	40%	399	383	401	NA	398	388
440	50%	401	387	405	NA	399	391

Table 3: IBP and recovery temperatures for the second distillation

Reaction Temperature (°C)	Distillate of Reactor products					
	300	300	300	320	320	320
Reaction Time (h)						
IBP (°C)						
Recovery Percentage						
T_{Recovery} (°C)						
10%	277	265	265	285	288	280
20%	288	279	280	300	300	286
30%	299	288	292	305	315	296
40%	303	299	304	315	321	304
50%	NA	308	NA	321	NA	315

and it's indicated that that catalytic cracking mechanism didn't happened at that functional group [10]. Figure 2 shows that relative to the reference peak, the peak at 1375 cm^{-1} in the spectra of reactor product (b) is higher than the same peak in the spectra of palm oil (a). It probably indicated that there was an increasing amount of $-\text{CH}_3$ group during the reaction. This fact estimated that hydrogenation reaction took place after the cracking cause of existence of loaded Ni, Mo catalyst in catalyst. Product Identification and Yield Calculation: To identify the hydrocarbon content of the biogasoline, GC-MS analysis was conducted. GC-MS analysis was also used to identify the hydrocarbon content of palm oil before the reaction for comparison. The results of the analysis of the palm oil and biogasoline are shown in Table 4 and Table 5, respectively.

Table 4: Result of GC-MS analysis of the palm oil

No.	Hydrocarbon molecule (as fatty acids)	Composition (%weight)
1	C ₁₄	5.96
2	C ₁₆	63.09
3	C ₁₈	29.47
4	Others	1.48

Table 5: Result of GC-MS analysis of the biogasoline

No.	Hydrocarbon molecule	Composition (% weight)
1	C ₈	5.13
2	C ₉	37.97
3	C ₁₀	4.60
4	C ₁₃	5.06
5	C ₁₅	37.26
6	C ₁₇	7.54
7	C ₁₉	2.44

It should be noted that the hydrocarbon molecules in Table 4 are commonly not independent. They are linked to the triglyceride molecules as fatty acids, three fatty acids for each triglyceride.

The result of GC-MS analysis of biogasoline in Table 5 can also be used to calculate the yield of simultaneous cracking and hydrogenation reaction in producing gasoline-grade hydrocarbon. Yield of reaction is defined in following equation:

$$\text{Yield(Vol\%)} = \frac{Y}{P} \times 100\% \quad (1)$$

where P is the palm oil feed volume and Y is the gasoline-grade hydrocarbons volume in the reactor products.

Gasoline-grade hydrocarbons are the hydrocarbon molecules having 6 to 10 carbon atoms within their structure. Table 5 shows that the amount of these hydrocarbons in the biogasoline (the final distillate of 30 ml product sample) is approximately 47.7%. The biogasoline volume was 7.5 ml.

Thus: The volume of gasoline-grade hydrocarbons in 30 ml product sample = $0.477 \times 7.5 \text{ ml} = 3.58 \text{ ml}$. The total volume in 30 ml reactor product = 11.93 %.

Reaction Mechanism: Based on the result of GC-MS analysis on the palm oil, there are three main fatty acid molecules in the palm oil triglyceride: miristic acids (C₁₄) that have no double bond in the structure, palmitic acids (C₁₆) also with no double bond and oleic acids (C₁₈) that

have one double bond in the middle of the carbon chain. The H-zeolite in the catalyst pore was expected at least to be able to crack the double bond in the oleic acids structure of catalyst pore trapped triglyceride because double bonds are easier to be cracked compared to single bonds [11]. In this case, triglyceride molecule could be entered zeolite catalyst pore ($\pm 0.56^\circ \text{A}$, diameter [12]), cause of its longitudinal section diameter (around 5.3-7.4 $^\circ \text{A}$) and its chain length (around 30-45 $^\circ \text{A}$) was smaller than catalyst pore. One of the results of this cracking is nonene (C₉) which can be used as biogasoline. The presence of hydrogen and hydrogenation catalyst was expected to saturate the double bond in the nonene molecules that was removed from catalyst pore to form more stable molecules (nonane). Non-saturated molecules are not wanted in fuels because they tend to react with some impurities or even react to each other in a polymerization reaction forming unwanted big molecules [1].

The expected reaction mechanism above is illustrated in Fig. 3. However, the molecules found in the biogasoline were not only C₉. There were also C₈, C₁₀, C₁₃, C₁₅, C₁₇ and even C₁₉ in significant proportioned products. Therefore, in the reactor, there were also the other reaction mechanisms that were happened. One of the other possible mechanisms is the mechanism proposed by Idem, who tried to perform reaction mechanism of triglycerides in canola oil with K-zeolit catalyst at 350 $^\circ \text{C}$. Idem proposed that before light hydrocarbons (C₂-C₁₀) are formed, the triglycerides in the canola oil are cracked because of the high temperature (thermal catalytic cracking) into heavier hydrocarbon molecules (C₁₂-C₂₀). After the thermal cracking reaction was occurred, the catalytic cracking reaction takes over, changing the heavy molecules into light hydrocarbons [1].

This mechanism proposed by Idem could also happen in this experiment because the reaction temperatures were not so much different. Therefore, it can be concluded that some of the triglyceride molecules in the palm oil were thermally cracked to be C₁₃ to C₁₉. Parts of these molecules were cracked again into smaller molecules and some parts of them were indicated un-cracked. These un-cracked molecules were also vaporized in the distillation process and also composed the biogasoline. This was possible considering the high recovery temperature in the distillation processes which were higher than the recovery temperature of a common gasoline.

