

Synthesis *Bio-gasoline* from *Crude Palm Oil Offgrade* via *Catalytic Cracking* Using $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ Heterogeneous Catalyst

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Abstract. The continuous use of fuel reduces oil reserves which causes the availability of petroleum in Indonesia tend to decrease. To overcome the problem of oil supplies, renewable energy is needed as an alternative fuel, one of which is bio-gasoline as a substitute for gasoline. Bio-gasoline can be made from Crude Palm Oil offgrade via catalytic cracking that has the advantage of simple tools and shorter processes cracking. Heterogeneous catalyst $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ made of alkaline calcium oxide which can reduce the acidity of biogasoline and $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles acidic which can trigger the breakdown of the hydrocarbon chain. This study aims to synthesize bio-gasoline from CPO offgrade through catalytic cracking reactions using $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ heterogeneous catalyst. The results showed that bio-gasoline has been successfully produced by the cracking method with a yield of 46.18%. Based on GC-MS analysis of the product it is suspected to contain mixed compounds from the biogasoline such as heptane, octane, decane, nonane, and undecane. Physico-chemical characteristics of the biogasoline product for fraction III (F₃) include density, viscosity, acid number, iodine number, and refractive index respectively of 0.73 g/mL; 2.76 cSt; 15.639 mg KOH/g sample; 2.29 g Iod/100g sample; and 1.465. The Biogasoline characterization is close to the Gasoline quality standard No. 0177.K/10/DJM.T/2018.

1 Introduction

Energy is a strategic sector and has an important role in various fields to maximize its utility. Energy needs in Indonesia are increasing from year to year in line with economic growth and population growth. Currently, the most widely used energy sources are fossil fuels such as oil, gas and coal. Fossil fuels are non-renewable energy with dwindling supplies [1]. Indonesia has oil reserves of 3.6 billion barrels which are expected to run out in the next 13 years [2]. Fuel oil is the main energy source used in various countries, including Indonesia. The continuous use of fuel reduces oil reserves which causes the availability of petroleum in Indonesia to decrease from 2000 to 2014 [2]. Renewable energy is needed as an alternative fuel to overcome the problem of oil supply shortages, one of which is Bio-gasoline [3].

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Bio-gasoline is a fuel oil composed of short chain hydrocarbons starting from C₅ until C₁₂ which is made from animal fats or vegetable oils that can be renewed so that they can be used as alternative energy to replace gasoline or petrol for motor vehicles [4]. Bio-gasoline, which is currently being developed, uses crude palm oil or crude palm oil as raw material Crude Palm Oil (CPO). The use of CPO as raw material for Bio-gasoline can compete with the use of CPO as food. To avoid this, the raw material for Bio-gasoline is CPO off-grade. CPO off-grade is the result of residual sorting consisting of abnormal fruit, fruit that is too young or too old, and rotten fruit that is no longer used. CPO off grade also contains high fatty acids, therefore CPO off grade very potential as an alternative raw material for the manufacture of Bio-gasoline.

Bio-gasoline can be synthesized from triglyceride oil or free fatty acids through reactions cracking. Reaction cracking can be done through several methods. Reaction cracking carried out at high temperature ($\pm 800^{\circ}\text{C}$) and low pressure (700 kPa) are called thermal cracking. Reaction cracking is carried out at elevated temperatures and pressures by flowing H₂, which is called hydrocracking. The reaction is carried out using a catalyst called catalytic cracking. Method thermal cracking has drawbacks, namely its use requires a series of tools that are resistant to high temperatures and requires large amounts of energy to obtain high temperatures and pressures. Method hydrocracking has drawbacks, namely its use requires a series of modified distillation apparatus powered by hydrogen gas so that it requires a large amount of money. Therefore, the method is used catalytic cracking because it is simpler in terms of reactor because it does not require high temperature and pressure and the cost is affordable. The catalytic cracking method also has advantages, namely the process cracking which is shorter because it is assisted by a catalyst which can speed up the reaction making it faster and more efficient. Method catalytic cracking is a process cracking which uses the help of a catalyst as a reaction accelerator so a catalyst is needed that has thermal stability at high temperatures, an adequate amount of acid sites, and pores to the active site that is easily accessible by reactants [5].

