Monoglyceride contents in biodiesel from various plants oil and the effect to low temperature properties

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Abstract. Monoglyceride is a by-product component of biodiesel process that relates to sedimentation problem at low temperature environment. To prevent the problem in using biodiesel-diesel fuel blends, it is necessary to limit of the monoglyceride content. The factor affecting monoglyceride content in biodiesel is the transesterification reaction and also the plant that is used. In this study, we investigate the monoglyceride content in biodiesel made from 4 plant oils; kemiri sunan (Reutealis trisperma) oil, coconut oil, nyamplung (Calophyllum inophyllum) oil, and waste cooking oil. These oils are purified and checked for its critical properties then converted to biodiesel. The biodiesel tested refer to Standard National of Indonesia for biodiesel (SNI 7182:2015). The monoglyceride content of biodiesel from kemiri sunan (Reutealis trisperma) oil, coconut oil, nyamplung (Calophyllum inophyllum) oil, and waste cooking oil, are 8.86%, 0.69%, 4.0%, and 2.69% consecutively. The low temperature properties represented by viscosity (@40 °C) for the 4 samples in the same order as before are 6.1 cSt, 2.7 cSt, 4.71 cSt, and 4.90 cSt. The cloud point is measured with the result of 30 °C, -20 °C, -60 °C and 30 °C respectively. The conclusions indicate that monoglyceride content can affect the low temperature properties of biodiesel.

1. Introduction
The use of biodiesel blends with diesel fuel for transportation sector rise in many countries in the last 10 years, spread from European countries, United States, and mostly in Asian countries. From all countries implementing the biodiesel blends, Indonesia is the first country in the world to implement the biodiesel blends in the percentage of 20% on its regular diesel fuel nationally [1]. This policy was established in the Decree of Minister of Energy and Mineral Resources no.12/2015 [2], which set a target of 20% biodiesel blending for transportation sector that started effectively from January 2016. To support this program, the improvement on the biodiesel specification was established. One of the parameter being added on the specification is monoglyceride content.

Monoglyceride is one of the impurities in the biodiesel caused by the reversible reaction from triglycerides into glycerol which one of the step including the forming of diglyceride and monoglyceride [3]. Ramos et al studied that fatty acid composition in the vegetable oils influence the properties of biodiesel, and also mention that in Europe areas the olive, almond, corn, rapeseed, and...
sunflower oils are preferable to produce biodiesel. There are wide varieties all over the world on the feedstock of plant oils for biodiesel. Soybean oil that already known widely as biodiesel source in US and EU countries, is being enhanced on its production by using bentonite to promote methanolsysis [4]. Another study performed on conventional feedstock, rapeseed oil, introducing their novelty on using 11 different linear or branched alcohols (C₃-C₆) rather than methanol [5]. A non-edible feedstock also being investigated for the alternative source of biodiesel, Karanj oil (Pongamia pinnata) which composed of 15.6% free fatty acid and produced biodiesel with 2.63%-wt monoglyceride [6].

In Indonesia, the most available feedstock for biodiesel production are palm oil and Jatropha curcas [7]. Some researchers investigated the potentiality of other plant oils for biodiesel feedstock. In a review article, Atabani [8] listed some non-edible plants producing oils that is potential to converted for biodiesel such as Callophyllum inophyllum, Pongamia pinnata, Hevea brasiliensis, Ricinus communis, Azadirachta indica, and many more plants. Even the edible oils has the same potentiality to be used in a single-cylinder diesel engine with palm oil for biodiesel, namely coconut oil [9]. Another promising source is Callophyllum inophyllum, which has seed oil content as high as 40-75% in a dry weight basis [10]. On this study we focusing on using 4 plant oils with high availability in Indonesia to be processed to biodiesel and investigating its monoglyceride content; Reutealis sperma oil, Coconut oil, Callophyllum inophyllum oil, and waste cooking oil (WCO).

The physical and chemical characteristics of biodiesel depend largely on the composition profile of fatty acid methyl esters, while the fatty acid composition in the final products relate directly with the feedstock composition. Feedstock with highly saturated fatty acid structures (such as palm oil) produce biodiesel with poor cold flow properties [11]. Figure 1 shows us the average value of cold flow properties represented by Cloud Point and Pour Point of biodiesel from some feedstock. In countries having low temperature season, poor cold flow properties can affect the operability of diesel engine, starting from filter clogging to difficulty of fuel pumping from fuel tank to engine [12]. For blends of biodiesel and diesel fuel, cloud point (CP) had been considered as one of indicator parameter to evaluate the low temperature properties [13]. In a study by [14], they investigated the effect of saturated monoglyceride and other impurities on the precipitant formation on cold temperature of biodiesel, and concluded that saturated monoglyceride is the main component affecting cloud point and the final melting temperature (FMT). All the studies done then lead the biodiesel users to limit the monoglyceride content on the specification.

