Synthesis of kemiri sunan (*reutealis trisperma* (blanco) airy shaw) H-FAME through partially hydrogenation using Ni/C catalyst to increase oxidation stability

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Abstract. Hydrogenated FAME (H-FAME) synthesis of Kemiri Sunan (*Reutealis Trisperma* (Blanco) Airy Shaw) using Nickel/Carbon catalyst is one of the methods to improve the oxidation stability of Kemiri Sunan biodiesel. The partial hydrogenation reaction breaks the unsaturated bond on FAME (Fatty Acid Methyl Ester), which is a key component of the determination of oxidative properties. Changes in FAME composition by partial hydrogenation reaction are predicted to change the oxidation stability, so it does not cause deposits that can damage the diesel engine injection system, pump system, and storage tank. Partial hydrogenation reaction is under conditions of 120 °C and 6 bars with 100:1, 100:5, 100:10 % wt catalyst in the stirred semi-batch autoclave reactor. H-FAME synthesis with 100:5 % wt Ni/C catalyst can decrease the iodine number which is the empirical measure of the number of unsaturated bonds from 166.77 to 155.64 (g-I₂/100 g) with an increase of oxidation stability from 650 to 665 minutes.

1. Introduction

Biodiesel is a biofuel that reduces the level of exhaust emissions. In addition, biodiesel mixes perfectly with diesel oil (Solar) and works well on all types of diesel engines. The main biodiesel advantage is that engine modifications are not required to run diesel engines. To ensure the quality of biodiesel, Indonesia has implemented the National Standard SNI 04-7182-2006 which was first ratified in 2006 and revised in 2015 with changes in the value of several parameters.

In fact, biodiesel that has passed through the production process can be degraded into other compounds that result in changes of biodiesel components during the storage process even though the biodiesel meets the established standards. These changes happen because biodiesel is very easily degraded into compounds such as acids, aldehydes, ketones, esters, peroxides and alcohols [1]. Changes in the characteristics of biodiesel caused by the oxidation process include increasing the viscosity value, peroxide number, acid number and decreasing the induction period [2].

Pertamina currently produces Biosolar with 15% biodiesel and 85% of diesel. Furthermore, the government hopes to increase biodiesel percentage by up to 30%. However, this mixture should be further investigated because the mixture results in a low biodiesel oxidation stability effect in which diesel engines are adversely affected by the emergence of deposits and gums that would damage the injection system, pumping systems and storage tanks.

The oxidation process of biodiesel is influenced by long acid chain fatty acids (C₁₆ to C₂₄) which contain unsaturated compounds that have lower oxidation stability value. Therefore, to improve the
oxidation stability, it is necessary to modify the biodiesel component (FAME). One way that can be done is by a partial hydrogenation reaction in which the reaction will break the unsaturated bond on FAME which is a key component of the determination of oxidative properties. Changes in the composition of FAME will change the oxidation stability, cetane number, and biodiesel viscosity [3].

On the other hand, the raw materials used by the biodiesel industry are vegetable oils from palm oil. However, this is a problem because vegetable oil from palm oil is not only used in the biodiesel industry but also the food industry. Therefore, the biodiesel industry should look for alternative vegetable oils which availability is assured and the price remains stable. Reliable vegetable oil among other oil is Jarak Pagar oil (Jatropha Curcas L.) and Kemiri Sunan oil (Reutealis Trisperma (Blanco) Airy Shaw) but Kemiri Sunan oil has the largest production number among other oil that has the potential for biofuels, such as Jatropha, Nyamplung, Kosambi, Bintaro, Kranji, and Kepuh. Kemiri Sunan oil gives a 52.17% percentage of each Kemiri Sunan seedlings, while there are 12,187 liters / ha of Kemiri Sunan oil productions annually [4]. In addition, Kemiri Sunan oil has a low FFA (Free Fatty Acid) of 2.6%, so it does not need pre-treatment to produce biodiesel [4].

Thus, this study was conducted to prove the oxidative stability of the product to be compatible with biodiesel standards through the partial hydrogenation of FAME components with the source of biodiesel feedstock from Kemiri Sunan oil.

2. Methodology
2.1. Materials
This study was conducted in two steps namely the synthesis of H-FAME in a hydrogenation reactor and characterization of H-FAME product. The materials needed in this study were: Kemiri Sunan oil (Darma Prema Bioenergy), Palm Biodiesel (Wilmar), Ni/C (Pratama), Aquadest (CV. Dwinika), Chloroform (Merck), Wijs (Merck), Sodium Thiosulfate (Merck), Potassium Iodide (Merck), Starch (Merck), Potassium Hydroxide (Merck), Phenolphthalein (Merck).