Reaction catalytic cracking can use a catalyst or support catalyst derived from transition metals such as Pt, Pd, Ni, Co, Rh, Ru, Cu, and Fe. The catalyst can also be combined with metal oxides such as NiO, SiO₂, Al₂O₃ and CaO to produce Bio-gasoline. CaO is used as a catalyst in the cracking process because it can reduce the acidity of Bio-gasoline, has low toxicity, is easy to prepare, affordable, and has abundant availability [6,7]. Several studies have discussed the catalytic activity of the CaO catalyst, for example in Hassan's research (2020), which states that the synthesis of Bio-gasoline from used cooking oil using a CaO catalyst can reduce the acidity of Bio-gasoline. The research produces Bio-gasoline in the form of alkanes and alkenes with a yield of 4.5wt% at 350°C at a speed of 400 rpm. The components of Bio-gasoline produced using a CaO catalyst are also similar to the components of Bio-gasoline produced using a natural zeolite catalyst in Bielansky's study (2011), which include ethyl benzene, xylene, and propyl benzene [6]. The use of calcium oxide as a catalyst for the production of Bio-gasoline was also studied by Ge (2021), who stated that the CaO/SBA-15 catalyst could catalyze the reaction cracking used cooking oil into Bio-gasoline with a yield of 69.7% [8]. Zheng's research (2019) also showed that CaO tends to convert some fatty acids into ketones and methyl ketones [9].

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is an iron oxide which has magnetic properties and has good thermal stability so that it can be used as a *support* catalyst [10,11]. In Abdulloh's research (2017), stated that the $\alpha\text{-Fe}_2\text{O}_3$ /zeolite Y can catalyze the reaction *cracking* on palmitic acid and produce short chain hydrocarbon compounds or Bio-gasoline in the form of alkanes and alkenes with a yield of 37.59% [5]. In Wijayanti's research (2020), stated that Al₂O₃/Fe₂O₃ was successfully used to catalyze the reaction *cracking* so that it can break the hydrocarbon bonds and produce p-xylene, paraffin, and naphthalene compounds. The study confirmed that using Al₂O₃/Fe₂O₃ can break complex bonds in vacuum residue. Fe₂O₃ has large pores so

that compounds with large molecules can enter the pores [12]. In Cheng's research (2015), shows that Fe_2O_3 used as a pyrolysis catalyst plays an important role in the breakdown of hydrocarbons and as much as 9% $\text{Fe}_2\text{O}_3/\text{CaO}$ can produce 41.05% alkanes. This research also shows that the $\text{Fe}_2\text{O}_3/\text{CaO}$ has a catalytic effect in the cracking of polycyclic aromatic hydrocarbons. This is because the catalyst surface has a high density of active sites [13]. Previous studies have shown the respective activities of CaO and $\alpha\text{-Fe}_2\text{O}_3$. Combined research between CaO and $\alpha\text{-Fe}_2\text{O}_3$ has been carried out on pyrolysis. Research on the synthesis of Bio-gasoline using CaO and $\alpha\text{-Fe}_2\text{O}_3$ heterogeneous catalysts has never been done before. Based on the discussion that has been done, CaO and $\alpha\text{-Fe}_2\text{O}_3$ catalysts have good advantages so that it has the potential to be developed as a new catalyst in the reaction catalytic cracking formation of Bio-gasoline. To find out the best conditions for using $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ on reaction *cracking* and to determine the characteristics of the Bio-gasoline synthesized, it is necessary to carry out the synthesis through experiments to identify the characteristics of the Bio-gasoline. Therefore, this study is performed to synthesize Bio-gasoline from Crude Palm Oil Off grade via Catalytic Cracking using $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$.

