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Characteristics of Heterogeneous Catalysts Fly Ash Fraction of Light Shell and Fiber of Palm Oil Mill Solid Waste Grown on Peatlands

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ABSTRACT

Utilization of biomass from agricultural waste in Indonesia is still not optimal. Biomass from agricultural waste containing of Si and Ca can be used for the manufacture of heterogeneous base catalysts. The catalyst produced will be applied to the manufacture of biodiesel. A biodiesel quality test and Gas chromatography-mass spectroscopy (GC-MS) test are carried out, including chemical composition analysis test (X-RD), three-dimensional structure (SEM), material characterization (FT-IR), surface and basic properties (BET), and mass-weight change (TGA). The research method used is an experimental method, where this research was carried out in 3 stages; the first stage is to determine the test and characteristics of crude palm oil raw material, the second is on the manufacture of palm ash catalyst, and the third is the application of a heterogeneous catalyst based on palm fly ash in the manufacture of biodiesel. The results on the characteristics of crude palm oil after purification using 5% shell activated charcoal showed an increase in quality, including the number of free fatty acids 3.86% w/w, water content 0.0015%, impurities content 0.0485%. The acid number of 13.840mgKOH/g is still within the quality standard, while for the quality of the biodiesel produced, the calcination catalyst treatment at a temperature of 700ºC for 5 hours for the density parameter is 0.860g/ml, water content is 0.03%-wb, iodine number is 26.30gI2/100g, saponification number 90.88mgKOH/g, and free fatty acid number 0.38%w/w have values according to biodiesel standard ASTM D6751. Catalyst calcined at 700ºC 5 hours found mesopore (7.93 nm) with a surface area 25.288 m^2/g. It also has CaO around 36º peaks, where catalyst particles are spherical with a smooth surface.

1. Introduction

A catalyst added to biodiesel production generally increases the reaction speed in forming the desired product [1,2]. According to Gemy *et al*., [3], the primary purpose of using a catalyst in a reaction is to lower the activation energy to accelerate the reaction [4], but not to shift the position

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of the equilibrium [2]. Thus, the function of the catalyst is to increase the reaction rate, where in theory, the greater the amount of catalyst used will increase the reaction rate [5]. Catalyst raw materials play an essential role in the manufacture of biodiesel [6,7], where the catalyst is a substance that can significantly increase the reaction rate and can affect the transesterification process. In addition to homogeneous catalysts, recently, along with the progress of research results, the use of heterogeneous catalysts for biodiesel production has offered many alternatives to process raw materials and cheaper production processes, and of course, with a longer catalyst life [8]. Heterogeneous catalysts have advantages over homogeneous catalysts because the remaining catalyst contained in the product can be recycled, has a long catalyst life, is more stable, non-corrosive and environmentally friendly [1,9,10], are very easy to separate from the system at the end of the process or reaction and can be reused. The ease of separating the solid heterogeneous catalyst, because the separation is only sufficient by filtering it [11], is more economical because it has the potential to be used many times [10,12]. Another consideration is in the transesterification reaction; the use of heterogeneous catalysts is an option because this heterogeneous catalyst can reduce the cost of biodiesel production [13] and is also very environmentally friendly. This point is, of course, very relevant to the world program (The Sustainable Development Goals/SDGs) in anticipating pollution caused by industries that produce a lot of waste, both solid, liquid and gas, which are carried out continuously by industrial players in all countries in the world, especially heterogeneous catalysts derived from, abundant, renewable, and sustainable natural resources [2] is an alternative to homogeneous catalysts [14], where the heterogeneous catalyst has many advantages over homogeneous catalysts, as a catalyst in the manufacture of heterogeneous catalysts biodiesel. One of the advantages possessed by heterogeneous catalysts includes being able to overcome the problems faced by homogeneous catalysts [15] In addition; heterogeneous catalysts include renewable resources, non-toxic, reusable, high catalytic activity, stability in both acidic and basic conditions and high water tolerance properties, which depend on the amount and strength of the active acid or base. Heterogeneous catalysts have the general advantage of easy separation from the reaction medium and reuse. The use of heterogeneous catalysts does not lead to soap formation, and solid acid catalysts can replace strong liquid acids, eliminating corrosion problems. The advantage of using a solid acid catalyst is that it is not sensitive to FFA content and the separation of the catalyst is easier [16].

Heterogeneous catalysts with high activity can be produced from Ca-based waste biomass material by calcining at high temperatures [18]. The heterogeneous catalysts are abundant and have outstanding potential to be developed; besides being renewable, it is also environmentally friendly and inexpensive. In addition, it also has the advantage of being a catalyst that has high activity in the manufacture of biodiesel. According to Ho *et al*., [17], the CaO catalyst can be supported by fly ash from the combustion of light fractions from coir and shells in boilers that are not utilized from waste from processing palm oil mills. The research results that have been carried out, using boiler ash as a heterogeneous base catalyst in the transesterification reaction, have been proven to be more efficient, provide high yields, and have suitable characteristics for the biodiesel produced [18]. The presence of alkaline and alkaline earth elements in the ash is used for burning plant biomass waste sources so that the ash can be used as an ash-based catalyst for biodiesel production [19]. Utilization of these waste sources for catalytic materials is a solution and a primary concern nowadays, considering that apart from its abundant availability, it is environmentally friendly and sustainable. Fly ash produced in palm oil processing in palm oil mills can be used as an alternative carrier because it is rich in Al and Si [20]. Empty palm oil bunch ash from the boiler heating station can be used directly and is considered calcined when heating in the boiler [21]. Thus, the subsequent treatment was only

dried in the oven to reduce the moisture content of the material with a standard temperature of 105ºC, then added other ingredients until it was close to neutral or alkaline.

The use of KOH in oil palm empty fruit bunch ash as a catalyst, from research conducted by Shan *et al*., [19], obtained oil conversion of 98.34% only for ash. It certainly shows that the waste of oil palm empty fruit bunches can be used as a catalyst in the transesterification reaction to produce biodiesel. According to Ho *et al*., [17], the CaO catalyst can be supported with fly ash or fly ash from the combustion of light fractions from coir and shells in boilers that are not utilized from waste from palm oil mill processing. Likewise, according to Zahrina *et al*., [22]. Fly ash or fly ash from the combustion of light fractions from coir and shells in the boiler can be used as a source of silica in the manufacture of catalysts [14,23,27]. Besides that silica also potential to fabricates inorganic membrane with dual catalyst [24-26]; Therefore, the aims of this work is to fabricate, characterize and applicate of the heterogeneous palm ash catalyst for production of biodiesel. The catalyst that has the best quality will be tested for its chemical composition analysis using the X-ray Diffraction (XRD) method, and a Scanning Electron Microscopy (SEM) test will also be carried out to determine the three-dimensional structure of the fly ash catalyst [28]. Material characterization using Fourier Transform Infra-Red (FT-IR) was carried out in the solid phase, in the form of a powder that had been dried [29], the surface and basic properties of the catalyst using Brunaeur-Emmet-Teller (BET) [30], and Thermogravimetric analyzer (TGA) analysis to test changes in the weight of the catalyst mass.

