Conversion of Palm Oil (CPO) into Fuel Biogasoline through Thermal Cracking Using a Catalyst Based Na-Bentonite and Limestone of Soil Limestone NTT

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ARTICLE INFORMATION

ABSTRACT

Cracking catalytic palm oil (CPO) into hydrocarbon fuel by saponification pretreatment has been carried out with bentonite and limestone-based catalysts. The catalysts used were Na-bentonite and Limestone NTT which were first analyzed using XRF, XRD, and SEM. Saponification pretreatment was carried out on CPO to facilitate the cracking process using a catalyst. The saponification product in the form of a mixture of soap and glycerol was then analyzed by DSC to determine the degradation temperature. Catalytic cracking is carried out in two stages, namely, the first stage hydrocracking at a temperature of 250-350°C using a stainless steel reactor is the source of catalyst Fe / Cr. The resulting distillate was then cracked again using a Na-bentonite catalyst and a TKNTT catalyst. The resulting fuel is a hydrocarbon fuel which is confirmed from the FT-IR results which indicate the presence of long-chain hydrocarbon compounds. This data is also supported by the results of the GC-MS analysis which shows that the fuel fraction produced is mostly biogasoline. Where cracking using a Na-bentonite catalyst produces a biogasoline fraction of 61.36% and a biodiesel fraction of 38.63%, THAT produces a biogasoline fraction of 88.88% and a biodiesel fraction of 11.11%. The characteristics of the hydrocarbon fuels that have been analyzed show that the calorific value of combustion is 6101 cal/g which is determined using a bomb calorimeter, and the cetane index is 62 which is analyzed using CCI. Both types of hydrocarbon fuels have met the physical requirements that must be possessed by biogasoline fuel based on SNI standards.

1. Introduction

Fossil fuels have been used as the main energy source for many years but their use is unsustainable and causes environmental problems associated with burning fossil fuels. Fossil fuels are natural resources that cannot be renewed so that their availability is increasingly limited, while the demand for energy needs for various industrial activities and meeting the needs of human life is increasing day by day (Radionova et al., 2016). In addition, the use of fossil fuels is not environmentally friendly and harmful to health because the burning of fossil fuels produces hazardous compounds such as NOx, SOx, Pb, CO, and other particulate compounds (Donatus 2015). Due to the high demand for fossil fuels, alternative fuels are needed that can replace fossil fuels. Biofuels have been studied to have great potential as a substitute for fossil fuels. Biofuels consist of biofuels gas and biofuels liquid and are usually produced from renewable natural resources. Biofuel Gas Consists of methane and hydrogen and biofuel liquid consists of biogasoline and biodiesel (Ahmad et al., 2016). In addition, biofuel is an environmentally friendly fuel because it does not contain nitrogen and sulfur compounds (Junifa, S. 2020).

Crude Palm Oil (CPO) is one of the potential alternative energy sources to replace fossil fuels, this is because palm oil has a long carbon chain similar to the hydrocarbon chains in fossils. Therefore, Crude Palm Oil can be processed to produce alternative fuels (biofuels) such as biodiesel and biogasoline which are possible to replace fossil fuels (Nurjanah et al., 2013). In 2011, Oil World still
placed Indonesia as the main producer of CPO with a production volume of 23.9 million tons of CPO/year. This shows that Indonesia has enormous potential to produce biogasoline or other fuel oils derived from palm oil (Jamtiko, Qodri., 2021).

The process of making biofuel from palm oil has been carried out by various methods such as esterification, transesterification, and cracking. Cracking is the process of breaking a high molecular weight hydrocarbon compound into a lower molecular weight compound by breaking the carbon chain bonds (C–C). The cracking reaction is divided into 2, namely: thermal cracking and catalytic cracking. Thermal cracking or pyrolysis is a reaction to break the bonds of hydrocarbon compounds due to the influence of thermal (high temperature). The mechanism of the thermal cracking reaction is through the formation of free radicals in forming the final product. The catalytic cracking reaction is the reaction of cracking (cracking) using a catalyst material (heterogeneous catalysts) as the material is capable of accelerating the reaction rate to achieve equilibrium and produce a final product through the reaction of the carbonium ion formation mechanism. (S, Donatus. 2015). Catalytic cracking has advantages over the methods used to process triglycerides. Among them, the products of catalytic cracking are gas, organic liquid products, water, and soda. Organic liquid products include (Aldehydes, ketones, carboxylic acids, and hydrocarbons such as paraffin, olefins, and naphthenic) whose boiling points correspond to gasoline, kerosene, and diesel. Both reaction temperatures are lower than those of pyrolysis, and large molecules are broken down into simpler molecules through dehydration, dehydrogenation, deoxygenation, and decarboxylation (Jovás et al., 2015).

(Anando et al., 2016) have investigated the production of biogasoline from palm oil through a catalytic cracking reaction with a gamma-alumina catalyst and obtained the peak results of the compounds analyzed by GC-MS similar to the peaks of commercial gasoline and obtained straight-chain hydrocarbon compounds at C6–C11. Mancio et al., (2016) have done a catalytic thermal cracking of the crude palm oil at a pilot scale using a catalyst Na2CO3. This study produced a conversion of 60% and produced biofuel with an acid value of most rendah. Senyawa-hydrocarbons The resulting product has characteristics similar to petroleum diesel.