2.2. Partially Hydrogenated FAME
The reaction was performed in a 330 mL batch stirred reactor integrated with a condenser and furnace. Extensive stirring of the biodiesel and catalyst in the reactor was accomplished using a magnetically driven, stirred with a DC geared motor. Ni/C catalyst was purged using nitrogen for 30 minutes, and then the Ni/C catalyst was activated by hydrogen at 10 bars and 400 °C for 1 hour. Kemiri Sunan FAME was used as feed and Ni/C catalyst with variation ratio of 100:1, 100:5, and 100:10 % wt. Before the hydrogenation, the feed and the catalyst were purged using nitrogen to remove O₂ for 30 minutes. Stirring speed and pressure during the reaction were kept constantly at 800 rpm and 6 bars respectively. The reactions were performed at temperature 120°C for 2.5 hours. In this step, the double bonds that were presented in the FAME were saturated with hydrogen. To compare the double bond reduction in the Kemiri Sunan H-FAME, palm FAME (B100) that has complied SNI Biodiesel was used in partial hydrogenation using the same catalyst and operating conditions as Kemiri Sunan FAME. Figure 1 shows a schematic diagram of the apparatus.
The product is characterized by iodine number test to determine the double bond reduction, acid number test to determine the amount of free fatty acid in the oil, FT IR (Thermo Scientific) to know the effect of reaction to the presence of functional group in FAME, GCMS (Agilent Technologies) to identify components of sample, and oxidation stability test to determine the increased oxidative stability. Furthermore, the product is characterized by the density, viscosity, and cetane index to examine quality of combustion of the product.

3. Result and Discussion
The used catalyst was Nickel/Carbon. In test variations, the catalyst was activated first. A physical properties result of the catalyst that had been used in H-FAME synthesis is attached in table 1.

| Catalyst | Surface Area (m²/gram) | Pore Size (nm) | Crystal Size (nm) |
|----------|------------------------|----------------|------------------|
| Ni/C     | 285.85                 | 2.2            | 77.78            |

To facilitate an explanation of the characterization results of the H-FAME samples in the next section, the researcher made a standard naming sample based on the operating conditions presented in table 2.

| Products of Kemiri Sunan H-FAME | Products of B100 | Ni/C (% wt) |
|----------------------------------|------------------|-------------|
| H-FAME a                         | H-FAME d         | 100:1       |
| H-FAME b                         | H-FAME e         | 100:5       |
| H-FAME c                         | H-FAME f         | 100:10      |

3.1. Results of Characterization
Result of chemical characterization of H-FAME product can be seen in table 3.
Table 3. Chemical Properties of H-FAME

| Product          | Iodine Number (g-I2/100g) | Acidity Number (mg-KOH/g) | Oxidation Stability (minute) |
|------------------|---------------------------|---------------------------|------------------------------|
| Kemiri Sunan FAME | 166.77                    | 0.45                      | 650                          |
| B100             | 91.78                     | 0.33                      | 585                          |
| H-FAME a         | 162.18                    | 0.44                      | -                            |
| H-FAME b         | 155.64                    | 0.40                      | 665                          |
| H-FAME c         | 152.38                    | 0.40                      | -                            |
| H-FAME d         | 87.21                     | 0.30                      | -                            |
| H-FAME e         | 82.38                     | 0.26                      | 602                          |
| H-FAME f         | 80.64                     | 0.25                      | -                            |
| SNI 2015         | Max. 115                  | Max. 0.5                  | Min. 480                     |

Based on table 3, the iodine number decreased with the increasing of the amount of catalyst used. The highest decrease in iodine number was in the catalyst ratio of 100:5 wt%. The decreasing of iodine number showed a reduction in the number of double bonds in the FAME component.

The oxidation stability characteristic was only performed on H-FAME b, H-FAME e, Kemiri Sunan FAME, and Palm FAME (B100). It was based on the decreasing of the highest iodine number. The oxidation stability of Kemiri Sunan FAME and B100 were examined to know the initial data before the partial hydrogenation process. Based on the table 3, it was proved that the partial hydrogenation reaction could increase the oxidation stability of biodiesel.

