

Biodiesel from Pyrolysis Fatty Acid Methyl Ester (FAME) using Fly Ash as a Catalyst

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ABSTRACT

Biodiesel is an environmentally acceptable alternative fuel that has no negative health effects and may be used in vehicles to cut emissions when compared to regular oil. Biodiesel can be produced from the pyrolysis process of Fatty Acid Methyl Ester (FAME) using a fly ash catalyst. The purpose of this study was to obtain biodiesel with a low water content of hygroscopic nature. The pyrolysis process using fly ash catalyst occurs in a temperature range of 141-200°C, which has an initial boiling point (IBP) of 151°C. The results showed that the characteristics of the biodiesel produced were following the standards of the Director General of Oil and Gas, namely density 842,500- 847,500 kg/m³, viscosity 3.053-3,371 cSt, CCI of 48.7-49.7°C at 181-200°C, flash point 58-59°C, content water 223- 218 ppm, and sulphur content of 700 ppm.

Keywords: *biodiesel, FAME, fly ash catalyst*

1. INTRODUCTION

Human activities cannot be separated from the use of fuels derived from fossil energy. The intensity of uncontrolled use and lack of energy conservation poses a problem in fossil fuels availability. The limited reserves of this energy source require serious attention, such as looking for other alternatives by optimizing the use of renewable energy sources. However, the alternatives developed must be able to produce energy in large quantities at low costs and have minimal impact on the environment to replace the fossil energy [1]-[3].

The use of renewable energy sources in the form of biofuels needs to be increased. Considering that the need for fossil fuel sources is increasing every year and these fuels are limited and expensive, it encourages various research and developments to get fuel that is cheaper, environmentally friendly, and from renewable natural materials [4]-[6].

Biodiesel is a biomass-based fuel that can be used to replace petroleum-based diesel. One of the benefits of biodiesel fuel is that it is a renewable energy source that is more environmentally friendly than fossil fuels because it emits far fewer greenhouse gases than fossil fuels. As a result, biodiesel has the potential to solve

energy issues in emerging countries, particularly those that do not produce oil [7].

Biodiesel is an alternative fuel from renewable sources with fatty acid ester compositions from vegetable oils, including palm oil, coconut oil, jatropha oil, kapok seed oil. There are still more than 30 kinds of Indonesian plants that have the potential to be used as biodiesel [8]-[10].

The use of vegetable oils directly as fuel for diesel engines has problems, mainly related to the properties of vegetable oils, namely high viscosity, low volatility, and containing unsaturated compounds / more than one double bond (polyunsaturated). However, these properties can be improved in several ways, namely pyrolysis, microemulsification, dilution, and transesterification [11][12].

Based on the content of free fatty acids in vegetable oil, the commercial biodiesel production process usually uses homogeneous catalysts, such as esterification with an acid catalyst and transesterification with a base catalyst. However, the use of this homogeneous catalyst can cause problems in the resulting product, for example, a product that still contains a catalyst, so it must be separated again. In this study, a catalyst was used from coal ash waste (fly ash) which was activated

so that it would facilitate the separation of the catalyst from the product. Fly ash has a hollow structure composed of several porous oxides, such as SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , and CaO [13]-[15].

Making biodiesel from CPO can be done through esterification and transesterification reactions to convert oil (triglycerides) into fatty acid methyl esters. The content of free fatty acids (FFA) in CPO raw materials is one of the determining factors for the method of making biodiesel. One form of utilization of CPO is processed into FAME so that the specifications are close to petroleum diesel specifications. The study aimed to obtain biodiesel from Fatty Acid Methyl Ester (FAME) through a pyrolysis process using a fly ash catalyst that had been activated using 1M NaOH, the concentration of the catalyst used was 10%. This biodiesel product is tested for quality based on the value of density, flash point, boiling point, water content and sulphur content of each temperature range which refers to the characteristics and specifications of the quality requirements of the Director General of Oil and Gas [16]-[18].

2. MATERIAL AND METHOD

2.1. Material and Equipment

The FAME that will be utilized as a sample will be obtained from the tank drainer (the part of the tank that serves to take samples or materials in the tank). After allowing the sample to sit for three days, it was deposited. Figure 1 depicts the pyrolysis apparatus used in the conversion process. Supporting equipment for product analysis includes viscometers, density meters, flash point meters, X-ray sulphur, Karl Fisher Moisture Measurement, and calculated cetane index (CCI).