2 Experimental Method

2.1 Tools and Materials

The equipment used in this study was a beaker glass (*iwaki*), volumetric flask (*pyrex*), pipet volume (*iwaki*), measuring pipette (*iwaki*), erlenmeyer (*pyrex*), separating funnel, watch glass, thermometer 100°C, evaporating dish, crucible, filter paper, cardboard, universal indicator (*merck*), modified distillation apparatus, sieve 100*mesh*, burettes, stands and clamps, digital balance (*Durascale DAB 200*), Buchner, magnetic stirrer (*HMS-79*), mortar and pestle, stirring rod, spatula, plastic wrap, aluminum foil, label paper, desiccator, *furnace (Thermolyne)*, oven (*Memmert*), viscometer *Ostwald*, ultrasonic reactor, Abbe Refractometer, XRF (*Panalytical minipal 4*), XRD (*Panalytical Xpert-Pro*), (*Scanning Electron Microscopy*) SEM, FTIR (*Shimadzu*) and GC-MS (*Shimadzu QP2010S*).

The materials used are *Crude Palm Oil (CPO) off-grade* obtained from PT. Sawit Arum Madani Sutojayan Blitar Regency, CaO p.a (*Merck*), NaOH p.a, FeSO_4 p.a, FeCl_3 p.a, Na_2SO_4 p.a, KOH p.a, KI p.a (*Smartlab*), I_2 p.a (*Smartlab*), 96% technical ethanol, technical phenolphthalein indicator, chloroform (*Smartlab*), glacial acetic acid, bromine water, 1% starch indicator, and distilled water.

2.2 Experimental Procedure

2.2.1 Synthesis of Hematite $\alpha\text{-Fe}_2\text{O}_3$ and $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ catalyst

Hematite nanoparticles were synthesized by reacting 20 mL of FeSO_4 solution 0.25 M with 20 mL FeCl_3 0.5 M. Added 50 mL of 1.5 M NaOH solution slowly and stirred using a magnetic stirrer until homogeneous. The mixture is filtered through fine filter paper and neutralized. The residue obtained was dried using an oven at 60-65°C for 3 hours. Then the solid was calcined at 800°C for 4 hours. Nanoparticles $\alpha\text{-Fe}_2\text{O}_3$ characterized using XRF and XRD [10].

2.2.2 Impregnation CaO/ α -Fe₂O₃ catalyst

Synthesis CaO/ α -Fe₂O₃ carried out using the wet impregnation method by dissolving CaO into a 250 mL Erlenmeyer and adding nanoparticle powder α -Fe₂O₃ with a ratio of Ca and Fe as large as 1:2. The mixture is shaken handshaker for 15 minutes. Next, the mixture is ultrasonically treated at 65-70°C for 1 hour. The mixture is filtered, neutralized, heated in the oven at 100°C for 4 hours, and in-furnace with a temperature of 700°C for 4 hours. The catalyst was characterized using XRF, XRD, and SEM [14].

2.2.3 Production of Bio-gasoline via Catalytic Cracking

Production of Bio-gasoline uses a modified distillation reactor equipped with a temperature sensor in the reactor. A total of 70 grams of CPO off grade and 0.5% concentration catalysts CaO/ α -Fe₂O₃ were put into the reactor. The reactor is heated at a heating temperature of 600°C-2000°C for 2.5 hours using an electric stove. The steam that comes out of the flask is condensed using cold water. The condensate obtained is separated into each fraction based on the temperature difference.

3 Result and Discussion

3.1 Characterization of Hematite

CaO/ α -Fe₂O₃ is a heterogeneous catalyst made of CaO impregnated into hematite (α -Fe₂O₃). Calcium oxide (CaO) is used as a catalyst for the formation of Bio-gasoline because it can reduce the acidity of the product. CaO can enter hematite (α -Fe₂O₃) thereby increasing the surface area of the catalyst. The greater the surface area of a catalyst, the higher the active side and catalytic activity.

