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THE USE OF PALM OIL AS HYDROCARBON FUEL WITH SAPONIFICATION PRETREATMENT THROUGH CATALYTIC CRACKING WITH Fe/Cr CATALYST

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ABSTRACT

The catalytic cracking of palm oil to become hydrocarbon fuel with saponification pretreatment has been done by using Fe/Cr catalyst. Palm oil or triglyceride is very difficult to cut off with metal catalyst so that to do it should use chemical catalyst through saponification pretreatment to form triglyceride acetate salt which will be analyzed its DSC to find out its degradation temperature. Catalytic cracking was made in the acetate salt by using Fe/Cr catalysts in stainless steel receptacle of 304 austenitic types with the most dominant Fe/Cr component. The process of the catalyticcrackingreactionoccurredatthetemperatureof250- 360ºC which produced hydrocarbon fuel. The produced hydrocarbon fuel was analyzed by using FTIR which indicated that there was a functional group that stated that distillate produced from catalytic cracking contained hydrocarbon fuel–strong absorption in the wavelength of 2923cm^{-1} which indicated the existence of alkenes functional group and absorption peak in the area of 992 cm^{-1}and 906cm^{-1}which showed the existence ofC-H group as alkenes. GC-MS analysis was done to identify the compounds found in hydrocarbon fuel obtained from distillate in catalytic cracking. The hydrocarbon fuel contains11.71% of compound1-dodecene ($C_{12}H_{24}$). The heat of combustion value and Cetane Index of hydrocarbon fuel were 10,896.28 cal/gand 50.9 respectively.

Keywords: Catalytic Cracking, Catalyst Fe/Cr, Hydrocarbon Fuel, Palm Oil, Saponification.
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INTRODUCTION

Indonesian oil palm plantations have been developed in 22 provinces of the 34 provinces in Indonesia. Two main islands which are the center of oil palm plantations are Sumatera and Kalimantan. In 2015, the area of Indonesian oil palm plantations is in the neighborhood of 11.3 million hectares[1].In the process of its development, the Indonesian oil palm has undergone numerous problems. The biggest obstacle faced by the Indonesian government is the black campaign about Indonesian palm oil in the European countries. Consequently, the Indonesian crude palm oil (CPO) gets difficulties to be marketed in the European Union countries. This is because of a rumor which says that palm oil can cause plenty of carbon emission. In the case of palm oil, European Union countries link it with environmental problems[2]. In its development, European Union has agreed on EU Emission Trading System (EU-ETS), a policy which is agreed by all European Union members to support the products produced by the countries which have low carbon industrial sectors. The total emission of a country is limited so that it will cause allowance (the surplus of unused emission).

According to EU-ETS, the product of palm oil from Indonesia and Malaysia does not meet the standard. The combination of Indonesian-Malaysian palm oil is considered to produce carbon above the normal threshold of 0.86 metric ton or 860 kilograms of carbondioxide produced from oil palm plantations each day[3].Palm oil can become an alternative fuel equivalent to gasoline because it has a hydrocarbon structure that resembles crude oil. Most hydrocarbon contained in palm oil is in the form of triglyceride which is glycerol esters that consist of three triglyceride acetous contents and one glycerol content.

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Palm oil cracking to hydrocarbon has been done many times although it is on the laboratory scale. In Malaysia, the research conducted by Twaiq[4] tested the performance of zeolite catalyst in catalytic cracking of palm oil to become hydrocarbon. Cracking was used to explain the incidence of the reduction of hydrocarbon compounds to be shorter by cutting off the bond of the carbon in that compound. Cracking can occur through the mechanism of the establishment of ion carbonium as free radical in a relatively high temperature; however, cracking reaction can be accelerated by the acid power which is indicated by the capacity of proton transfer[5].