2. Materials and Methods

2.1 Method

The research method used is an experimental method, which in this study was carried out in 3 stages; the first research is to determine the test and characteristics of crude palm oil raw material, the second research is on the manufacture of palm ash catalyst, and the third is the use of a palm ash heterogeneous base catalyst in the manufacture of biodiesel. This study's materials and tools include palm fly ash from combustion at the boiler station taken at PT. Kayung Agro Lestari (PT. KAL) Manjau, Muara Pawan District, Ketapang Regency, West Kalimantan with GPS coordinates -1.448691392900511, 110.23248461639757, 98% alcohol, phenolphthalein indicator, H_2SO_4 solution, KOH solution, distilled water, filter paper, aluminium foil, methanol and phosphoric acid. The tools needed include analytical balance, magnetic steer, thermometer, viscometer, hot plate, desiccator, cup, knife, dropper, static, burette, stopwatch, condenser, pycnometer, three-neck flask, spatula, measuring flask, glass beaker, measuring cup, Erlenmeyer, pH meter, and a set of analyzers GC-MS, TGA, SEM, FT-IR, BET and X-RD.

2.2 The Manufacture of Catalysts

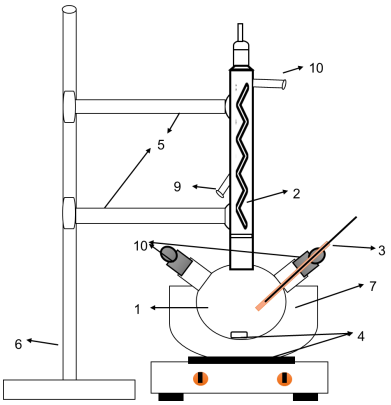
The research was carried out by preparing the raw materials for fly ash from the light fraction of shells and palm fiber which were taken directly from the palm oil mill first, then dried in the sun for 2-3 days to dry the fly ash from the light fraction of the shell and palm fiber, then sifted with a mesh size of -200+300 mesh. Process calcination is carried out by treating temperature and time, while the temperature used include 500ºC, 700ºC, and 900ºC while the length of time is 1 hour, 3 hours, and 5 hours. Making catalysts refers to research conducted by Harinda *et al*., [31]. The catalyst was made by sifting fly ash from the light fraction of shell and palm fiber using a sieve -200+300 mesh. Fly ash that escaped at the size of 200 mesh was then heated at a temperature of 540°C in the furnace for 1 hour. Furthermore, the first step is to neutralize the pH by adding H_2SO_4; neutralization will make the fly ash light fraction of the shell and palm fiber become neutral and can also remove some impurities

that can interfere with the reaction. The next step is chemical activation by mixing fly ash from the light fraction of shells and palm fiber with 50%-b NaOH. After the NaOH and fly ash were mixed and then calcined put into the furnace,

With temperature treatments of 500ºC, 700ºC, and 900ºC, the length of time is 1 hour, 3 hours, and 5 hours. After cooling, the fly ash NaOH mixture was pulverized. The addition of NaOH base was carried out to increase the ability of fly ash from the light fraction of shell and palm fiber so that its basicity increased.

2.3 Characterisation of catalyst during biodiesel fabrication

Testing of fly ash catalyst for a light fraction of shell and palm fiber that has been obtained in the manufacture of biodiesel is carried out by adding methanol added to crude palm oil in a ratio oil: methanol 1:9. In contrast, the reaction time carried out in the study was the length of the transesterification reaction time is 90 minutes, with a catalyst using 3% of the weight of the oil material. Transesterification was carried out using a series of three-neck flask, complete condenser, and heater stirred. After the filtration step is carried out, the transesterification solution is separated from biodiesel with glycerol using a separating funnel and allowed to stand until the solution forms two layers, of which the transparent top layer is the product biodiesel. The bottom layer is a glycerol product**.**



Caption:
1. Three-necked round flask
2. Condenser
3. Thermometer
4. Stirrer Magnetic + Hotplate
5. *Clamp*
6. *Stative*
7. *Bath oil*
8. Glass lid
9. Water, and
10. Steam

Fig. 1. Schematic circuit diagram for transesterification reaction process

2.4 Analysis of the Palm Fly Ash

The catalyst basicity of the catalyst was analyzed using Hammett (phenolphthalein) and pH indicators; besides that, the catalyst that has the best quality is based on the high acidity (base) value and the best biodiesel production test results are produced, then An analytical test was carried out to measure the change in mass weight of the sample/catalyst using TGA, it is a chemical composition using X-RD, and SEM test was also carried out to determine the three-dimensional structure of the fly ash catalyst, the light fraction of shells and palm fiber produced by combustion at the boiler station, while the characterization the material using FT-IR is carried out in the solid phase, in the form of a powder that has been dried. In contrast, the analysis of the surface and basic properties of the catalyst uses BET [23].

2.5 Analysis of Crude Palm Oil and Biodiesel Production Test Results

The crude palm oil raw materials analysis includes free fatty acid number, acid number, water content, and iodine number and analyzed using GC-MS to see changes in the type and composition of fatty acids in the oil crude palm oil. The biodiesel product that has been obtained is analyzed characteristics to determine the quality of crude palm oil biodiesel products with biodiesel standard ASTM D6751, including density value (g/ml), kinematic viscosity (mm^2/s), acid number (mgKOH/g), free fatty acid content (% w/w), iodine number ($gI_2/100g$), saponification number (mgKOH/g), water content (%-wb) and dirt content (%). Then, from the best quality results in the treatment, an analysis will be carried out using GCMS to see changes in the type and composition of fatty acids in the oil.

3. Results and Discussion

3.1 Characteristics of Crude Palm Oil

Crude palm oil is crude palm oil produced from the mesocarp or yellow palm fruit fiber, obtained by extraction and has not undergone a refining process, usually still contains dissolved and insoluble impurities in the oil [33]. The palm oil has the constituent components of palm oil, namely, 95.62% triglycerides, 4.00% free fatty acids, 0.20% water, 0.07% phosphatides, 0.03% carotenes, and 0.07% aldehydes. From the results of the research on the characteristics of palm oil, the results of the analysis of crude palm oil as a sample taken at the research site show that the oil has characteristic values of free fatty acids, water content, dirt content, saponification number, specific gravity, density, acid number and iodine number different.

Table 1
Characteristics of crude palm oil

Test Parameter	Unit	Analysis before purification	Analysis after purification	Quality standard CPO
Free fatty acids	% b/b	7,5139	3,8600	5 maks
Water content	%-wb	2,8700	0,0015	0,5 maks
Dirt level	%	0,0049	0,0485	0,5 maks
Saponification number	mgKOH/g	124,2100	17,5600	224-249
Density at 40ºC	g/ml	0,9400	-	-
Viscosity 40ºC	mm^2/s (cSt.)	114,0000	-	-
Acid number	mgKOH/g	19,7100	13,8400	6,9
Iodine number	$gI_2/100g$	36,0500	83,0977	50-55

In addition, analysis of crude palm oil was also carried out using GC-MS to see changes in the type and composition of fatty acids in crude palm oil.