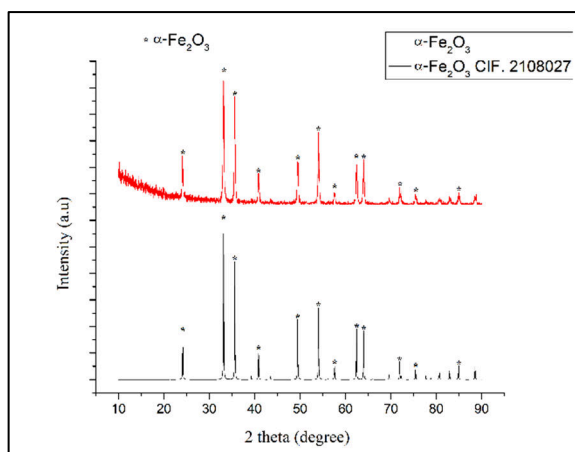


Fig. 1. Diffraction XRD of Hematite

The synthesis of hematite was carried out by reacting a FeSO₄ 0,25 M, FeCl₃ 0.5 M, and NaOH 1,5 M until magnetite (Fe₃O₄) then calcined at 800°C. Hematite then characterized using XRD and some peaks correspond in the hematite diffraction database. Results of characterization of hematite using XRD produces a diffraction pattern with a peak at an angle of 2 θ (24,14°; 33,15°; 35,63°; 40,86°; 49,46°; 54,05°; 57,58°; 62,42°; 63,99°; 71,94°; 75,45°;

and $84,90^\circ$) which corresponds to COD (Crystallography Open Database) with the number CIF.2108027 which is a database of hematite served on **Fig 1**. This shows that the hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3$) have been successfully synthesized. Hematite was characterized using XRF to determine the percentage of oxide composition in it. Characterization using XRF showed that the synthesized hematite nanoparticles had a purity of 97.05%.

3.2 Characterization of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ catalyst

The impregnation of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ via wet impregnation and sonochemistry using the ratio of $\text{CaO}:\alpha\text{-Fe}_2\text{O}_3$ 1:2. The color of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ before calcining it was in the form of reddish-brown powder and after calcining it was brown. Based on the XRD results, there are peaks at an angle of 2θ ($33,55^\circ$; $35,67^\circ$; $41,65^\circ$; $48,59^\circ$; $62,47^\circ$; $63,05^\circ$; $75,35^\circ$) which corresponds to the COD database (*Crystallography Open Database*) with the number CIF.9013281 which is a database of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ (**Fig 2**). This shows that catalyst has been successfully synthesized.

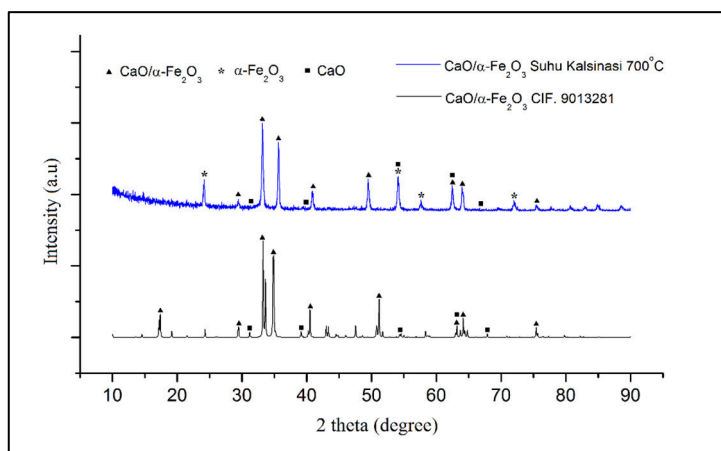


Fig. 2. Diffraction XRD of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ Catalyst

The $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ heterogeneous catalyst was also characterized using XRF to determine the percentage of oxide composition in it. Characterization using XRF showed that the catalyst contains the largest content, namely CaO and $\alpha\text{-Fe}_2\text{O}_3$ by 94.71%.

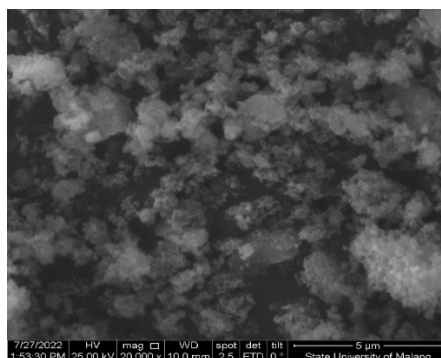


Fig. 3. Morphology SEM of $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ Catalyst

SEM characterization results (**Fig. 2**) indicate that the $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ has an irregular and interlocked particle shape which shows the effect of impregnation. This shows that the catalyst has the form of an amorphous (irregular) powder. These results are also similar to research conducted by Mahmudah (2016) which showed that the Fe_2O_3 impregnated CaO has a particle shape that looks like an irregular structure and is bound together to form aggregates.