The latest research was also carried out by Friskila, S (2020) namely the use of palm oil into hydrocarbon fuels with Saponification Pretreatment through the cracking of CPO with Fe/Cr catalyst. In this study, a chromatogram with the largest area was produced for the compound 1-Dodecane (C12H26) which was equivalent to the fraction biodiesel.

Jonathan, H (2021) also conducted a similar study, in which Crude Palm Oil was cracked using Na-Bentonite and Fe2O3 as catalysts. From this research, the result is that there is a dominant compound which is a straight-chain hydrocarbon compound, namely 1-pentadecane (C15H30).

The effect of pore size on catalytic cracking has been studied. (Sadamrelli, M, S. 2016) has investigated the effect of catalyst pore size on n-octane catalytic cracking activity using ZSM-5, HZMS-5, and Hβ catalysts with small, medium, and large pore sizes. The selectivity of olefins increases with a decrease in the pore size of the catalyst. Another study also examined the effect of aluminum (Al) in the catalyst and concluded that a lower amount of aluminum (Al) in the catalyst resulted in higher olefin production, this was due to the slightly lower amount of aluminum (Al) in the acid site in the catalyst. the catalyst which results in higher selectivity for olefins. In this study, researchers will crack CPO by comparing the use of two catalysts, namely Na-bentonite and Al2O3 from limestone soil of NTT. Researchers want to compare the amount of conversion of CPO into biogasoline and biodiesel fractions produced on each catalyst.

The purpose of this study was to determine the characteristics of the fuel produced using Na-bentonite and TKN TT catalysts.

Over the centuries, fossil fuels have been used in many aspects of life, but these fuels are non-renewable and will eventually run out. The scarcity of fuel now makes people have to look for alternative energy sources that are easily renewable (renewable fuels), one of which is biofuel. In recent years, many developments have been carried out on raw materials for making biofuels from plants, especially oil palm, this is because this fuel is non-toxic and does not contain nitrogen and sulfur compounds. Palm stearin is a derivative product of palm oil which is solid at room temperature and can be used as a raw material for the production of biofuel (Chuckling and Ratnawali, 2014).

Alternative fuels (biofuels) can be produced from various varieties of renewable natural resources. Among them, triglycerides have a very important role and are compounds that are commonly found in vegetable and animal oils (Doronin et al, 2012). Several techniques have been studied to convert vegetable oils and animal fats into biofuels. One of the most promising techniques for producing alternative fuels from vegetable and animal oils is pyrolysis. Pyrolysis is also known as thermal cracking and catalytic cracking. (Xu et al, 2013).

2. Research methods
Preliminary analysis was carried out on the CPO samples to determine the value of free fatty acids. Then put 100 g of CPO sample into a glass beaker and then heated at a temperature of 90°C then added 30 g of NaOH and then heated while stirring with a
magnetic stirrer until the soap was formed. The soap was allowed to stand for 24 hours and then put into a stainless steel reactor and then heated on a gas stove at a temperature of 250°C-360°C for 2 hours while connected to a distillation device. The resulting distillate is accommodated. Each 100 mL of the resulting distillate was added with 5 g of Na Bentonite and 5 g of NTT lime soil. Cracked by heating on a gas stove at a temperature of 250-350°C for 2 hours while connected to a distillation apparatus. The resulting distillate is accommodated. The resulting distillate was analyzed using GC-MS, FT-IR, and Calculated Cetane Index (CCI).

This research was conducted from March to May 2021 at the Laboratory of Inorganic Chemistry, FMIPA USU, Medan. Analysis of FT-IR and GC-MS performed in the laboratory of Organic Chemistry UGM. Analisa Calorimeter conducted at the Laboratory of Chemical Physics Research and Technology UGM. The DSC analysis was carried out in the laboratory Electron Microscope PTKI, Medan. The analysis was Calculated Cetane Index carried out in the PT. SUKOFINDO, Bekasi. XRD and SEM EDX analyses were carried out at the Physics Laboratory of the State University of Medan.

2.1 Tools and Materials

2.1.1 Tools
Stainless Steel-Reaktor 13 cm
-HotplateStirrer
-Statif and Klem
-Kondensor
-Spatula
-Batang Mixer Glass
-Termometer 3600C Alla
-Neraca Analytical 220 g Radwag
-Gelas Measure 30 mL Pyrex
-glass Beaker to 500 mL Pyrex
-Corong Pisah 1000 mL Duran
-gas Stove Rinnai
-Aluminum Foil -Perekat
gas -Tabung 3 kg LPG
-Spectrometer-IR Bruker
-Calculated Cetane Index ASTM D4737-10-2016
- gas chromatography mass spectroscopy Shimadzu

2.1.2 Materials
-crude palm oil (crude Palm Oil)
- Bentonite -
-Limestone from NTT
- Technical
-NaOH - NaOH 0.1 N -
-Isopropyl alcohol (pro analysis)
-Pheoftalen indicator -
-Silicon Grease -
-Aquadest -
-NaOH 30%

2.2 Free Fatty Acid Analysis of CPO
Weighed 5 g of CPO sample in an Erlenmeyer flask. Added 50 mL of isopropyl alcohol then added 3 drops of PP indicator. Titrate with 0.1 N NaOH solution. Record the volume of NaOH used. Experiments were 3 times.