In Indonesia, the same type of research was done by Tambun[6]which revealed that the mixture of palm oil and ABE (Acetone, Butanol, Ethanol) could be cracked catalytically to become a gasoline hydrocarbon product with Alumina/ZSM-5 catalyst. Saipulloh[7] proved that trans-etherification and the addition of methanol in palm oil can yield gasoline with catalytic cracking by using B_2O_3/Al_2O_3catalysts. Yussuf[8] produced hydrocarbon of gasoline fraction from palm oil with saponification pretreatment through catalytic cracking with B_2O_3/Al_2O_3catalysts. With the existence of the chemical base, cracking can be done without the incidence of polymerization and polycondensation reactions. It most possibly occurs due to the existence of the active cluster. Therefore, it is expected that it can supplement the yield and the conversion of triglyceride cracking reaction to fuel.

The research was about the process of palm oil cracking to become hydrocarbon with saponification pretreatment, using a chemical base that has not been much informed. Therefore, the writers were very interested in researching the use of palm oil for hydrocarbon fuel with saponification pretreatment, using NaOH chemical base, through catalytic cracking with Fe/Cr catalyst. The chemical base, NaOH, has chemical properties which can absorb CO_2, and since it highly relies on methanol and ABE compounds used in previous researches, the use of these compounds is considered economical so that they have to be changed to other compounds. One of the promising alternatives is by using the chemical base compound.

The chemical base compound used in this supplement is functioned to neutralize or stabilize active molecules or functional groups in triglyceride. It was also expected that this research could increase the value-added of palm oil. In this research, NaOH was added to 100g of palm oil and left in 24 hours until it was hardened and produced soap. The hardened soap was cracked catalytically at the temperature of 250º-360ºC by using Fe/Cr catalyst.

EXPERIMENTAL

Instrumentations

DSC instruments by Mettler Toledo, FT-IR model Shimadzu IR Prestige-21, Cetane Index analysis by CID 510, and GC-MS instruments model Pegasus BT GC-TOF Mass Spectrometer, Bomb Calorimeter model 1341 Parr.

Methods

One hundred grams of Crude Palm Oil is added with 30 g technical NaOH then heating at 90ºC on a hot plate and stirring using a magnetic stirrer until it mixes homogeneously. Then allowed to stand for 24 hours until it hardens and produces soap, DSC analysis is done on the soap that has been formed. Then the mixture that has been obtained is put into a stainless steel container which is the source of the Fe/Cr catalyst assembled into a distillation apparatus. Then heated at high temperatures ranging from 250-360ºC. Left the cracking process occurs, marked by the end of the distillate droplets. The resulting distillate was characterized by FT-IR, Bombcalorimeter, cetane number and GC-MS.

RESULTS AND DISCUSSION

The saponification reaction between palm oil and NaOH is as follows:

NaOH base serves to stabilize the reactive groups contained in triglycerides and prevent the polymerization and polycondensation reactions that are triggered by the state of the reactive group. The reactive groups found in palm oil are esters, hydroxyl groups and unsaturated carbon bonds.

Thermal Analysis with DSC

Thermal analysis of the soap resulting from saponification reaction with DSC can be seen in Fig.-1.