In Figure 2. The graph of the analysis of crude palm oil shows that there are nine peaks to determine the composition of crude palm oil, including at peak 1 myristate fatty acid was 0.61%, peak 2 palmitate fatty acid was 44.14%, peak 3 palmitic fatty acid was 0.45%, peak 4 oleic fatty acid was 49.73%, peak 5 nonadecanoic fatty acid was 4.12%, peak 6 hexadecenoic fatty acid was 0.52%, peak 7 dihydromalvalate fatty acid was 0.13%, and peak 8 arachidic fatty acid was 0.30%.

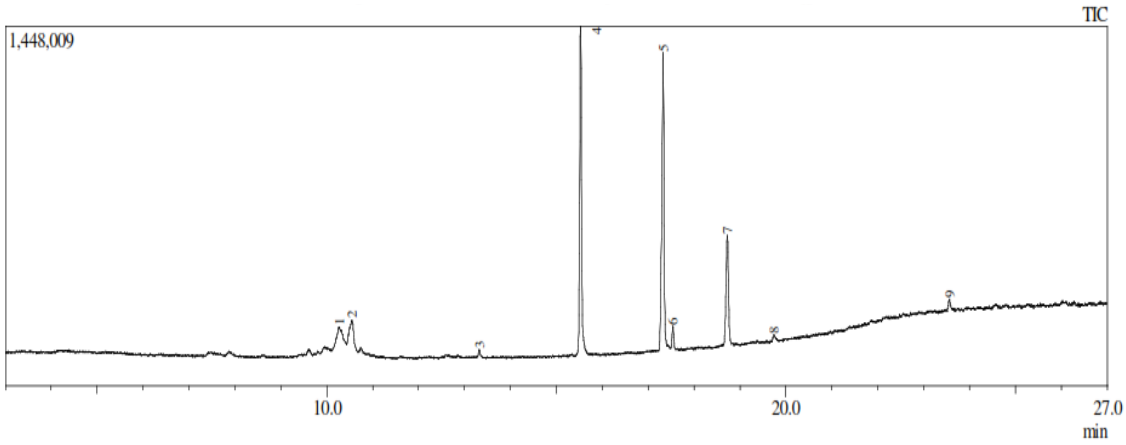


Fig. 2. Graph of crude palm oil analysis results

3.2 Characteristics of Palm Fly Ash Catalyst

Ash catalyst of a light fraction of shell and palm fiber added to biodiesel production generally increases the reaction speed in forming the desired biodiesel product [1,34]. Where is research on the manufacture of palm biomass-based catalysts from combustion residues at this boiler station, there is also CaO [35], Ca which is calcined at high temperatures [17-19], Al and Si [20]. The presence of heterogeneous catalysts, especially heterogeneous catalysts derived from waste biomass from processing in palm oil mills, is a wasteful, renewable, and sustainable natural resource [36], is more efficient and provides higher yields [37].

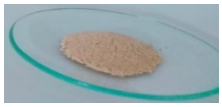
The characteristics of the fly ash catalyst from the light fraction of shell and palm fiber from the calcination, the calcination catalyst treatment at a temperature of 500ºC with a time of 1 hour, 3 hours and 5 hours tend to get brown coloured catalyst with a pH value of 12 while for the calcination catalyst treatment the temperature is 700ºC with a time of 1 hour, 3 hours and 5 hours with the same colour but a higher pH value of 13 (base), as for the cal curing temperature 900ºC with a time of 1 hour, 3 hours and 5 hours lighter colour (light brown) with a decreased pH value but still alkaline (pH 9-12). As for the fly ash catalyst test for the light fraction of shells and palm fiber in the manufacture of biodiesel, the best treatment was based on the quality of the biodiesel (parameter density g/ml, moisture content %-wb, iodine number gI_2/100g, saponification number mgKOH/g, and acid value). Free fat % w/w) the catalyst was obtained by calcination in the calcination catalyst treatment at a temperature of 700ºC for 5 hours, so that later the palm fly ash catalyst treatment was carried out by BET, X-RD, TGA, SEM, and FT-IR tests.

3.3 Characteristics of Fly Ash Catalyst from the Light Fraction of Palm Shells and Palm Fiber

Area the surface area and pore size of the catalyst can be carried out using Brunauer Emmett Teller (BET) [31], where the surface area of the solid catalyst has a direct impact on its catalytic activity [37]. In Figure 3a. Graph analysis of runaeur emmet teller test on the catalyst of a light fraction of shell and palm fiber with heating treatment at 700ºC for 5 hours shows that the calcination catalyst is microporous because pore size = 7.93 with surface area = 25.288 m^2/g. Hysteresis loop type H3. The larger surface area provides more catalytically active base sites for transesterification to occur, thus increasing the conversion rate [16]. Calcination time can affect the particle surface area, where a high calcination duration will reduce the BET surface area. During calcination, the particles can undergo condensation until the hydroxyl groups are removed, and the binding and

rearrangement of the particles result in a more stable configuration [28]. In addition, the increase in calcination temperature makes the catalyst gradually turn into stable crystals and an increase in surface area, where the closing of the pores of the catalyst by CaO crystals causes a decrease in the surface area of the catalyst. Therefore, the large catalytic surface area obtained is due to the possibility of CaO being uneven throughout the pores [38].

Table 3
Characteristics of calcined palm fly ash catalyst

No	Treatment	Analysis results	Colour	pH
1	Calcination catalyst temperature 500ºC with 1 hour		Chocolate	12
2	Calcination catalyst temperature 500ºC with 3 hours		Chocolate	12
3	Catalyst calcination temperature 500ºC with a time of 5 hours		Chocolate	12
4	Calcination catalyst temperature 700ºC with a time of 1 hour		Chocolate	13
5	Calcination catalyst temperature 700ºC with 3 hours		Chocolate	13
6	Calcination catalyst temperature 700ºC with a time of 5 hours		Chocolate	13
7	Calcination catalyst temperature 900ºC with a time of 1 hour		Slightly light brown	12
8	Calcination catalyst temperature 900ºC with 3 hours		Light brown	9
9	Calcination catalyst temperature 900ºC with a time of 5 hours		Light brown	9