2.3 carried out the preparation of Limestone Soil Samples in NTT (TKNTT). TKNTT
samples were dried at a temperature of 100°C using an oven and then crushed using a pestle and mortar, filtered, and then characterized using SEM, XRD, and XRF.

2.4 Preparation of Na-Bentonite
Put 50 g Bentonite into Erlenmeyer then add 200 mL 30% NaOH allowed to stand 6 hours then filtered using filter paper, and then heated in an oven at 105°C and then pulverized with a mortar and pestle, then filtered and then characterized using SEM, XRD, and SEM.

2.5 CPO cracking with NaOH pretreatment
weighed 100 g CPO, inserted into a glass beaker, added 30 g NaOH in technique then heated at a temperature of 90°C above the hotplate while stirring with a magnetic stirrer. After the soap is formed, then let stand for 24 hours. The resulting soap was analyzed using DSC and Bomb Calorimeter. The resulting soap is put into a stainless steel reactor and connected to reactor stainless steel with a condenser. Heated on a gas stove while measuring the temperature using a thermometer. The resulting distillate was accommodated in an Erlenmeyer flask until the last drop of the distillate was collected.

2.6 Cracking of CPO with Na-Bentonite
Measured 100 mL of CPO distillate then put into a reactor stainless steel and then added 5 g of Na-bentonite. It is connected to reactor stainless steel with a set of distillation equipment and then heated on a gas stove while the temperature is measured using a thermometer. The resulting distillate was collected using an Erlenmeyer flask until the last drop of distillate was collected. The resulting distillate was characterized using GC-MS, FT-IR, and CCI (calculated cetane index).

2.7 CPO cracking with TKNTT
Measured 100 mL of CPO distillate then put into a reactor stainless steel and then added 5 g of TKNTT. The reactor is connected stainless steel to a set of distillers and then heated on a gas stove while the temperature is measured using a thermometer. The resulting distillate was collected using an Erlenmeyer flask until the last drop of distillate was collected. The resulting distillate was characterized using GC-MS, FT-IR.

2.8 Free Fatty Acid Analysis of CPO

5 g CPO

\[\text{dimasukkan ke dalam labu erlenmeyer} \]
\[\text{ditambahkan 50 mL isopropil alkohol} \]
\[\text{ditambahkan 3 tetes indikator PP} \]
\[\text{dititrasi dengan larutan standar NaOH 0,1 N} \]
\[\text{dicatat volume NaOH yang terpakai} \]

Hasil
2.9 TKNTT Sample

- Tanah Kapur NTT
  - dikeringkan pada suhu 50°C
  - dihaluskan menggunakan alu dan lumpang
  - disaring

Hasil

- dikarakterisasi XRF, SEM, XRD

Hasil

2.10 Preparation Na-Bentonite Production of

- 50 g Bentonit
  - dimasukkan kedalam erlenmeyer
  - ditambahkan 200 mL larutan NaOH 30%
  - didiamkan selama 6 jam
  - disaring dengan menggunakan kertas saring
  - dikeringkan didalam oven pada suhu 105°C
  - dihaluskan dengan alu dan lumpang
  - disaring

Na-bentonit

- dikarakterisasi XRD, SEM

Hasil
2.11 CPO Pretreatment with Saponification

100 g CPO

- dimasukkan kedalam beaker glass
- ditambahkan 30 g NaOH teknis
- dipanaskan pada suhu 90°C
- diaduk dengan magnetik stirrer sampai terbentuk sabun
- didiamkan selama 24 jam

Sabun

dikarakterisasi DSC

Hasil

- dimasukkan sabun yang terbentuk kedalam reaktor stainless stell
- dihubungkan dengan kondensor
- dipanaskan di atas kompor gas sambil diukur suhu
- ditampung destilat menggunakan labu erlenmeyer

Destilat CPO
2.12 Production of Biogasoline with Na-Bentonite Catalyst

- 100 mL destilat CPO
  - dimasukkan ke dalam wadah stainless stell
  - ditambahkan 5 g Na-bentonit
  - dihubungkan wadah dengan kondensor
  - dipanaskan di atas kompor gas sambil diukur suhu
  - ditampung destilat menggunakan labu erlenmeyer

Biogasoline

- dikarakterisasi GC-MS, FT-IR, CCI, dan Bom Kalorimeter

Hasil

3. Results and Discussion

3.1 Free Fatty Acid Analysis of CPO

The results of the analysis of CPO fatty acids were determined using the following calculations:

\[
\text{ALB content} = \frac{V \times N \times \text{NaOH} \times 25.6}{\text{Weight of CPO Samples}}
\]

Determination of free fatty acids of CPO samples was carried out 3 times analysis then the value of free fatty acids was determined from the average value.