A study by Hoekman [11] revealed that biodiesel from Palm Oil produce highest cloud point and pour point among other 11 biodiesel samples from various feedstock (including: camelina, canola,coconut, corn, jatropha, rapeseed, safflower, soy, sunflower, tallow and grease). Considerable compositional variability is observed on this wide range of feedstock. Hoekman et al pointed that fatty acid composition is the main factor affecting the biodiesel parameters, most affected are the low temperature properties. Indonesia as a country that implement the biodiesel diesel fuel blends policy to 20% volume is very strict to keep the biodiesel quality being blended to fulfill its specification. Biodiesel specification in Indonesia followed the SNI 7182:2015 [15]. The specification was prepared by the technical committee with consideration to domestic production of biodiesel quality. It already limiting the monoglyceride content by maximum 0.8% mass. However, in current time biodiesel used for blending mostly come from palm oil. Considering that Indonesia has a lot of plants which contain high oil content, it is necessary to study whether the derived biodiesel from various plants can fulfilled the specification especially cloud point and monoglyceride contents. These 2 parameters are considered to represent the low temperature properties along with viscosity that in practical perspective can detect the change of biodiesel properties causing by low temperature easily.

In this study we focusing on 4 (four) different plant oils to be converted through transesterification process to biodiesel and measuring the critical parameters of the produced biodiesel that relate to low temperature properties. The plant oils used in the study were: kemiri sunan (Reutealis trisperma) oil, coconut oil, nyamplung (Calophyllum inophyllum) oil, and waste cooking oil (WCO). We emphasize to measure the monoglyceride content on the biodiesels produced to know whether the 4 plant oils can fulfill the monoglyceride limitation on the biodiesel specification in SNI 7182:2015. The novelty of
this research is based on the limitation of references that provide us the variation of monoglyceride content in biodiesel especially when produced from various feedstocks. By doing so, we hope that the result on this research which including only 4 feedstock can be explore widely for other potential feedstock available in Indonesia.

2. Methodology

2.1. Measurement of the properties of plant oils

The plant oils used in this study were collected from small scale oil milling. The oil were processed through pressing and mechanical purification from the remaining impurities. All of the plant oils were measured for the acid value, kinematic viscosity, saponification value, iodine value and density. This parameters are needed to determine the stage of transesterification and also the amount of alcohol and catalyst used for conversion.

2.2. Optimization of transesterification process

After getting the critical properties of the feedstock, we continue to optimize the transesterification process condition to get the highest yield of biodiesel. The fatty acid components in each feedstock is different, this lead to different process condition of each feedstock to get the best result of biodiesel yield.

2.3. Measurement of biodiesel properties

The biodiesel produced in the optimum process then continued to be measured of the critical parameters relate with the low temperature properties. In relation to the composition of the feedstock used to the low temperature properties we measured the monoglyceride content of all samples. The methods used in this study conform to SNI 7182:2015.

3. Results and discussion

Table 1 shows us the result of the measurements for the plant oils used in this study.

| No. | Test Parameters       | Unit          | Test Methods | Plant Oils | Coconut | C.inophyllum | R.trisperma | WCO      |
|-----|-----------------------|---------------|--------------|------------|---------|--------------|-------------|----------|
| 1   | Acid Value            | mg KOH/gr     | ASTM D664    |            | 0.021   | 0.006        | 0.022       | 0.011    |
| 2   | Viscosity @50 °C      | cSt           | ASTM D445    |            | 19.4    | 27.8         | 49.2        | 31.5     |
| 3   | Saponification Value  | mg KOH/gr     | SNI 7182:2012|            | 228     | 171          | 185         | 191      |
| 4   | Iodine Value          | gr 1/100 gr   | SNI 7182:2012|            | 78.80   | 190.82       | 330.2       | 240.26   |
| 5   | Density @40 °C        | kg/m3         | ASTM D4052   |            | 0.90893 | 0.92786      | 0.9192      | 0.90021  |

From table 1, we may observe that the acid value for the samples vary with the lowest belongs to Calophyllum inophyllum oil and the highest belongs to Reutealis trisperma oil. The acid value indicated the quantity of the fatty acid component of the plant oils, but cannot describe us the composition of fatty acid construct the oil. The information of the acid value is used to determine the transesterification steps needed for the biodiesel conversion. Because all samples possess low acid value then the transesterification can be performed in one stage.

The Saponification Value is used to calculate the average Molecular Weight (MW) of the oils, which then is used to calculate the methanol needed to convert the triglycerides of the oils into fatty acid methyl ester. The Iodine Value indicates the double bonds exist on the oils which also indicates the oxidation stability of oils. Among the samples, Reutealis trisperma (kemiri sunan) shows the highest Iodine Value that indicates this oil possess the highest double bonds among others. Kinematic viscosity is measured here as indicator the successfulness of the transesterification process, because the biodiesel produced should have required viscosity refer to the specification which is far lower than the origin plant oils.
All of the samples then being optimized for the transesterification process with the optimization parameter is the molar ratio of methanol to plant oil. Temperature of the reaction was fixed at 60 °C. Table 2 shows us the yield of biodiesel production for variations of molar ratio of reactants for each plant oils. For each plant oils we start the optimization with molar ratio 6:1 that is in general used for palm oil biodiesel.