2.2. Sampling Method

The pyrolysis process is carried out in a pyrolysis unit with a 7-liter capacity. The cracking process at temperatures ranging from 161 to 170 °C, 171 to 180 °C, 181 to 190 °C, and 191-200 °C. The volume of liquid fuel produced was measured and recorded. In addition, the condensate is measured with a measuring cup in order to quantify its volume and study its qualities.

2.3. Sampling Testing

The density, viscosity, cetane number, flash point, water content, and sulphur content of the fuel product produced from the pyrolysis process with FAME as the raw material are all measured to determine biodiesel quality. To establish the quality of biodiesel obtained from the pyrolysis process, a study examined at the qualities of biodiesel fuel parameters. The parameters of the resulting fuel are compared to those of PT Pertamina

RU III biodiesel to see if there is a drop in quality or if they remain the same, including water content. For 5 days, data was retrieved at temperatures ranging from 161°C to 200°C [19].



Figure 1. tool

Caption:

1. Reactor,
2. Condenser,
3. Preheater,
4. Stainless steel shell,
5. Pressure control,
6. Thermo Control,
7. Control Valve,
8. Water cooler (inlet),
9. Water cooler (outlet),
10. Output Product,
11. Liquid fuel product tank

3. RESULTS AND DISCUSSION

3.1. Characteristic of Fly Ash as Catalyst

The fly ash catalyst, which is coal fly ash from the boiler combustion chamber, was tested for its characteristics. Using an Inductivity Coupled Plasma (ICP) instrument, a characteristic test is performed to determine the components present in the fly ash catalyst.

Table 1. The results of an ICP investigation of the Fly Ash catalyst's properties

| Sample | Analysis Parameters | Method | Unit | Results |
|---------|---------------------|--------------------------|------|---------|
| Fly Ash | Al | IP 501/ASTM D 5184 | % | 7.52 |
| | Si | | % | 24.44 |
| | Fe | | % | 46.18 |
| | Ca | | % | 16.36 |
| | K | | % | 0.32 |
| | Mn | | % | 0.44 |
| | Ni | | % | 0.88 |
| | Cu | | % | 0.08 |
| | Zn | | % | 0.01 |
| | V | | % | 0.01 |

Based on the table, the content of Fe and Si elements is more significant percentage than other elements. Furthermore, can be concluded based on the composition *fly ash* entry class f ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}$) > 70 % derived from bituminous coal [19].

3.2. Characteristics of FAME as raw material

Characteristic results obtained after deposition of at least 3 (three) days to determine the characteristics of FAME before using raw materials. The results obtained for the cetane number, density, viscosity, sulphur content, flash point and color are still within the minimum and maximum limits, while the water content is still above the maximum limit, the value can be seen in Table 2.

Table 2. Result of FAME analysis as raw material

| Characteristics | Units | Results |
|--|----------------------|---------|
| Cetane Number | -- | 58.3 |
| Density @ 15 °C | kg/m ³ | 854 |
| Viscosity @ 40 °C | mm ² /sec | 4.83 |
| Sulphur Content | % m/m | 0.07 |
| Evaporation point @ Distillation 90% (vol) | °C | 333 |
| Flash Point | °C | 152 |
| Moisture Content | mg/kg | 623 |
| Colour | - | 1 |

3.3. The density of biodiesel from FAME pyrolysis at temperature range of 141-200 °C

The calorific value and power produced by the combustion process of fuel are affected by density. A high density value indicates that the fuel contains a large number of components. This component will increase the calorific value of the fuel combustion process by extending the atomization process of the fuel components during the combustion process.

According to the Director General of Oil and Gas's quality standard, the required density for biodiesel is 815-860 kg/m³ at 15 °C. A density value that meets the required quality standards can produce a complete combustion reaction in the engine, whereas a density value that exceeds the standard causes the combustion reaction to become imperfect, increasing emissions and engine wear. Figure 2 depicts the results of the analysis of the density value of biodiesel fuel [20].