| Experimental | Sample Weight | Volume (mL) | NaOH | Normality NaOH | ALB value |
|--------------|---------------|-------------|------|----------------|-----------|
| 1            | 5,214         | 8.6         | 0.1  | 4.24           |
| 2            | 5,514         | 9.04        | 0.1  | 4.20           |
| 3            | 5,120         | 8.44        | 0.1  | 4.22           |
| Average      |               |             |      | 4.22           |

ALB levels in the CPO samples used in this study were 4.22%. ALB levels indicate the level of product damage due to the breakdown of triglycerides into glycerol and free fatty acids. A high acid number indicates that the free fatty acids present in vegetable oil are also high so that the quality of the oil is even lower (Winarno, 2004). According to widya (2015), There are various grades of CPO (Crude Palm Oil) that can be used as an alternative to raw materials, biofuel namely standard CPO (FFA < 5%), off-grade CPO (FFA 5-20%), waste CPO (FFA 20-70). Determination of free fatty acids can be carried out using the alkaline titration method (NaOH). In principle, this method analyzes free fatty acids based on the amount of NaOH used in the titration to form a pink sample color. This is in accordance with the statement of Maligan (2014) which stated that the principle of acid-base titration is the analysis of the amount of free fatty acids in a sample which is equivalent to the amount of base (NaOH) added in the titration which is marked by a change in the color of the sample to pink.
3.2 Pretreatment of CPO with Saponification

The first step of this research is to perform cracking of CPO samples with saponification pretreatment. At this stage, a distillate will be produced. According to Friskilla’s research (2020), the distillate used The resulting biodiesel fraction. Furthermore, the resulting distillate will be cracked using Na-Bentonite and TKNTT catalysts. At this stage, Palm Oil / Crude Palm Oil is reacted with NaOH base to form soap (salt of fatty acid triglycerides). Palm Oil Saponification Reaction produces soap (triglyceride fatty acid salt) based on the following reaction:

\[
\begin{align*}
H_2C &- O - C - R_1 \\
\mid & \\
HC &- O - C - R_2 + 3 \text{NaOH} \rightarrow \\
\mid & \\
H_2C &- OH \\
\mid & \\
R_1 &- C - O - Na \\
\mid & \\
R_2 &- C - O - Na \\
\mid & \\
H_2C &- OH \\
\mid & \\
R_3 &- C - O - Na
\end{align*}
\]

The saponification reaction of CPO uses NaOH base which functions to stabilize the reactive groups found in triglycerides. Stabilization or neutralization of these reactive groups is important because it can prevent polymerization and polycondensation reactions triggered by the state of the reactive groups. The reactive groups in question are ester, hydroxyl, and unsaturated carbon bonds (double bonds).

![Figure 4.1 Reaction Saponification](image)

Figure 4.1 Reaction Saponification

![Figure 4.2 Thermogram of DSC from CPO saponification.](image)

Figure 4.2 Thermogram of DSC from CPO saponification.
Thermal analysis with DSC on the results of CPO saponification in the form of soap is shown in Figure 4.2. This shows that there is a peak indicating the glass transition \(T_g\) at 94.45°C, crystallization peak at 413°C, peak melting \(T_m\) at 475.43°C, and a decomposition peak at 527.43°C. Based on the data obtained, it shows that the temperature required for the process of cracking soap into fuel without using a catalyst is 527.43°C. This data is in accordance with previous research (Supeno et al., 2021). The addition of a catalyst in the cracking process is needed to reduce the activation energy so that the temperature required for the cracking process can be lowered. CPO catalytic cracking process of saponification pretreatment results conducted in the temperature range 250-350°C. Determination of the cracking temperature was envisaged from the boiling point of biodiesel is similar to diesel fuel in the range of 270-350°C.

### 3.3 Catalytic Cracking CPO saponification results

This research does catalytic cracking in stages, where the results of catalytic cracking using a Fe/Cr catalyst against the saponified CPO will be carried out again by catalytic cracking using Na-bentonite and TKNTT catalysts.

During the cracking process, the CPO saponification products in the form of soap and glycerol will be converted into hydrocarbon compounds in the presence of a Fe/Cr catalyst from reactor stainless steel. Based on the results of research conducted by Supeno et al. (2021), catalytic cracking at this stage produces a biodiesel fuel fraction. In this study, the cracking process was carried out again using Na-bentonite and TKNTT catalysts, where biodiesel fuel would be converted into biogasoline fuel which was analyzed using GC-MS.

The catalytic cracking process occurs at a temperature of 250-350°C and is able to produce energy that causes excitation of electrons from the catalyst (Fe / Cr, Na-bentonite, TKNTT). These electrons will fill the empty orbitals of the carbon atoms that make up the long hydrocarbon chain until the orbitals are full and become saturated. At this time there will be a cracking process.