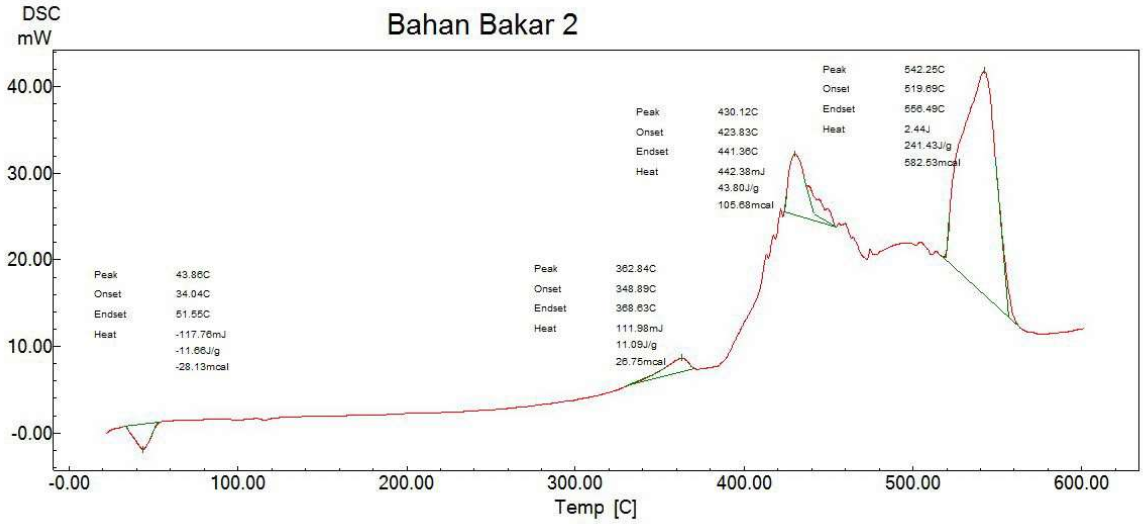
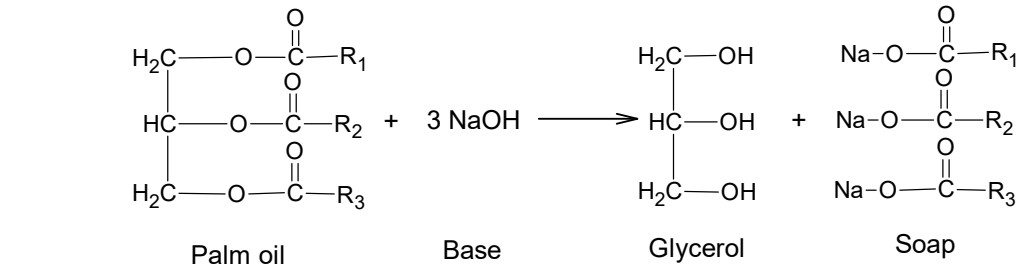


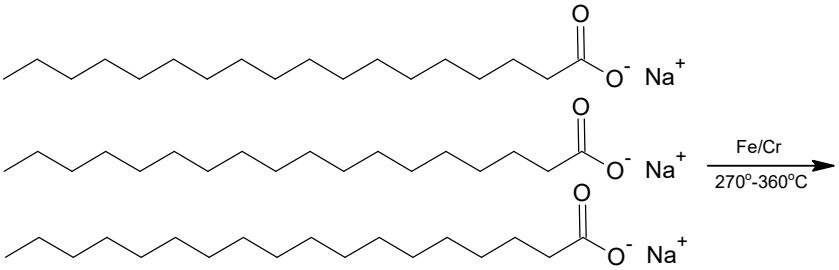
Fig.-1: The Results of the Thermal Analysis with DSC on Soap resulting from Saponification Reaction

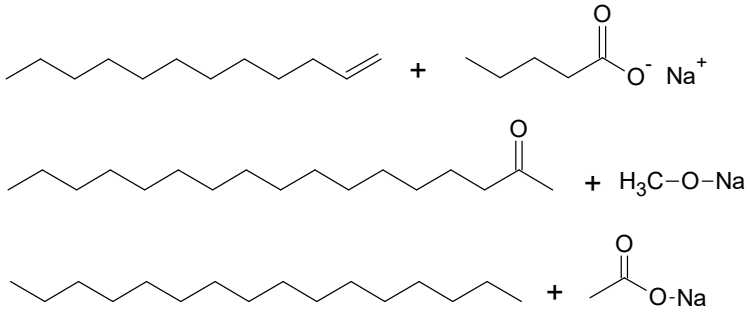
From Fig.-1, we can see peaks showing glass transition at 51.5ºC, crystallization peaks at 368.63ºC, melting peaks at 441.36ºC, and decomposition peaks at 556.49ºC. From the data obtained as a result of DSC analysis, it was found that the decomposition temperature of the pretreatment soap is at a temperature of 556.49 ºC, but because this study using the catalytic cracking process, which in the process uses a catalyst that serves to reduce the activation energy, so the temperature which is used in the catalytic cracking reaction process in this study is 250-360ºC. It also considers the boiling point of biodiesel which has nearly the same properties as diesel and other diesel oils which is 270-350ºC. The solar fraction has a boiling point of 250-400ºC with C atom ≥ 12 and functions as the life of a diesel engine[9].