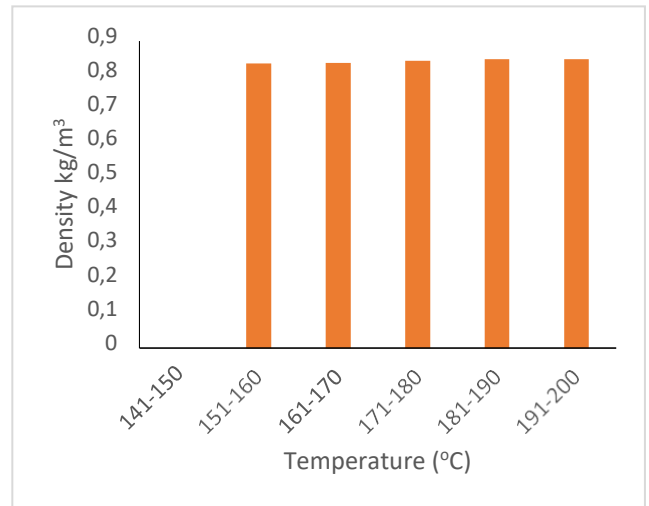


Figure 2. Biodiesel Density Result of FAME Pyrolysis

Figure 2 shows that for the composition of FAME raw materials with Fly Ash catalyst starting from a temperature of 151-160°C with a density of 0.8350 kg/m³, 161-170°C density 0.8360 kg/m³, 171-180°C density 0.8425 kg/m³, 181-190°C density 0.8465 kg/m³ and 191-200°C density 0.8475 kg/m³. All of them obtained the results of density analysis between the minimum and maximum limits of the required quality standards. When viewed from the temperature range, the density value of the biodiesel product is heavier if the biodiesel product is obtained at a higher temperature [21].

3.4. Viscosity of biodiesel resulting from FAME pyrolysis at temperature range of 141-200 °C

A high viscosity will increase friction loss in the pipe, make the pump work harder, and complicate the filtering process, increasing the possibility of dirt settling and fuel fogging. A low viscosity causes the lubrication to thin, causing wear and damage to the combustion engine [22].

FAME's kinematic viscosity is nearly twice that of diesel oil, which is critical for engine lubrication. FAME is a vegetable-derived material with low sulphur and aromatics content. Furthermore, the level of Particulate Matter emissions produced is lower (PM). The required biodiesel viscosity value at 40 °C, according to the Director General of Oil and Gas, is 2.0-4.5 cSt.

Figure 3 depicts the results of an analysis of the viscosity value of biodiesel fuel. Figure 3 shows that for the composition of FAME raw materials with Fly Ash catalyst starting from a temperature of 151-160°C with a viscosity of 2.459 cSt, 161-170°C viscosity 2.652 cSt, 171-180°C viscosity 3.053 cSt, 181-190°C viscosity 3.262 cSt and 191-200°C viscosity 3.371 cSt. When viewed from the temperature range, the viscosity value of biodiesel products is greater if the biodiesel yields are obtained at higher temperatures [23].

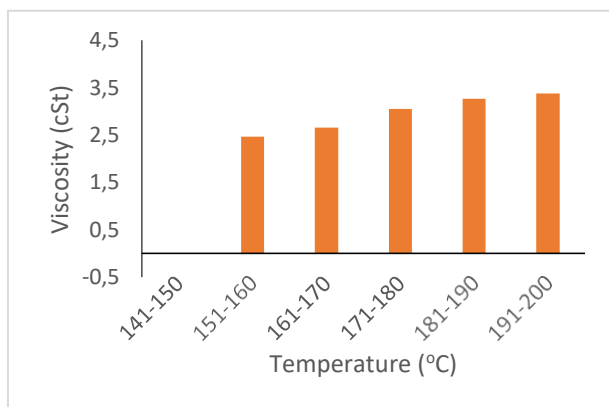


Figure 3. Biosolar Viscosity of FAME Pyrolysis

3.5. Calculated cetane index (CCI) of biodiesel from FAME pyrolysis at temperature range of 141-200 °C

The cetane number is a number that shows the results of testing the combustion quality of a diesel fuel by comparing the reference fuel with the known cetane number in advance. The FAME cetane number according to SNI is at least 51, while the standard for petroleum diesel according to the Director General of Oil and Gas is at least 48 and the Calculated Cetane Index (CCI) is at least 45.

The cetane number indicates how quickly diesel engine fuel can be injected into the combustion chamber so that it burns spontaneously in the engine. The cetane number of petroleum diesel is influenced by the structure of the constituent hydrocarbons. The lower the cetane number, the lower the ignition quality because it requires a higher ignition temperature.