Pretreatment distillate catalytic cracking process CPO produce a yield of 77% calculated as follows:

\[
\text{Yield} = \frac{\text{Volume CPO before cracking}}{\text{Volume CPO after cracking}} \times 100\%
\]

\[
\text{mass CPO sample} = 100 \text{ g}
\]

\[
\text{density of oil} = 0.9 \text{ g/mL}
\]

\[
V_{\text{CPO}} = \frac{\text{mass} (\text{g})}{\text{Volume (mL)}} = \frac{70 \text{ mL}}{90 \text{ mL}}
\]

\[
\text{Yield} = \frac{0.77 \times 100\%}{100\%} = 77.77\%
\]

The distillate obtained is then cracked back on heating 180-240°C using different catalysts namely Na-Bentonite and TKNTT so that the distillate is obtained as follows:

| Cracking catalyst | The volume before cracking (mL) | Volume after cracking (mL) | Yield (%) |
|-------------------|---------------------------------|---------------------------|-----------|
| Na bentonite      | 70                              | 65                        | 72.2%     |
| TKNTT             | 70                              | 67                        | 72.2%     |

Yield Na-bentonite = \( \frac{65}{90} \times 100\% \)

Yield Na-bentonite = 72.2%

Yield TKNTT = \( \frac{67}{90} \times 100\% \)

Yield TKNTT = 74.4%

### 3.4 Analysis X-Ray Fluorescence (XRF)

The chemical elements in bentonite and limestone soils of NTT analyzed using XRF are shown in Table 4.2. The results of X-ray diffraction using X-Ray Fluorescence (Panalytical minipal IV) base metal in Appendix 1 show that bentonite was identified as dominant elements in the form of Si, Al, Fe, P, Ca, and Ti, while the TKNTT samples identified elements as Ca and Si only. It can be seen that bentonite for Si elements has an intensity of 7.529 cps/mA while other elements have an intensity of fewer than 7.529 cps/ A, so it can be assumed that the largest constituent of bentonite is Si. This is in accordance with the results of previous studies (Abukhadra et al., 2019). The element Ca is the largest constituent of TKNTT with an intensity of 37.359 cps/A.

| XRF test results for chemical elements in bentonite and TKNTT. | Table 4.3 XRF test results for chemical elements in bentonite and KTNTT. |
|---------------------------------------------------------------|---------------------------------------------------------------------|
| Cracking catalyst | The volume before cracking (mL) | Volume after cracking (mL) | Yield (%) |
|-------------------|---------------------------------|---------------------------|-----------|
| Na bentonite      | 70                              | 65                        | 72.2%     |
| TKNTT             | 70                              | 67                        | 72.2%     |

Yield Na-bentonite = \( \frac{65}{90} \times 100\% \)

Yield Na-bentonite = 72.2%

Yield TKNTT = \( \frac{67}{90} \times 100\% \)

Yield TKNTT = 74.4%
Based on XRF test results, it can be concluded that bentonite is assumed to have dominant compounds in the form of SiO$_2$ (Quartz), CaO (Lime), Fe$_2$O$_3$ (Hematite), FeTiO$_3$ (Ilmenite), and Al$_2$O$_3$ (Corundum). While TKNTT has dominant compounds in the form of CaO, CaCO$_3$ (Calcite), and Ca(OH)$_2$ (Portlandite). Where the presence of these compounds is discussed further in XRD analysis.

### 3.5 Analysis of X-Ray Diffraction (XRD)

Na-Bentonite and TKNTT XRD diffractograms are shown in Figure 4.3.

![XRD Diffractogram of Na-Bentonite Catalyst and TKNTT](image)

Figure 4.3 XRD Diffractogram of Na-Bentonite Catalyst and TKNTT

From the XRD analysis, there is a diffraction peak at 2θ = 8.1°; 19.7°; and 34.6° with diffraction planes (001), (110), and (110) respectively being the diffraction pattern of Na-bentonite with a hexagonal structure (JCPDS No. 79-1910) (Guo et al., 2019). This
shows that the pillarization of bentonite with Na metal has been successfully carried out. However, there is a diffraction peak at 2θ = 20.7°; 26.5°; and 28.2° which is the diffraction peak of bentonite material (JCPDS No. 29-1499). This shows that there is still bentonite that does not react to form Na-bentonite (Naik & Meivelu, 2020).

Based on the results of XRF and XRD analysis, Na-bentonite indicates the presence of Quartz as the most dominant compound. Other crystalline phases such as Lime, Corundum, Hematite, and Ilmenite were identified as impurities. Diffraction peaks Quartz with a hexagonal structure are at 2θ = 20.7°; 26.5°; and 42.7° with the respective lattice planes (100), (011), and (200) according to JCPDS data No. 46-1045 (Wijaya et al., 2021). Mineral compounds Corundum with the rhombohedral structure are indicated by the presence of 2θ diffraction peaks at angles of 26° (012) and 37.8° (110) (JCPDS No. 10-0173). Minerals Hematite and Ilmenite with a hexagonal structure were also found, each with a characteristic 2θ diffraction peak at an angle of 24.2° (10-2); 33.2° (104), and 61.7° (12-4) according to JCPDS data No. 96-101-1241 for Hematite and JCPDS No. 96-101-1034 for Ilmenite.

The TKNTT diffractogram shows that CaCO₃ (Calcite) is the most dominant mineral compared to other minerals such as Portlandite and Lime. 2θ diffraction peak which is owned by the form of the mineral TKNTT calcite with rhombohedral crystal system is shown at an angle of 22.8°; 29.3°; 43.1°; 46.9°; and 56.5° have lattices with planes (012), (104), (202), (024), and (211) (JCPDS No. 47-1743). While the 2θ diffraction peak which indicates the mineral Ca(OH)₂ is 18°; 34.3°; and 62.6° with (001), (101), and (201) respectively are diffraction patterns Portlandite with a hexagonal crystal system according to JCPDS data No. 44-1481 (Li et al., 2015). The 2θ diffraction peak at an angle of 32.1° with the lattice plane (111) on both catalysts indicated the presence of CaO (minerals Lime) (JCPDS No. 96-100-0045). The presence of these compounds is in accordance with the results of testing using XRF.