Table 2. Optimization of molar ratio of methanol-plant oil.

| No | Plant Oils          | Reaction Temperature (°C) | Molar Ratio (CH₃OH: Oil) | Yield (%) |
|----|---------------------|---------------------------|-------------------------|-----------|
| 1  | Coconut Oil         | 60                        | 6:1                     | 90        |
| 2  | *Reutealis trisperma* | 60                        | 6:1                     | 15        |
|    |                     |                           | 10:1                    | 20        |
|    |                     |                           | 15:1                    | 30        |
|    |                     |                           | 20:1                    | 60        |
| 3  | *Calophyllum inophyllum* | 60                        | 6:1                     | 10        |
|    |                     |                           | 10:1                    | 30        |
|    |                     |                           | 15:1                    | 85        |
| 4  | Waste Cooking Oil   | 60                        | 6:1                     | 75        |

The optimum molar ratio for each plant oils are marked grey. We may observe that for coconut oil, first trial with molar ratio 6:1 resulting 90% yield of biodiesel which is high for biodiesel so we choose this as optimum. For *Reutealis trisperma*, the optimum molar ratio is higher, achieved at 20:1 means that more methanol is needed to convert the fatty acid in origin oil. For *Calophyllum inophyllum*, we have to mention that before optimizing the molar ratio on the main reaction, this plant oil require pre-treatment by extraction using methanol 1:1 up to 3 times extraction to eliminate the resin components on original oil. The waste cooking oil also use the optimum molar ratio of 6:1 to produce 75% yield to biodiesel.

As important part after transesterification process finish, the washing process should eliminate the remaining impurities from the final product. The impurities include unreacted methanol, glycerol, and also the catalyst. In this study, we performed washing process using warm water at temperature 60-70 °C in 3 stages of washing. After washing process we perform the last purification stage by heating the biodiesel to 80 °C for 30 minutes.

The biodiesel produced from the optimum process and passing the washing process then measured for the monoglyceride content, kinematic viscosity, and cloud point using the method listed in SNI 7182:2015.

In figure 1 is showed the result of monoglyceride content for each sample compare to the standard limitation established in SNI 7182:2015. Using the limit value of maximum 0.8 % mass, the biodiesel prepared in this study that can fulfill the limit is only from coconut oil. Other biodiesel fail to satisfy the limit. Monoglyceride content in biodiesel depends on some factors; reaction condition (temperature, molar ratio, type and quantity of the catalyst), and also other impurities that disturb the triglyceride conversion to fatty acid methyl ester). The failure of biodiesel from *Calophyllum inophyllum*, *Reutealis trisperma* and waste cooking oil may challenge us to perform variations over wider range to find optimum biodiesel yield not only from the quantity but also quality especially monoglyceride content.
From figure 2 we can observe the kinematic viscosity of all biodiesel prepared from plant oils in this study. The red line is the limit value for kinematic viscosity established in SNI 7182:2015 with value of maximum 6.0 cSt. Only one sample biodiesel fail to fulfill the limit; biodiesel of *Reutealis trisperma* which has kinematic viscosity 6.1 cSt. Investigation from the original plant oils in table 1 reveals that *Reutealis trisperma* oils has the highest kinematic viscosity among other samples with value of 49.2 cSt. Eventhough the biodiesel slightly exceed the limit, but the transesterification process in this study can reduce the kinematic viscosity of original oils.

Cloud point of all biodiesel samples is showed in figure 3. Here we can observe that all samples fulfill the limit required in specification with maximum value 18 °C. Until here we can take a look to the monoglyceride contents of each samples. In figure 1 the monoglyceride content that fulfill the limit in Indonesian biodiesel specification is only biodiesel from coconut oil. We can observe the cloud point of coconut oil is -2 °C. The highest monoglyceride content which belongs to *Reutealis trisperma* related with the cloud point in 3 °C. So the relation of the monoglyceride contents with low temperature properties is not showed clearly using cloud point, we can try to show the realtionship using other method such as Cold Filter Plugging Point (CFPP). This fact may lead us that this can be explained from the fact that most of the study in the literature use plant oils from different climates with Indonesia. It becomes our benefit too that in tropical climate such in Indonesia won’t be affected much with low temperature properties of the biodiesel. Only some areas in high altitude still need our concerns to provide good quality of biodiesel that is already covered in our specification.
4. Conclusion

The monoglyceride content from biodiesel prepared from 4 different plant oils (coconut oil, nyamplung/Calophyllum inophyllum, kemiri sunan/Reutealis trisperma and waste cooking oil) is measured with the result of only one biodiesel fulfill the maximum limit in Indonesian specification which belong to coconut oil (0.70 %mass). Kinematic viscosity of the samples can fulfill the limit in the specification except for biodiesel from Reutealis trisperma with value of 6.1 cSt. The cloud point of all samples can fulfill the limit in the specification.

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