FAME has a higher cetane number or calculate cetane index (CCI) than petroleum diesel, making it ideal for boosting auto-ignition in diesel engines. The more devils there are, the longer the fatty acid's carbon chain is and the more saturated the molecule is [24].

The results of the CCI analysis of biodiesel fuel at various temperature ranges can be seen in Figure 4.

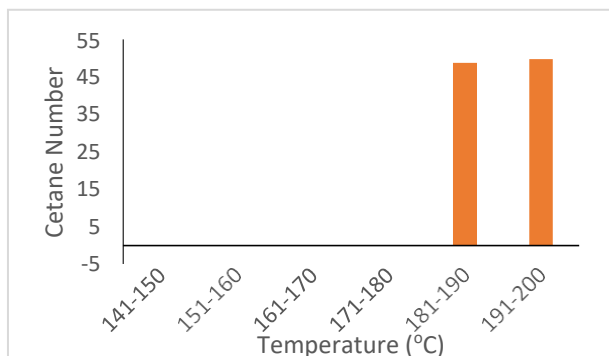


Figure 4. Calculated Cetane Index (CCI) of FAME Pyrolysis

The ASTM D613-80 method is a measurement method in determining the quality of biodiesel combustion or also said to determine the cetane number of diesel fuel, for the composition of FAME raw materials with Fly Ash catalyst starting from a temperature of 181-190°C with a cetane number of 48.7 and 191-200°C a cetane number of 49.7. The temperature range obtained by the CCI analysis value is above the minimum quality limit required by the Director General of Oil and Gas.

3.6. Flash point of biodiesel from FAME pyrolysis at temperature range of 141-200 °C

The flash point value of FAME is much higher than the flash point value of petroleum diesel, so the blending formulation with more FAME composition will result in the flash point of the biodiesel produced also increasing. The flash point of biodiesel also increased every week for one month of storage. Referring to the quality requirements of the Director General of Oil and Gas, the flash point of each biodiesel product composition has passed the minimum required limit [25]. In the quality requirements of the Director General of Oil and Gas, the flash point value is set at a minimum value of 52°C for petroleum-based diesel fuel. The flash point value (flash point) of biodiesel fuel that has been obtained from this study can be seen in Figure 5.

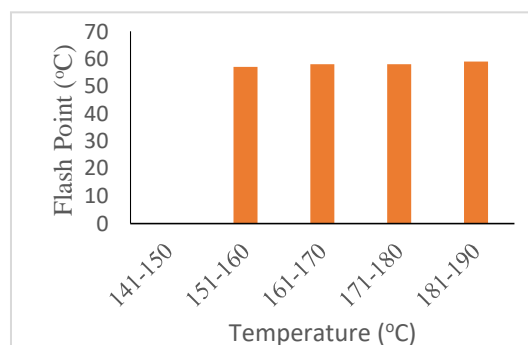


Figure 5. Flash Point of Biodiesel Results of Pyrolysis

Figure 5 shows that for the composition of FAME raw materials with Fly Ash catalyst starting from a temperature of 151-160°C with a flash point of 57°C, 161-170°C flash point 58°C, 171-180°C flash point 58°C, 181-190°C flash point 58°C and 191-200°C flash point 60°C. All of them obtained the results of flash point analysis above the minimum required quality standard. When viewed from the temperature range, the flash point value of biodiesel products is higher if the biodiesel yields are obtained at higher temperatures [26].

3.7. The water content of biodiesel from FAME pyrolysis at temperature range of 141-200 °C

In some countries with winters, the water content in diesel engine fuel might crystallize, obstructing the passage of fuel via the injectors. Furthermore, water can promote corrosion and the growth of microorganisms, which can clog the combustion chamber and prevent fuel from entering. Clogging and engine damage can also be caused by sediment [27].