3.6 Analysis Scanning Electron Microscope (SEM)

Analysis of Na-bentonite catalyst morphology and TKNTT using SEM with a magnification of 500 and 2000 x shown in Figure 4.4.

Figure 4.4 Microstructure of SEM catalyst a). Na-Bentonite and b). Summit at 500 and 2000 x magnification.

Na-bentonite micrographs have surface characteristics that appear as groups of agglomerated particles consisting of layers with smooth surfaces that are stacked on top of each other. From Figure 4.4 a, it can be seen that there is a porous character and the catalyst crystals are sphere-like crystals. Compared to Figure 4.4 b, the TKNTT catalyst has a rougher surface. This is assumed to come from the combination of CaCO₃, CaO, and Ca(OH)₂ which has a surface structure like a cube (cubic).
3.7 Catheterization of Alternative Fuels
3.7.1 Analysis Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectra of the fuel (BB) resulting from the catalytic cracking of the CPO pretreatment distillate are shown in Figure 4.5. The FT-IR spectra of the two fuels resulting from catalytic cracking have identical characteristics in terms of the presence of functional groups present in the fuel. The summary of FT-IR spectra shown in Table 4.4 explains that there are absorption peaks at wave numbers 2924.09 and 2854.65 cm\(^{-1}\) which are identified as vibrations stretching CH asymmetric of the methylene group and vibrations stretching CH symmetry of the methyl group in the compound, alkane. This data is reinforced by the vibrations bending asymmetric and CH symmetry of the methyl group at wavenumbers 1458.18 and 1373.32 cm\(^{-1}\) (Stuart, 2005; Withrow, 2016). The weak absorption peak in the wavenumber region of 1720.50 cm\(^{-1}\) indicates that the fuel produced has a C=O group. The presence of the C=C group shown at wave number 1643.35 cm\(^{-1}\) indicates that there are olefin hydrocarbon compounds. The absorption peaks at wave numbers 964.41 and 910.40 cm\(^{-1}\) indicate the presence of a CH group. The presence of an absorption peak at a wavenumber of 725.23 cm\(^{-1}\) indicates that the fuel resulting from catalytic cracking is a long chain hydrocarbon compound, \((\text{CH}_2)_n\). Each absorption peak contained in the fuel is a characteristic possessed by hydrocarbon compounds (Supeno et al., 2021).

![Figure 4.5 FTIR Spectra of Fuel from catalytic cracking using Na-Bentonite and TKNTT.](image)

### Table 4.4 Summary of FT-IR spectra of fuel catalytic cracking

| Wave Number (cm\(^{-1}\)) | Type of Group | Vibration Type |
|---------------------------|---------------|----------------|
| BB Na-bentonite           | BB TKNTT      |                |
3.7.2 Analysis of Gas chromatography-mass Spectrometry (GC-MS)

Alternative fuel (biofuel) produced from the cracking process using Na-bentonite and TKNN catalysts then analyzed using the GC-MS instrument to analyze the fuel fraction contained in the sample and its constituent compounds. The chromatogram of the fuel produced from the catalytic cracking of the CPO distillate is shown in the figure below.

![Chromatogram of GC-MS fuel resulting from catalytic cracking using Na-bentonite as a catalyst.](image)

The chromatogram in Figure 4.6 shows that there are 44 compound fractions identified in the fuel resulting from catalytic cracking using a Na-bentonite catalyst. The results of the GC-MS analysis showed that there were 5 constituent compounds with the highest peaks, which are summarized in Table 4.5.

![Chromatogram of compounds with the highest peaks from BB Na-bentonite catalyst.](image)

| Peak | No. | The highlight of the compound name | Molecular formula | Retention Time (Minutes) | Time Area (%) |
|------|-----|-----------------------------------|-------------------|--------------------------|--------------|
| 1    | 27  | 1-Undekena                        | C_{11}H_{22}       | 29.759                   | 15.48        |
| 2    | 28  | n-Decane                           | C_{10}H_{22},957  | 22                       | 13.17        |
| 3    | 18  | 1-Dodecane                         | C_{12}H_{24}       | 27.052                   | 10.29        |
| 4    | 14  | n-Nonana                           | C_{9}H_{20}        | 24.423                   | 7.71         |
| 5    | 13  | 3-Undecane                         | C_{11}H_{22}       | 24.170                   | 5.35         |

Figure 4.7 Chromatogram of GC-MS fuel resulting from catalytic cracking using TKNN catalyst.
The chromatogram in Figure 4.7 shows that there are 36 fractions of compounds identified in the fuel resulting from catalytic cracking using TKN TT catalyst. The results of the GC-MS analysis show that there are 5 constituent compounds with the highest peaks which are summarized in Table 4.6.