3.3 Characterization Biogasoline Product Catalytic Cracking

Process *cracking* can convert fatty acids in CPO *off grade* with a long carbon chain into a hydrocarbon compound with a short carbon chain, namely $\text{C}_3\text{-C}_{12}$. Process *cracking* using $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ which are acidic and basic to produce good quality biogasoline. Acid catalysts in process *cracking* are effective for breaking or terminating hydrocarbon bonds, while base catalysts are effective for producing bio-gasoline in the form of alkanes and alkenes. The CaO compound in the catalyst also acts as an alkaline substance which can reduce the acidity of Bio-gasoline. Product *catalytic cracking* is dark yellow in Fraction I, yellow in Fraction II, while for Fraction III it is clear yellow. Product *catalytic cracking* is in the form of a waterier liquid and does not freeze at room temperature (25°C). The synthesized Bio-gasoline smells like fuel. Furthermore, the resulting product *cracking* using a $\text{CaO}/\alpha\text{-Fe}_2\text{O}_3$ calcination temperature 700°C with a concentration of 0.5% produces a yield of 46.18%. The Biogasoline obtained was added up for the yield calculation and then its chemical properties were characterized, consisting of density, viscosity, acid number, iodine number, and refractive index which is summarized in **Table 1**.

Table 1. Physico-chemical characteristics of Bio-gasoline

Parameter	Mark			
	CPO <i>off grade</i>	Faction I (f_1)	Faction II (f_2)	Faction III (f_3)
Density (g/mL)	0,912	0,72	0,73	0,73
Viscosity (cSt)	56,02	2,15	2,25	2,76
Acid number (mg KOH/g sample)	76,07	48,79	43,57	15,64
Iodine number (g iodine/100 g sample)	23,86	15,86	5,08	2,29
Refractive index (at 25°C)	1463	1,429	1,430	1,431
Distillation temperature ($^\circ\text{C}$)	-	100-125	126-150	151-200
Weight per fraction (gram)	-	4,65	3,34	24,34

Product *catalytic cracking* CPO *off grade* is then identified using the FTIR instrument which aims to determine the functional groups in the product *catalytic cracking*. The peaks in the IR spectrum can be used to predict the functional groups in the compounds resulting from the reaction *cracking*. Based on the results of FTIR spectrum analysis (**Figure 3**). Components of the resulting product catalytic cracking based on FTIR analysis containing functional groups C-H sp^2 , C-H sp^3 , C=O, OH and C-C-C so that they are classified as alkanes, alkenes, carbonyl compounds in the form of carboxylic acids, esters, and ketones.

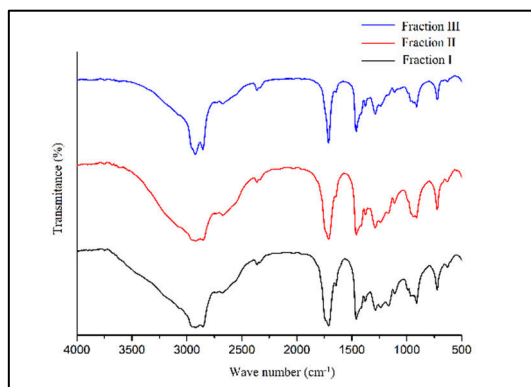


Fig. 4. FTIR Result of Biogasoline

In the FTIR spectrum of Fractions I, II, III for the wave number region 2500-3300 cm^{-1} there are peaks with weak and very wide intensities indicating characteristic of the stretching vibration of the O-H bond for carboxylic acid compounds. In addition, the absorption in the area around 3300 cm^{-1} and obliquely into the aliphatic C-H absorption band also shows the characteristics of the O-H bonds of carboxylic acid compounds. This indicates that the compounds contained in the cracking products have O-H groups for carboxylic acids.