Table 4. Identification of Functional Groups on H-FAME Products

| Bonds   | Functional Groups | Wave Number (cm⁻¹) | Kemiri Sunan FAME | B100   | H-FAME b | E     |
|---------|-------------------|--------------------|-------------------|--------|----------|-------|
| =CH₂    | Alkene            | 991-723            | √                 | √      | √        |   √   |
| C-O     | Alcohol           | 1169-1243          | √                 | √      | √        |   √   |
| C=O     | Carbonyl          | 1740               | √                 | √      | √        |   √   |
| C-H     | Alkane            | 1360-1459          | √                 | √      | √        |   √   |
|         | Alkane            | 2853-2932          | √                 | √      | √        |   √   |

Identification of functional groups using FTIR indicated that the partial hydrogenation reaction did not break the functional group bond but only broke the double bond of the FAME component which was a key component of oxidative properties.

Table 5. Component Identification of Sample BKS and H-FAME b and e

| Components          | Kemiri Sunan FAME | B100   | H-FAME b | H-FAME e |
|---------------------|-------------------|--------|----------|----------|
| % Methyl Palmitate (18:0) | 13.97             | 33.17  | 13.36    | 33.29    |
| % Methyl Stearate (18:0)     | 8.14              | 9.78   | 7.81     | 9.70     |
| % Methyl Oleate (18:1)      | 0                 | 38.63  | 1.44     | 39.81    |
| % Methyl Linoleate (18:2)   | 28.17             | 0.28   | 26.10    | 0.22     |
| % Methyl 9,11,13 Octadecatrienoate (18:3) | 38.70        | 0.23   | 37.82    | 0.18     |

According to table 4, the percentage of Methyl Linoleate and Methyl 9,11,13 Octadecatrienoate components were decreased, while the components of Methyl Oleate, Methyl Stearate, and Methyl Palmitate were increased. These results indicated that the partial hydrogenation reaction had broken
the saturated bond on the FAME component into an unsaturated bond. These results also confirmed the result of the decrease in iodine number.

Table 6. Physical Properties of H-FAME

| Products          | Density (kg/m³) | Viscosity (CSt) | Cetane Index |
|-------------------|-----------------|-----------------|--------------|
| Kemiri Sunan FAME | 878.94          | 6.5             | 47.06        |
| B100              | 856.96          | 4.5             | 52.51        |
| H-FAME a          | 879.56          | -               | -            |
| H-FAME b          | 884.78          | 6.8             | 49.04        |
| H-FAME c          | 883.95          | -               | -            |
| H-FAME d          | 858.21          | -               | -            |
| H-FAME e          | 863.69          | 4.6             | 55.59        |
| H-FAME f          | 864.43          | -               | -            |
| SNI 2015          | 850-890         | 2.3-6.0         | Min. 51      |

Based on the results of physical properties, density of H-FAME product increased, this was because the FAME component bound to hydrogen. While the viscosity of the product increased due to the increasing number of saturated methyl ester components and partial hydrogenation. The breakdown of unsaturated bonds into saturated bonds will increase the oxidation stability of biodiesel but it decreases flow properties, so it is necessary to obtain optimum conditions for both parameters to meet the specification [5]. In addition, the cetane index increased after the partial hydrogenation reaction showed that the more saturated components of the FAME, the more cetane index of the FAME which indicated combustion quality.

Table 7. Conversion, Selectivity and Yield of Product

| Products  | % Conversion | % Selectivity | % Yield |
|-----------|--------------|---------------|---------|
| H-FAME b  | 92.74        | 10.87         | 10.08   |
| H-FAME e  | 93.26        | 10.58         | 9.87    |

The calculation of selectivity was based on the amount of addition of the methyl oleate component, since methyl oleate is the desired component by the partial hydrogenation reaction in biodiesel. If the FAME component gets saturated, it will cause a high viscosity of biodiesel thereby imparting the flow properties [5].

4. Conclusion
Partial hydrogenation Kemiri Sunan (Reutealis Trisperma (Blanco) Airy Shaw) FAME using Ni/C catalyst under conditions of 120 ºC and 6 bars with 100:5 % wt catalyst in the stirred semi-batch autoclave reactor decreased the iodine number which was the empirical measure of the number of unsaturated bonds from 166.77 to 155.64 (g-I₂/100 g) with an increase of oxidation stability from 650 to 665 minutes. These conditions with activated Ni/C led to dominant yield of 10.08%, conversion of 92.74%, and selectivity of 10.87% of methyl oleate (18:1). The decrease of iodine number on Palm H-FAME (B100) indicates that the catalyst can react to various types of biodiesel, whether it is compliant with SNI or not yet fulfilled.

5. Acknowledgements
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6. References

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