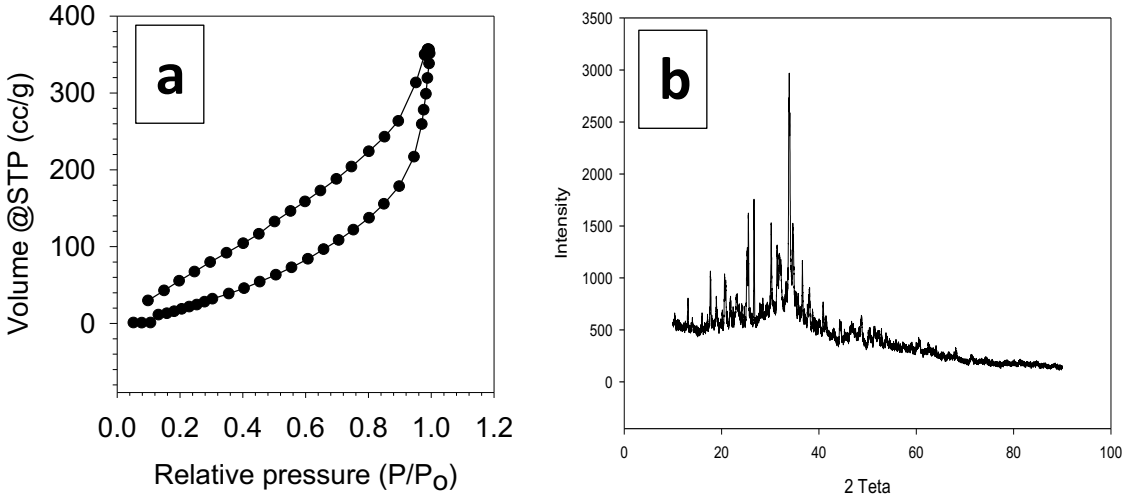


Fig. 3. Graph of a catalyst with 700ºC heating treatment for 5 hours a. brunaeur-emmet-teller test, and b. x-ray diffraction

The purpose of x-ray diffraction (X-RD) analysis is to obtain information about mineral changes and crystal structure characteristics of raw materials and products [39]. In Figure 3b. The graph of the analysis of the x-ray diffraction test (X-RD) on the catalyst by heating treatment at 700ºC for 5 hours shows that the catalyst has CaO at around 36◦ peaks. The increase in the active catalyst site is likely to occur at a higher reaction rate, and more products will be produced, while according to Setyoningrum *et al*., [40], CaO components will be impregnated in the SiO_2 pores. in fly ash [23]. According to Marwaha *et al*., [18], Boiler ash can be either bottom ash or fly ash, and although in a lower amount than bottom ash, it diffuses into the atmosphere along with the flue gases at high temperatures, with the composition of fly ash on a dry basis is 55,19% SiO_2, 30.01% Al_2O_3, 4.58% Fe_2O_3, 2.74% TiO_2, 2.12% Na_2O, 1.91% MgO, 1.40% K_2O, 1.28% BaO, and 0.77% CaO, while the results of other X-RD analysis showed that CaO formed at temperatures in the range of 550-670°C was relatively abundant [41].

Scanning electron microscope (SEM) analysis aims to determine the structure and surface morphology of the CaO catalyst [42]. Research by analyzing using SEM that has been carried out by Marwaha *et al*., [18] shows that the catalyst is filled with CaO, which is activated by calcination treatment at a temperature of 700°C for 2 hours. In Figure 4. The graph of the scanning electron microscopy analysis on the catalyst by heating treatment at 700ºC for 5 hours shows that the morphology of the calcination catalyst at a magnification of 1000 times the calcined catalyst particles in this sample is round with a smooth surface.

In Figure 5. The graph of the analysis of the thermographic analysis (TGA) and dTGA tests on a catalyst with a heating treatment of 700ºC for 5 hours shows that the catalyst shows the calcination catalyst weight loss, which is divided into 3 phases, including green line, in phase 1 catalyst material, the water loss is about 13.87%, occurs below 150◦C, phase 2 water loss, volatile, primary pyrolysis is about 2.37%, occurs at temperatures between 150-580 C, and phase 3 primary pyrolysis and material decomposition is about 7.55% at a temperature above 580◦C. While on the black line, dTGA shows a peak related to the mass change rate of about 138.2 for phase 1, 775.5 C for phase 3.

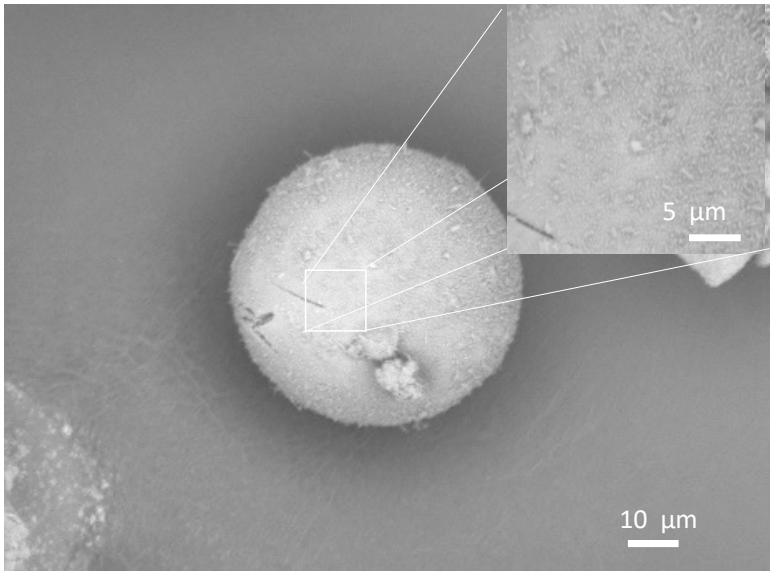


Fig. 4. Scanning electron microscopy test analysis of catalyst with heating treatment at 700ºC for 5 hours a. at 1000x magnification and b. at 5000x magnification