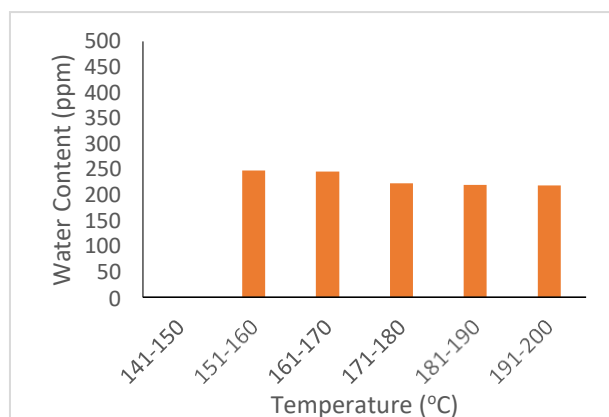


Figure 6. Water content of FAME Pyrolysis Results

Figure 6 shows that for the composition of FAME raw materials with Fly Ash catalyst starting from a temperature of 151-160°C with a water content of 248 ppm, 161-170°C water content 245 ppm, 171-180°C water content 223 ppm, 181-190°C water content 219 ppm and 191 -200°C water content 218 ppm. All water content analysis results are below the maximum required quality standard and are in accordance with the objectives of this study. When viewed from the temperature range, the value of the water content of biodiesel products is less if the biodiesel yields are obtained at higher temperatures.

3.8. Sulphur content of biodiesel resulting from FAME pyrolysis at a temperature range of 141-200 °C

Sulphur is the biggest adversary of diesel engines, as the higher the sulphur concentration, the more acidic the engine will become. Engine components, from scale to fuel lines, will be damaged as a result of this circumstance. Crust in the fuel lines can obstruct the flow of fuel into the cylinders, resulting in a direct impact on engine performance, ranging from lower power to more significant damage. Premature combustion, often known as knocking, occurs here, causing the engine to tickle [9].

Injector components can be damaged by high sulphur levels, resulting in poor combustion. The cleaner the exhaust gas emissions, fuel lines, diesel filters, and combustion chamber are, the lower the sulphur content. Sulphur also affects engine life. The

higher the sulphur which is acidic, the more the engine will rust easily [14].

High sulphur levels in diesel fuel have consequences that go beyond vehicle harm. When combustion gases from an engine are mixed with air, sulphur dioxide (SO₂) is formed, and when SO₂ is coupled with water vapor, an acidic composition is formed, which is damaging to the body [26].

FAME is devoid of nitrogen and aromatic molecules, with a sulphur content of less than 155 ppm (parts per million) [9]. FAME also includes 11% oxygen by weight, which lowers energy content while also lowering exhaust gas emissions such as carbon monoxide (CO), hydrocarbons (HC), particulates, and soot. Biodiesel has a lower energy content than diesel, but its fuel efficiency is similar to petroleum diesel, which implies that the power and torque produced are proportionate to the calorific value content of the combustion.

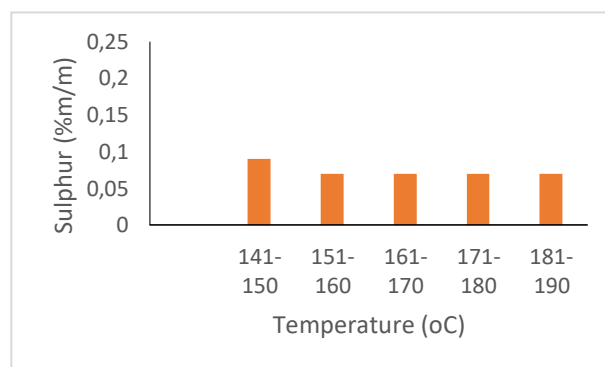


Figure 7. Sulphur content of biodiesel from FAME pyrolysis

Figure 7 shows that the composition of FAME raw materials with Fly Ash catalyst starts at a temperature of 151-160°C with a sulphur value of 0.09% w/w, and 161-200°C a sulphur value of 0.07% w/w. Everything is obtained from the analysis that the sulphur content of biodiesel is far below the maximum required limit.

4. CONCLUSION

Biodiesel is an environmentally friendly diesel fuel, according to the pyrolysis results, because it creates lower exhaust pollutants, namely free sulphur. The sulphur content of 0.1 percent w/w is well below the quality standard limit's maximum value. According to the findings, the viscosity density value of the cetane number, flash point of water content, and sulphur value of biodiesel are still within the range of the Director General of Oil and Gas' quality criteria.

AUTHORS' CONTRIBUTIONS

All of the authors are involved in the process of designing the equipment and analysis biodiesel. The first and corresponding author contribution is

responsible for data processing and manuscript writing. The second author is responsible for equipment design and data processing. The third author is responsible for analysis biodiesel sample. The fourth author is responsible for funding arrangement.

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