In the FTIR spectrum of Fractions I, II, III for the wave number region 1735-1750 cm^{-1} there is 1 peak with a strong and sharp intensity which shows the characteristic C=O bond stretching vibration of carboxylic acids and their derivatives. This indicates that the compounds contained in the cracking products have a carbonyl group as a carboxylic acid or its derivatives. In the Fraction II spectrum, for the wave number region 1735-1750 cm^{-1} there is 1 peak with a strong and sharp intensity which shows the characteristic stretching vibration of the C=O bond as an ester derived from a carboxylic acid. This indicates that the compounds contained in the cracked product have C=O bonds as esters.

In the FTIR spectrum of Fractions I, II, III for the wave number region 1395-1440 cm^{-1} there are peaks with moderate and sharp intensity which show the characteristic bending vibrations of the C-O-H bond of carboxylic acids. This indicates that the compounds contained in the cracked product have C-O-H bonds as carboxylic acids. In the Fraction III spectrum for the 1100 cm^{-1} wave number region, there are medium and sharp peaks showing the characteristic bending vibrations of the C-C-C bond of ketones. This indicates that the compounds contained in the cracking products have C-C-C bonds as ketone compounds.

Product cracking was also identified using the GC-MS instrument to determine the compounds formed due to the process of catalytic cracking. The compounds formed were identified based on the peaks that appeared at a certain retention time in the GC-MS chromatogram. The results of the GC-MS chromatogram analysis of fractions I, II, and III showed the constituent compounds present in the product catalytic cracking each fraction. Product constituent components catalytic cracking Fractions I, II and III are summarized in **Table 2**.

Table 2. Compound Product Cracking Based on GCMS

Fraction I	Fraction II	Fraction III
1-Octene	1-Heptene	Heptane
Octane	Octane	Octane
Nonana	3-Undecene	Decane
1-Decene	Nonanoic acid	Nonane

Heptanoic Acid	Nonane	Undecanoic acid
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The results of the GC-MS analysis of fractions I, II, and III showed that the yield compounds *cracking* impure *Bio-gasoline* but rather a mixture of the Bio-gasoline fraction (C₅-C₁₂), diesel (C₁₂-C₁₈), and heavy gas oil (>C₁₈) served on **Table 3**. To separate these fractions, it is necessary to carry out further distillation to produce distillate products with a higher purity for each fraction.

Table 3. Compounds from Catalytic Cracking Based on GC-MS Analysis

Fraction	I	II	III
Bio-gasoline (C₅-C₁₂)	79,40 %	68,44 %	83,17 %
Biodiesel (C₁₃-C₁₈)	20,60 %	30,58 %	16,83 %
Heavy Gas Oil (>C₁₈)	-	0,98 %	-
Compounds contained	Alkane Alkene Carboxylic acid	Alkane Alkene Carboxylic acid Ester	Alkane Alkene Carboxylic acid Ketones

The character of the synthesized Bio-gasoline is compared with the Gasoline quality standards of the Directorate General of Oil and Gas, Ministry of Energy and Mineral Resources Number 0177.K/10/DJM.T/2018. From the data that has been obtained, the physicochemical characteristics of Bio-gasoline are close to the Gasoline quality standards in Indonesia.

4 Conclusion

Bio-gasoline has been successfully synthesized from CPO off grade through reactions catalytic cracking. The yield of bio-gasoline as a result of the reaction cracking CPO off grade the highest using CaO/ α -Fe₂O₃ with concentration of 0.5% is 46.18%. Physicochemical characteristics of Bio-gasoline product catalytic cracking for fraction III (f3) include density, viscosity, acid number, iodine number, and refractive index respectively of 0.73 g/mL; 2.76 cSt; 15.639 mg KOH/g sample; 2.29 g Iod/100g sample; and 1.465. The Bio-gasoline characterization is close to the MEMR Gasoline quality standard no. 0177.K/10/DJM.T/2018.

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