Catalytic Cracking Process using Fe / Cr Catalysts

The catalytic cracking reaction of the soap resulting from the saponification reaction using the Fe / Cr catalyst is as follows:







Scheme-1

Based on the above reaction, the catalytic cracking process using Fe / Cr catalyst, occurs in the presence of heating at a temperature of 250-360ºC then the free electrons contained in Fe / Cr will be released (Fe / Cr acts as a lewis base ie donating or releasing free electron pairs) and will fill in the empty orbitals contained in the carbon atom, until the empty orbitals are full and become saturated and cracking happens Characteristics of Hydrocarbon Fuels Results of Catalytic Cracking Process.

FT-IR Analysis

The picture above is the FT-IR spectrum product that results from the experiment. In the spectra shown the absorption peak at region number 2923.94 cm^{-1} indicates the C-H group in alkanes, the absorption peak at area number 1718.18 cm^{-1} indicates the absorption of weak group C=O on ketones, peak absorption at area number 1456.28 cm^{-1} indicates the sharp absorption of C-H groups in the alkyl, the absorption peaks in the region of 992.19 cm^{-1} and 906.03 cm^{-1} indicate the presence of C-H groups[10]. Each absorption peak shows the functional groups found in the sample, namely hydrocarbon compounds.

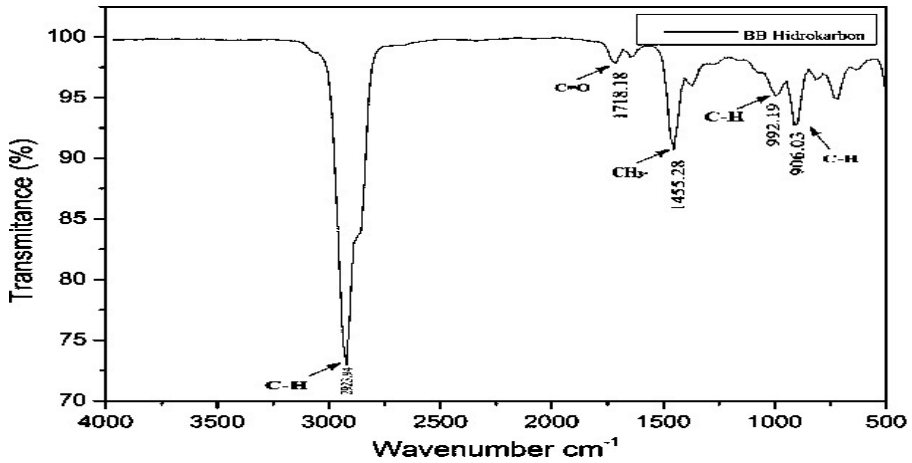


Fig.-2: FT-IR Spectrum of Hydrocarbon Fuels as a Result of the Catalytic Cracking Process using Fe / Cr Catalyst

BombCalorimeter Analysis

This Bombcalorimetry Analysis is carried out to test the heating value whose purpose is to find out the number stating the amount of heat/calories produced from the combustion process of a certain amount of fuel with air/oxygen.

Table-1: Bomb Calorimeter Analysis Results Data

Sample	Type of Analysis	Unit	Heating Value
Hydrocarbon fuel	Heating Value	Cal/g	10,896

Calorie value of fuel oil ranges from 10,160–11,000 cal / g. The heating value of biodiesel is influenced by the high oxygen content of biodiesel fuels[11]. The test results obtained by the heating value of combustion for biodiesel are 10,896 cal / g. From the test data obtained that the biodiesel obtained meets the specified standards.

GCMS Analysis

The chromatogram in the picture above shows that there are 69 compounds contained in hydrocarbon fuel obtained from catalytic cracking of CPO, with different retention times and areas. The results of GC-MS analysis of catalytic cracking hydrocarbons using catalyst Fe / Cr showed that in the hydrocarbon fuel distillate there were four compounds with the highest peak, which can be seen in the Table-2.