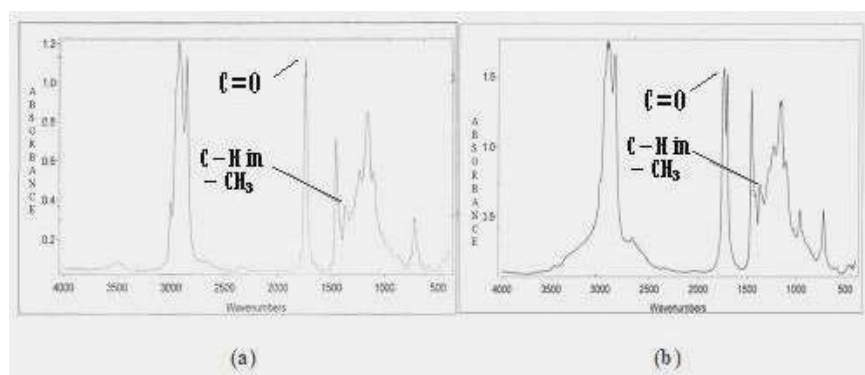


Fig. 2: FTIR spectra of palm oil: (a) before reaction, (b) after reaction (320°C, 1.5 h)

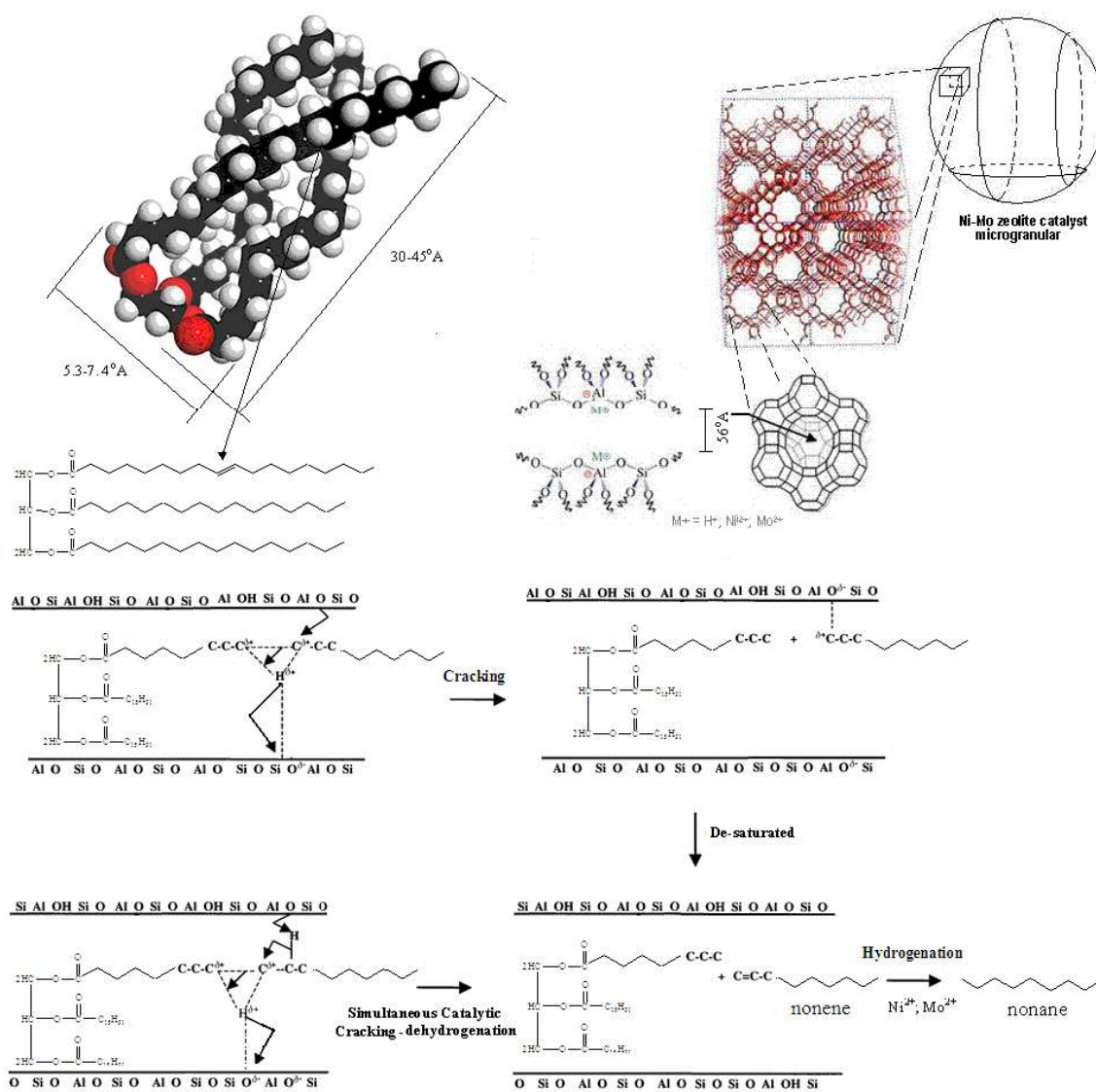


Fig. 3: Expected mechanism of the simultaneous catalytic cracking and hydrogenation reaction

CONCLUSIONS

Using NiMo/zeolite catalyst, this process could be successfully used in a synthesizing gasoline-grade hydrocarbons (biogasoline) through simultaneous cracking-hydrogenation reaction even in atmospheric pressure. The biogasoline produced contains C₈ to C₁₀, which was also composed the gasoline from crude oil, with the yield of 11.93%. However the biogasoline still contains large proportion of heavy hydrocarbons (C₁₃, C₁₅, C₁₇ and C₁₉) that are different from hydrocarbon content of crude oil's gasoline. To minimize these heavy hydrocarbons, an additional distillation can be modified to produce more high content biogasoline, but the amount of energy needed will be greater.

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