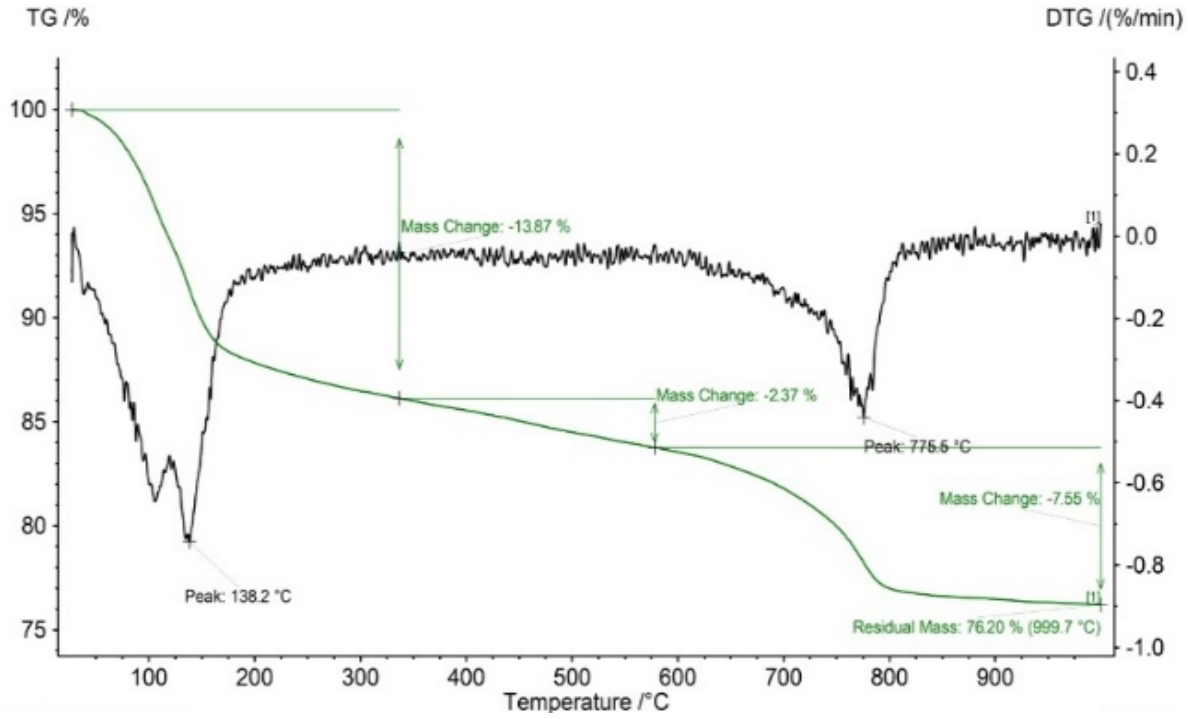


Fig. 5. Graph of thermographic analysis (TGA) and dTGA analysis of palm fly ash with heating treatment at 700ºC for 5 hours

Fourier transforms infrared (FT-IR) analysis aims to reveal the infrared spectrum pattern of the catalyst and identify the chemical bonds of a compound at a specific wavelength [42]. In Figure 6. The graph of the fourier transforms infrared test of the catalyst with a heating treatment at 700ºC for 5 hours shows that the catalyst has a bending vibration of the siloxane group at 432-590 cm-1, the carbonate group at 1400-1500 cm-1. The study results of the FT-IR spectra of the CaO catalyst

supported by fly ash were to characterize the surface absorbing species, such as carbonate and hydroxide CaO supported on fly ash [43].

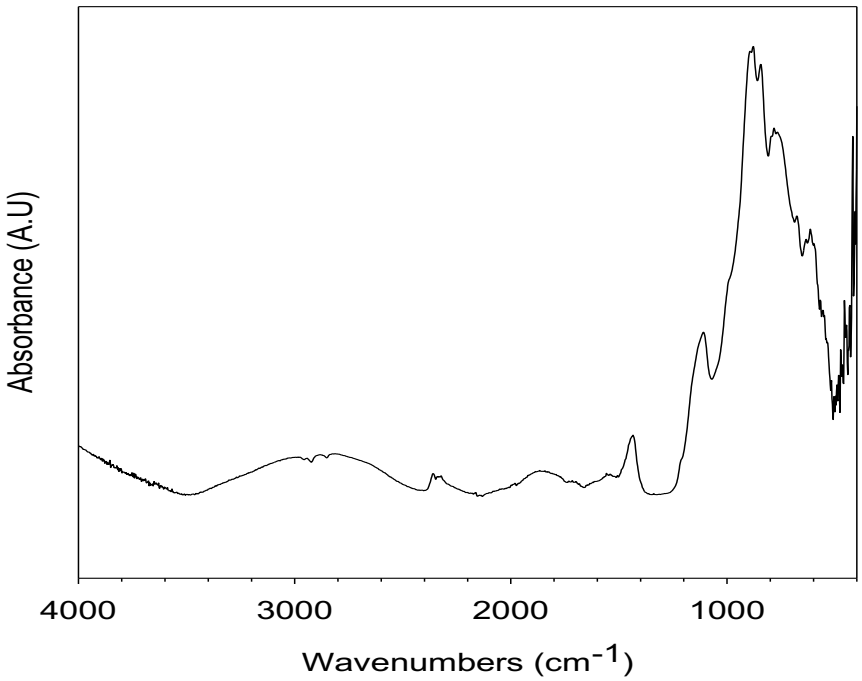


Fig. 6. Graph of analysis of the Fourier transforms infra-red test catalyst with heating treatment at 700ºC for 5 hours

3.4 The Use of Palm Fly Ash Catalyst in Biodiesel Production

Proses The process of forming biodiesel using a calcined palm fly ash catalyst is best carried out through a transesterification reaction, where the presence of the catalyst influences its success, so that in large-scale use, the catalyst used must, of course, be considered in terms of lower costs, and environmentally friendly [44]. The research was carried out by making biodiesel in a round bottom flask batch reactor equipped with a heater, magnetic stirrer and cold condenser water, by adding the best-calcined palm fly ash catalyst and mixed methanol as well as heating treatment up to 60ºC, the volume ratio of oil: methanol 1:9, and catalyst 3% w/w oil for 90 minutes. Density is one of the parameters for the success of the transesterification reaction in the manufacture of biodiesel, where specific gravity is the main property of the fuel, which directly affects the performance characteristics of the engine or the fuel itself [45] and affects the quality of atomization and combustion that occurs in the engine [46,47]. Density is related to the calorific value and the resulting power [48,49], viscosity value, where the greater the density value, the greater the viscosity value [5]. Figure 7a. The graph of the density value of biodiesel shows that the highest value of biodiesel density is 0.9133 g/ml at a temperature treatment of 500ºC with a heating time of 3 hours, while the lowest value is 0.8400 g/ml at a heating treatment of 700ºC with a heating time of 3 hours. Meanwhile, the optimum biodiesel density value meets the standards of SNI 04-7182-2006 (0.815-0.875 g/ml), namely the samples treated at 700ºC for 5 hours, 900ºC for 3 hours and 900ºC for 5 hours. with values, respectively: 0.8600 g/ml, 0.8633 g/ml, and 0.8667 g/ml. According [50], biodiesel fuel with a density that exceeds the specified standard will cause incomplete combustion reactions, so that it can increase emissions and wear of diesel engines due to conditions where the amount injected into the combustion

chamber is also greater so that the energy produced by combustion is getting bigger [51]. In addition, the density of biodiesel is known to be highly dependent on the ester content and residual alcohol, so the initial selection of vegetable oils for raw materials needs to be selective [45].