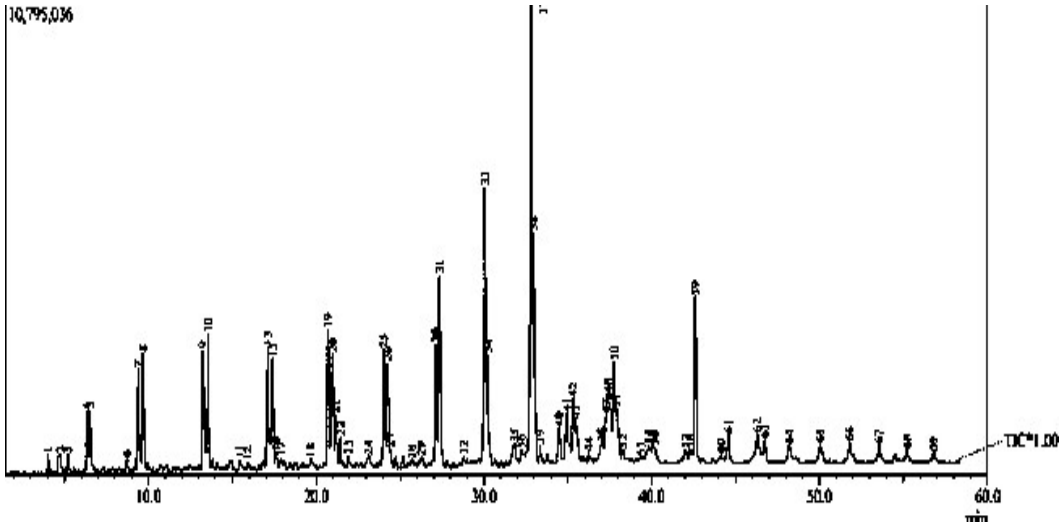


Fig.-3: Chromatogram GC-MS Hydrocarbon Fuels

Table-2: The Chromatogram of Compounds with the Highest Peak

Highest Peak	Peak	Name of Compound	Molecule Formula	Retention Time (minutes)	Area (%)
1	37	1-dodecene	$C_{12}H_{24}$	32.823	11.71
2	33	1-undecene	$C_{11}H_{22}$	30.059	6.29
3	38	n-hexadecane	$C_{16}H_{34}$	32.975	4.29
4	31	dodecane	$C_{12}H_{26}$	27.385	4.19

Cetane Index Analysis

The cetane number of a fuel is influenced by the elements contained in the fuel, such as the carbon element which is a source of combustion energy. The standard sedan index that must be possessed by diesel or biodiesel fractions is at least 51.

Table-3: Data of Cetane Index

Parameter	Results	Method
Cetane Index	50.9	ASTM D4737-10 (2016)

The Calculated Cetane Index analysis data above shows that the hydrocarbon fuel product produced in this study has a cetane index of 50.9. These results state that the cetane index of the product of this study is close to the Indonesian National Standards.

CONCLUSION

The result of saponification pretreatment of crude palm oil (CPO) by using NaOH base produced soap (triglyceride acetous salt) for which catalytic cracking was done by using Fe/Cr catalyst toward the soap as the result pretreatment.

Fe/Cr catalyst is the heterogeneous catalyst that is used to accelerate the incidence of cracking reaction in the temperature of 250ºC-360ºC by decreasing activation energy. In the result of catalytic cracking, using FE/Cr catalyst toward the soap as the result of pretreatment in the form of liquefied distillate which had been analyzed qualitatively by using FT-IR, there was a functional cluster which indicated that distillate as the result of catalytic cracking contained hydrocarbon fuel: strong absorption in the wavelength of

2923.94cm-1 which indicated the existence of alkenes functional cluster. Meanwhile, the absorption peak in the wavelength of 1456.28 cm-1 indicated that there was incisive absorption of C-H cluster in the Alkyl. The analysis on GC-MS was done to identify compounds that were found in hydrocarbon fuel obtained from distillate as the result of catalytic cracking. The result showed that hydrocarbon fuel contained 11.71% compound 1-Dodekena ($C_{12}H_{24}$).

The characteristics of hydrocarbon fuel which had been analyzed showed that the heat value of combustion was 10,896.28 cal/gr which was determined by using bomb-calorimeter, and Cetana Index was 50.9, determined by using Calculated Cetana Index Analysis. Both types of hydrocarbon fuel had met physical requirements which have to be possessed by biodiesel fuel.

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