| Peak | No. Peak | Name of compound | Molecular formula | Retention time (minutes) | Area (%) |
|------|----------|------------------|-------------------|--------------------------|----------|
| 1    | 14       | 1-Nonene         | C₉H₁₈              | 17,836                   | 6,49     |
| 2    | 10       | Undecene         | C₁₁H₂₂             | 14,241                   | 6,02     |
| 3    | 29       | 1-Dodecene       | C₁₂H₂₄             | 29,725                   | 5,86     |
| 4    | 20       | 3-Undekena       | C₁₁H₂₂             | 21,121                   | 5,33     |
| 5    | 7        | 1-Oktena         | C₈H₁₆              | 10,373                   | 5,28     |

The results of the analysis of the fuel from the catalytic cracking of the CPO pretreatment distillate using the Na-bentonite catalyst showed that the biogasoline and biodiesel fractions were 61.36% and 38.63%, respectively. Meanwhile, using the TKN TT catalyst produced biogasoline and biodiesel fractions of 88.88% and 11.11%, respectively. Thus, in this study, the catalytic cracking of the CPO pretreatment distillate has the potential to produce more gasoline fractions than biodiesel fractions. The study of Supeno et al., (2021) produced fuel with a major fraction in the form of biodiesel from CPO using a Fe/Cr catalyst. Likewise, research conducted by Hutabarat (2021) conducted catalytic cracking using Na-Bentonite on saponified CPO to produce biodiesel fuel fraction. In this study, catalytic cracking was carried out in stages, where the results of the catalytic cracking using a Fe/Cr catalyst against the saponified CPO will be carried out again by catalytic cracking using Na-bentonite and TKN TT catalysts. From these data, it can be concluded that the catalytic cracking of saponified CPO produces a biodiesel fuel fraction, while the second catalytic cracking stage using Na-bentonite and TKN TT catalysts produces a major fraction of fuel in the form of gasoline.

3.7.3 Analysis of Bomb Calorimeter and CCI

Bomb calorimeter analysis was carried out to test the calorific value with the aim of knowing the number that states the amount of heat generated from the combustion process of a certain amount of fuel with oxygen. The standard calorific value of fuel based on the SNI-04-7182-2006 standard is 10,498 BTU/lb or about 5,832 cal/g. In this study, the calorific value of biodiesel combustion was 6101 cal/g using a Na-bentonite catalyst. Thus the fuel produced meets the Net Calorific Value according to the standard.

The cetane number (CN) is used to describe the ignition quality of diesel fuel. The ignition quality of diesel fuel can also be calculated using the Cetane Index (CI) method (EN ISO 4264, ASTM D 4737). The cetane number of a fuel is influenced by the elements contained in the fuel, such as the element carbon which is a source of combustion energy (Supeno et al., 2021). The standard cetane index that biodiesel must have is >45. Based on the CCI test results, the cetane index value was 62 using Na-bentonite catalyst. Based on the data obtained and summarized in Table 4.5, it can be concluded that the fuel obtained in this study can be used as an alternative fuel candidate in the form of biogasoline that has met the specified standards.

4. Conclusion

1. The results of XRD and XRF analysis show that Na-bentonite is mostly composed of Quartz (SiO₂) minerals, while TKN TT is mostly composed of CaCO₃ minerals. The morphology of the catalyst analyzed using SEM showed that both catalysts had a large and porous surface. Where the Na-bentonite catalyst appears as crystals that are shaped like spheres (sphere-like crystals) while the TKN TT catalyst is in the form of a cube (cubic).

2. In accordance with the results of the FT-IR and GC-MS analysis, it can be concluded that the fuel fractions produced are biogasoline and biodiesel fractions. The biogasoline fraction is 88.88% (TKN TT) 61.36% (Na-Bentonite) and the biodiesel fraction is 11.11% (TKN TT) and 38.63% (Na-Bentonite). combustion was 6101 cal/g determined using a bomb calorimeter, and a cetane index of 62 which was analyzed using CCI. Both types of hydrocarbon fuels have met the physical requirements that must be possessed by biogasoline fuel based on SNI standards.

References
[1] Abukhadra, MR, Ibrahim, SM, Yakout, SM, El-Zaidy, ME, & Abdeltawab, AA (2019). Synthesis of Na+ trapped bentonite/zeolite-P composite as a novel catalyst for effective production of biodiesel from palm oil. Effect of ultrasonic irradiation and mechanism. Energy Conversion and Management, 196(June), 739–750. https://doi.org/10.1016/j.enconman.2019.06.027

[2] Atkins, PW (1997). Kimia Fisik Jilid 1. Edisi Keempat. Terjemahan Irma KartohadiProdjo. Jakarta : Erlangga

[3] BC Clark and AB Baird. (1992) Ultraminiaturize X-ray fluorescence spectrometer for in-situ geochemical analysis on Mars, Earth and Planetary Science Letters, vol. 19, no. 3, 359–368

[4] Benson, TJ, Hernandez, R, French, WT, Alley, EG, Holmes, WE, (2009). Elucidation of the catalytic cracking pathway for unsaturated mono-, di-, and triacylglycerides on solid acid catalysts. J. Mol. Catal. A: Chem. 303, 117–123

[5] Chua K., J, Ratnawali, S. (2014). Biogasoline from Catalytic Cracking of Refined Palm Oil Using H-ZSM-5 Catalyst. International Journal of Advanced In Chemical Engineering and Biological Sciences (1), 114–118

[6] Dachriyanus. (2004). Analisa Struktur Senyawa Organik. Padang: Lembaga Pengembangan Teknologi Informasi dan Komunikasi (LPTIK) Universitas Andalas

[7] Doronin, VP, Potapenko, OV, Lipin, PV, Sorokina, TP, (2013). Catalytic cracking of vegetable oils and vacuum gas oil. Fuel 106, 757–765.