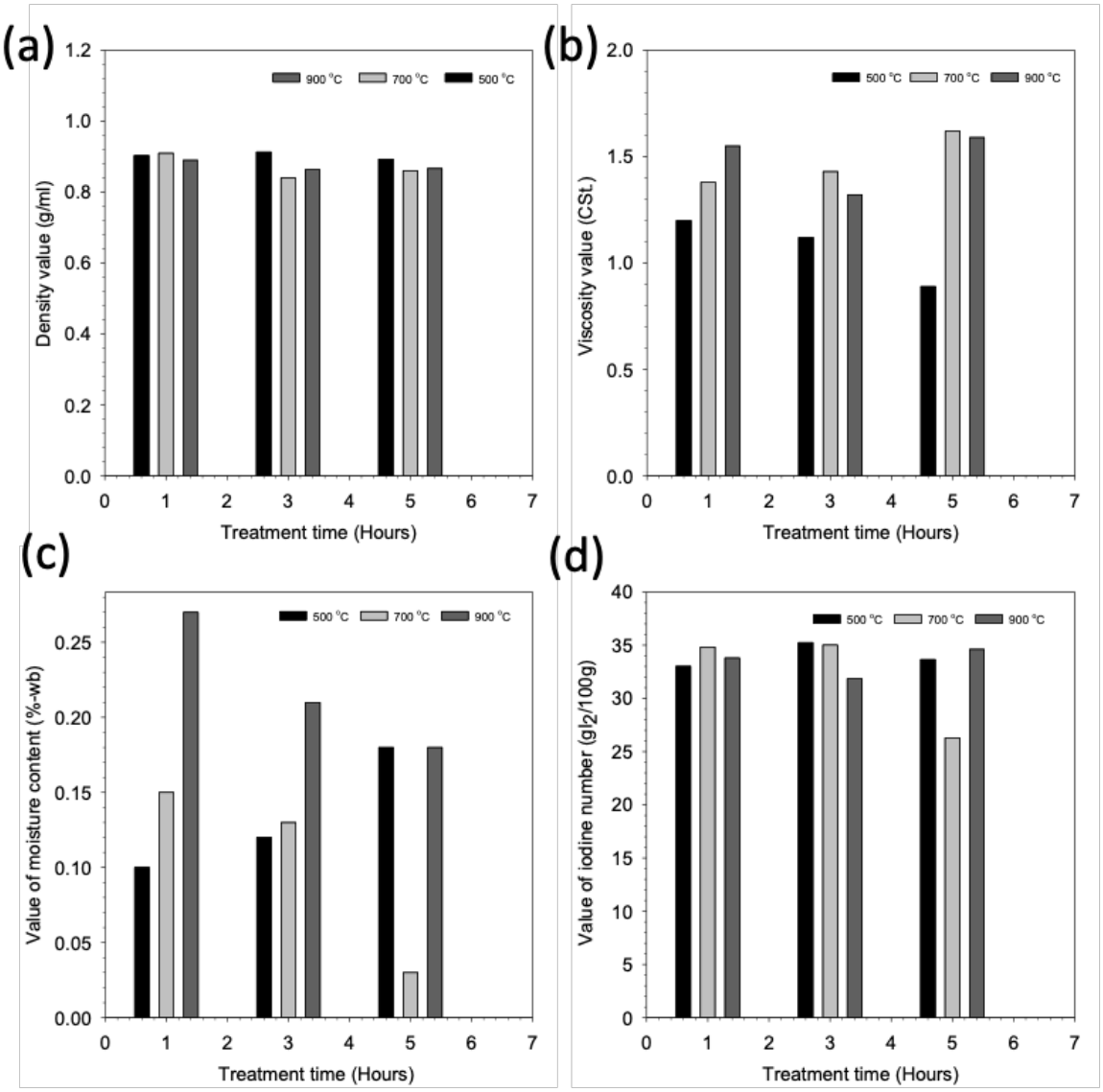


Fig. 7. a). Graph of biodiesel density with palm fly ash catalyst; b). Kinematic viscosity; c). water content; d). iodine value

Viscosity testing is one of the characteristic tests on oil to determine the level of viscosity of the oil [51], which according to Warsito *et al*., [52], viscosity is a physical property that occurs due to the interaction of molecules in the fluid so that it can withstand the fluid flow that causes the fluid to flow. Can be expressed as an indicator of viscosity, affecting the level of ease of engine flame, the quality of spraying, the size of the particles coming out of the nozzle, and the quality of the combustion engine used [45,53], affects the speed of fuel flow through the injector so that it can affect the atomization of the fuel in the combustion chamber, and viscosity also has a direct effect on the ability of the fuel to mix with air [54]. Figure 7b. The graph of the kinematic viscosity value of biodiesel shows that the heating temperature treatment of 500ºC with a time of 5 hours has the lowest viscosity value with a value of 0.8930 Cst, while the highest value of 1.6163 CSt is obtained at a heating treatment temperature of 700ºC with a time of 5 hours, and the treatment This is closer to

a good biodiesel quality standard according to SNI 04-7182-2006, which is between 2.3-6.0 CSt. The higher the viscosity value, the thicker and more challenging the biodiesel will flow [5,55], friction losses in the pipe, pump work will be heavy, filtering is complex, and large amounts of dirt may be deposited, and it is challenging to atomize fuel [56]. High viscosity usually above 5.5 CSt is not expected because it can hinder the engine running and make it difficult for fuel injection into the combustion chamber [57], resulting in larger droplets that can cause incomplete combustion [58], forms deposits in the engine [59], affects the fast work of the injection tool and makes it difficult to ignite fuel [31], causing wear [51], and aggravates pump performance [60]. On the other hand, if the viscosity value of biodiesel is lower than the minimum value of the quality standard, it indicates the presence of impurities in excess in the form of light fractions in biodiesel, especially in the form of residual methanol [61], causing a leak in the fuel injection pump [28], wear and tear on some parts of the fuel pump [60,62] , where the biodiesel fuel produced is not able to provide lubrication for the injection pump [58].

In Figure 7c. The graph of the value of the water content of biodiesel shows that the water content value at a heating temperature of 700ºC for 5 hours has the smallest water content value of 0.03%, while the highest value is 0.27% at a heating temperature of 900ºC for a long time. 1-hour time. A good quality standard of biodiesel according to SNI 04-7182-2006 for water content, which is a maximum of 0.05%, so samples with a heating treatment of 700ºC with a duration of 5 hours meet these standards. The presence of a high-water content in biodiesel fuel used as fuel will cause a decrease in the heat of combustion, foaming, corrosive if it reacts with sulfur because it will form acid and provide space for microbes to grow so that it will become an impurity for biodiesel [48,60]. The presence of excess water content in biodiesel fuel, then the transesterification reaction causes the catalyst used to be more dilute so that the reaction slows down and also causes a hydrolysis reaction of triglycerides followed by a saponification reaction [63,64]. This reaction will result in an odor; hydrolysis will produce a rancid flavour and odor in the oil [64]. From the results of previous research, it shows that the longer the transesterification reaction time in the manufacture of biodiesel can cause a decrease in the value of the water content of biodiesel, besides that the duration of the perfect transesterification reaction and the presence of heat in the reaction will cause water to be broken down into its original elements [65].