[8] Gerper. (2004). Biodiesel Production Technology. USA: Iowa State University

[9] Guo, Y., Guo, Y., Tang, D., Liu, Y., Wang, X., Li, P., & Wang, G. (2019). Sol-gel synthesis of new ZnFe2O4/Na-bentonite composites for simultaneous oxidation of RhB and reduction visible of Cr(VI) under light irradiation. Journal of Alloys and Compounds, 781(Vi), 1101–1109. https://doi.org/10.1016/j.jallcom.2018.12.050

[10] Gunstone FD, Padley FB. (1997). Lipids Technologies and Applications. New York: Marcel Dekker Inc.

[11] Han U. (2015). Quality Improvement Of Oil Palm Shell- derived Pyrolysis oil via catalytic deoxygenation over NiMo/S-Ál2O3, Fuel 143,512–518

[12] Hariyadi P. (2009). Mengenal Minyak Sawit dengan Beberapa Karakter Unggulnya. Jakarta : Gabungan Pengusaha Kelapa Sawit Indonesia (GAPKI)

[13] Hassan S.N. (2015). Biogasoline: an out of the Box Solution to the Food Fuel and Land Use Competitions. Energy Conversion and Management, 89, 349–367

[14] Heny. (2007). Proses Perengkahan Minyak Sawit menggunakan Katalis Jenis DH Prosiding Seminar Nasional Fundamental dan Aplikasi Teknik Kimia’. Surabaya : Institut Teknologi Sepuluh November

[15] Hutabarat, JAR (2021). Pembuatan Biofuel dari Minyak Kelapa Sawit melalui Proses Hydrocracking dengan Katalis Ni/Mg/- Al2O3. Jabatan Teknik POMITS Vol 3

[16] Knothe G, Gerpen Jv, Krahl J. (2005). The Biodiesel Handbook, 9–10 Champaign Illinois USA: AOCS Press

[17] Kurt C, Bittner. (2006). Sodium Hydroxide In Ullmann’s Encyclopedia of Industrial Chemistry. Wiley Online Library: Bayer Material Science SG, Leverkusen Germany

[18] Li, H., Niu, SL, Lu, CM, & Cheng, SQ (2015). The stability evaluation of lime mud as transesterification catalyst in resisting CO2 and H2O for biodiesel production. Energy Conversion and Management, 103, 57–65. https://doi.org/10.1016/j.enconman.2015.06.039

[19] Lovás, P., Hudec, P., Hadvinová, M., Ház, A., (2015). Conversion of rapeseed oil via catalytic cracking: effect of the ZSM-5 catalyst on the deoxygenation process. Fuel Process. Technol. 134, 223–230.

[20] McGee, H. (2004). On Food and Cooking: Thes Science and Lore of the Kitchen. Scribner. United States of America

[21] Naik, BD, & Meivelu, U. (2020). Experimental studies on sodium methoxide supported bentonite catalyst for biodiesel preparation from waste sunflower oil. Environmental Progress and Sustainable Energy, 39(4), 1–14. https://doi.org/10.1002/ep.13390

[22] Nugroho, K. (2014). Pembuatan Biofuel dari Minyak Kelapa Sawit melalui Proses Hydrocracking dengan Katalis Ni-Mg/- Al2O3. Jurnal Teknik POMITS Vol 3 No. 2

[23] Nurhadi M. (1999). Pembuatan dan Karakterisasi Katalis Kromium Zeolit Alamin Perengkahan Fraksi Minyak Bumi. Tesis S2 Program Pasca Sarjana Universitas Gajah Mada : Yogyakarta

[24] Ong, YK, Bhatia, S., (2010). The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils. Energy 35, 111–119.

[25] Perry RH, Green DW, (1984). Perry’s Chemical Engineer’s Handbook. 6th. ed. Mgraw Hill Co., International Student Edition, Kogakusha, Tokyo.

[26] Pradita O, S. (2008). Studi Komparasi untuk Kerja Mesin dan Pengaruh Kenaikan Cetane Number pada Campuran Biodiesel Minyak Jagung dengan Minyak Solar Murni. Essay. Jakarta : Teknik Mesin Universitas Indonesia Renewable and Sustainable Energy Reviews. Volume 12,2404–2421

[27] Reeves J. B. (1979). Agriculture handbook. Dalam JB Reeves, Consumer and Food Economics Institute (hal. 4). Washington, DC: US Dept. of Agriculture.

[28] Sastrosatomo S. (2003). Budidaya Kelapa Sawit. Jakarta: Agromedia Pustaka. Halaman 3