Lod number is a chemical property present in the oil to determine the number of double bonds or unsaturated bonds in oil [66,67], including showing the level of unsaturation or the number of double bonds of fatty acids making up biodiesel. A high iodine number is an unfavourable property for fuels, including biodiesel fuel, where oil containing unsaturated fatty acids or having a high number of double bonds will be easily oxidized when the oil is in contact with oxygen [48]. Likewise, according to Purnomo *et al*., [68], biodiesel with a high iodine number is more easily oxidized when in contact with air or oxygen. The iodine number according to the SNI standard 04-7182-2006, which does not exceed the value of 500, the higher the iodine value, the higher the number of double-bonded fatty acids contained in the oil [48]. Meanwhile, from the analysis results, as shown in Figure 7d. The graph of the value of the biodiesel iodine number shows that all treatments are included in the biodiesel quality standard of SNI 04-7182-2006. The higher the iodine number, the lower the oxidation stability will lower the quality of biodiesel products. In addition, the results of research conducted by Suleman *et al*., [67] show that the increase in the value or number of iodine is in line with the increase in the concentration catalyst; this is because the fatty acid bonds are not completely degraded during the heating process. This condition causes the iodine number to increase.

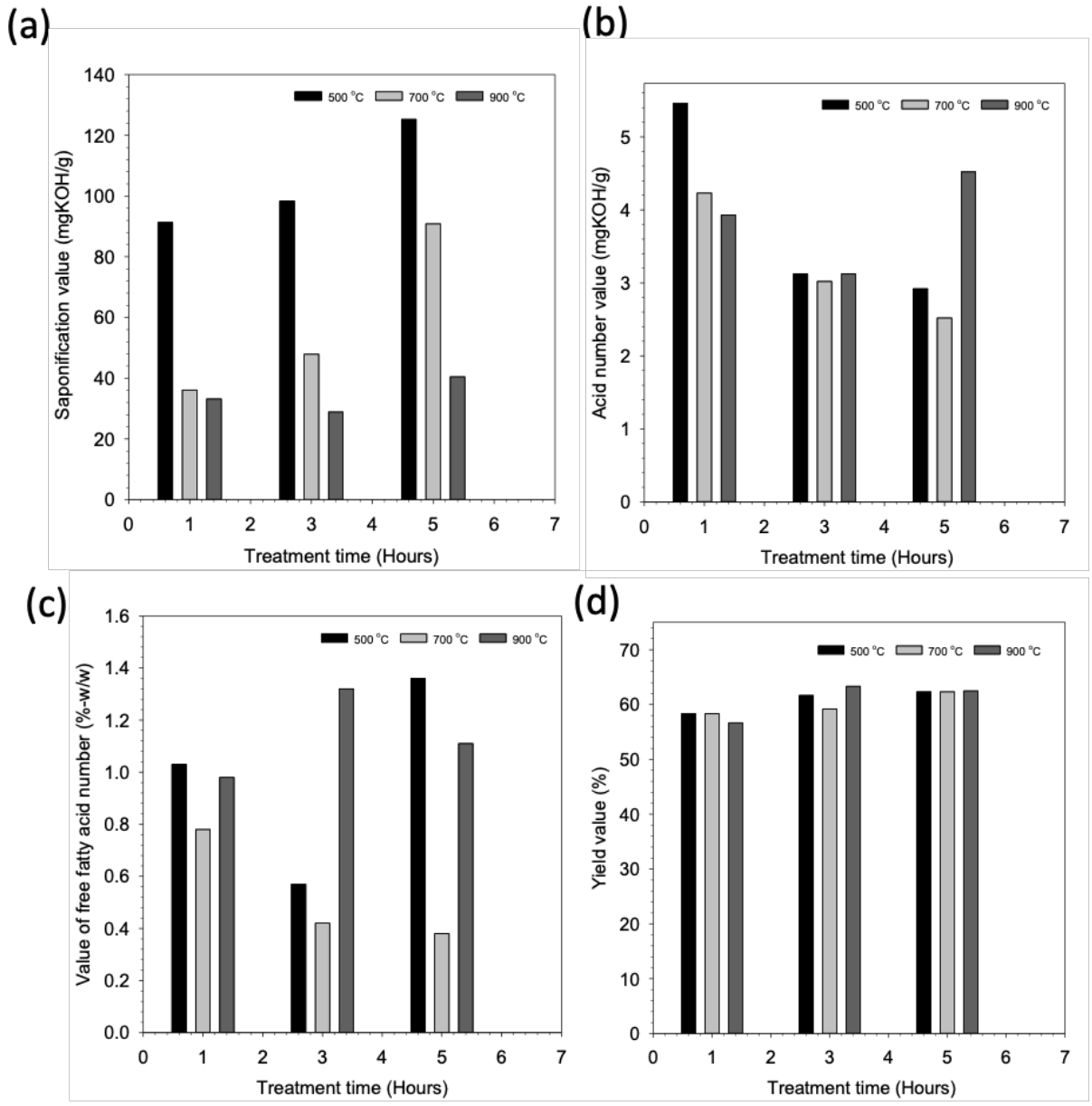


Fig. 8. a). Graph of saponification number of biodiesels with palm fly ash as a catalyst; b). acid number value; c). free fatty acid value; d). yield value

The saponification number in biodiesel products is related to the molecular weight of the product; where biodiesel has a higher molecular weight, it will have a lower saponification number, and vice versa [50,66], the low number of saponification obtained was due to the high content of intermediate compounds in biodiesel. In biodiesel products, the larger the soap product, it will cause the methyl ester washing process to be complicated because the soap will bind the methyl ester product with water [65,69,70]. If there are fewer short-chain compounds in biodiesel, it shows that the free fatty acid content in the oil is getting less [67,71], the better the combustion process in a diesel engine [72]. Meanwhile, according to the Indonesian national standard, namely SNI-04-7182-2006, the biodiesel quality requirement for saponification is less than 115. In Figure 8a. The graph of the saponification number value for biodiesel shows that the saponification number value in all treatment ranges from the smallest 28.88 mg-KOH/g at a heating temperature of 900ºC with a long heating time of 3 hours to 125.28 mg-KOH/g at a heating temperature of 500ºC with a heating time

of 5 hours. Hence, all of these treatments were still below the 115 mg-KOH/g for the saponification number parameter. The results of research conducted by Oktaningrum [73] show that the increase in the number of saponification along with the addition of catalyst concentration, especially alkaline catalysts, is due to the use of excessive alkaline catalysts, and high temperatures in the transesterification reaction will cause a saponification reaction in the manufacture of biodiesel. The value of the numbers of saponification in the sample should decrease with the lower concentration of the catalyst used. The process that occurs during the transesterification reaction is binding free fatty acids with a base as a reaction catalyst so that soap will be formed [70].

The acid number dramatically affects the quality of biodiesel, where if the acid number is high, the biodiesel quality will be lower. The acid number indicates corrosive properties [60]. In addition, the presence of an acid number in biodiesel, it is inevitable that there will be free fatty acid content in the biodiesel, so that it can result in the formation of ash during combustion [54]; and also determine the level of damage during storage [65], which will result in the process of rusting or corroding the engine [56]. According to Andalia and Pratiwi [64], the parameter or value limit for the higher acid number is if the acid number or number contained in the biodiesel is more than 0.8 mg KOH/g, so it will cause the formation of ash during combustion, fuel deposits fuel and reduce the life of the fuel pump and filter. In Figure 8b. The graph of the acid number value of biodiesel with a palm fly ash catalyst shows that all treatments carried out, both temperature and heating time, still did not exceed the acid value below 0.8 mg-KOH/g. In this case, the presence of a high acid number is biodiesel that still contains free fatty acids [74]. The high acid number may occur because of the amount of catalyst added to the biodiesel manufacturing process [72,75]. While the acid number is below 0.8 mg-KOH/g, indicating that the biodiesel product is not corrosive does not cause damage injector [50], indicating that free fatty acids can be removed or reduced through pretreatment. That has been done before [48]. In the transesterification process, fatty acids present in triglycerides will react with methanol to produce methyl esters, so this condition will also impact decreasing the value of the acid number produced [70].

In Figure 8c. The graph of biodiesel's free fatty acid value shows that the free fatty acid value ranges from 0.38%-w/w to 1.36%-w/w, where the value is the lowest at 700ºC heating treatment. With a length of time of 5 hours and the highest was in the treatment at a heating temperature of 500ºC for a long time of 5 hours, while the optimum free fatty acid value and met the biodiesel quality standard according to SNI-04-7182-2006 (maximum 0.74%-w/w), including the treatment at a heating temperature of 500ºC for 3 hours, a temperature of 700ºC for 3 hours, and a temperature of 700ºC for 5 hours with successive values of 0.57%-w/w, 0.42%-w/w, and 0.38%-w/w. According to Andalia and Pratiwi [64], biodiesel with low free fatty acid content is good biodiesel to be used as fuel [76]. The content of free fatty acids in raw materials is one of the determining factors for the type of biodiesel production process. Generally, pure oil has a low free fatty acid content of about 2% so that it can be directly processed by the transesterification method. If the free fatty acid content of the oil is still high, a pre-esterification process was previously carried out [77,78]. According to Sundaryono *et al*., [79], the value of the fatty acid content If the free fatty acid content is less than 2%, it can be directly transesterified using an alkaline catalyst. However, if the free fatty acid content turns out to have a value greater than 2%, it needs to be esterified first using an acid catalyst such as an H_2SO_4 catalyst [80]. The number of double bonds determines the level of saturation and the length of the carbon chain, namely the distribution of atoms in the compound, where the length of the carbon chain used for biodiesel production varies depending on the source feedstock [81,82]. Free fatty acids are essential factors that determine the amount of catalyst, the type of catalyst to be used, and biodiesel storage stability [83]. The higher the acidity value of the oil, the higher the amount of catalyst consumption, and it will be easy to form more soap during the transesterification process.

Dramatically affects the low conversion rate and yield in transesterification [6], and oils with a free fatty acid content of more than 2% require an esterification and transesterification reaction process.

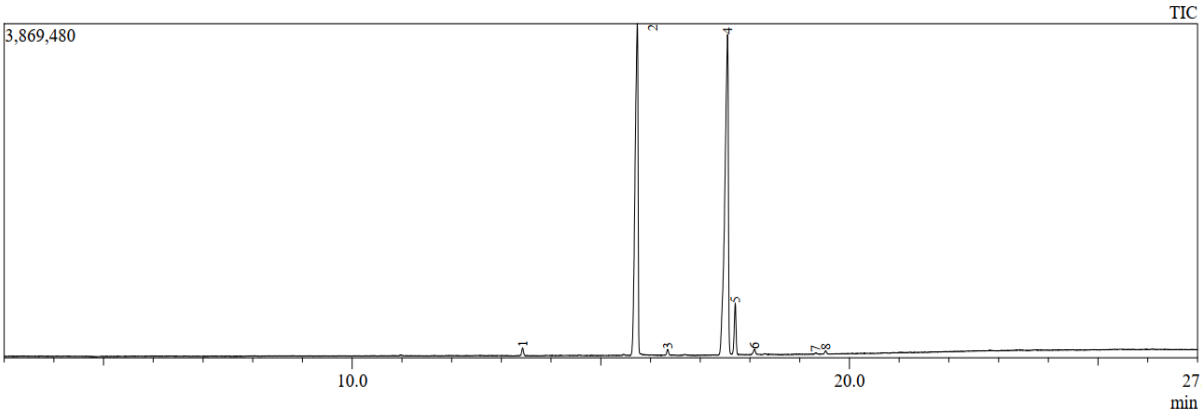


Fig.9. Graph of GC-MS analysis of palm oil biodiesel

The analysis results on biodiesel were also carried out using gas chromatography-mass spectroscopy (GC-MS) to see changes in the type and composition of fatty acids in the biodiesel product. In Figure 9. The graph of the analysis of crude palm oil biodiesel based on fly ash catalyst, a light fraction of shells and palm fiber, it appears that there are six peaks to determine the composition of biodiesel, including at peak 1 myristate fatty acid methyl ester 0.61%, peak 2 palmitate fatty acid methyl ester 44.14%, peak 3 palmitate fatty acid methyl ester 0.45%, peak 4 oleic fatty acid methyl ester 49.73%, peak 5 acid methyl ester nonadecanoate fat 4.12%, peak 6 hexadecenoate fatty acid methyl ester 0.52%, peak 7 dihydromalvalate fatty acid methyl ester 0.13%, and peak 8 arachidic fatty acid 0.30%.

4. Conclusion

This research was carried out in 3 stages; the first stage is to determine the test and characteristics of crude palm oil raw material, the second is on the manufacture of palm ash catalyst, and the third is the application of a heterogeneous catalyst based on palm fly ash in the manufacture of biodiesel. Fabrication of heterogeneous catalysts derived from fly ash fraction of light shell and fiber of palm oil mill solid waste which obtained from peat wetlands are successfully acquired in this work. The characteristics of crude palm oil after purification using 5% shell activated charcoal an increase in quality, including free fatty acid number (3.86 wt%), water content (0.0015%-wb), impurities content (0.0485%), and acid value (mgKOH/g) is 3.8600; 0.0015; 0.0485; and 13.8400, respectively. The quality of biodiesel produced in the calcination catalyst treatment with a temperature of 700ºC for 5 hours for the parameters of density (0.860 g/ml), water content (<0.05 %-wb), iodine number (<30 gI^2/100g), saponification number < 115 mgKOH/g), and number free fatty acids (<0.4% w/w) have a value according to the Indonesian biodiesel standard SNI 04-7182-2006, with consecutive values: 0.8600; 0.03; 26.30; 90.88 and 0.38. Meanwhile, the heterogeneous fly ash fraction of light shell and fiber of palm oil mill solid waste catalysts have micropore structure with average pore size 7.93 nm with surface area 25.3 m^2/g. The morphology of catalyst particles is spherical with a smooth surface.

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