The Influence of Sorbitan Monooleate as a Surfactant and Octanol as a Co-surfactant to Restore Biodiesel’s Flow Properties at the Cold Temperatures

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Abstract - The application of the biodiesel-diesel mixed fuel at the cold temperatures causes problem stoppage in the diesel engine. This is caused by the precipitation of agglomerate Saturated Monoglycerides (SMG). From the previous study, the addition of 1% Sorbitan Monooleate (SMO) could reduce the Cloud Point (CP) and Cold Filter Plugging Point (CFPP) respectively by 4.2°C and 2°C. In this study, SMO was used as a surfactant with octanol as a co-surfactant. For each biodiesel with 0.4-0.6% MG, the SMO was varied by 0.1-1% v/v. The molar ratio of the SMO/octanol is 1:1. Samples of biodiesel were stored at the cold temperatures (±16°C). The effect of addition SMO and octanol was analyzed by Differential Scanning Calorimetry (DSC) and the changes of MG’s droplet particle size were analyzed by Particle Size Analyzer (PSA). As the results, the addition of SMO and octanol reduced CP by 4.6°C and CFPP by 3°C. The PSA and DSC method proved that there were changes in MG’s particle diameter and onset temperature respectively from 8.18-68.30 µm to 0.29-8.88 µm and from 9.79°C to 4.97°C. The changes indicate that the SMO and octanol have roles in reducing the agglomeration of MG in biodiesel.

Keywords Biodiesel, flow properties, sorbitan monooleate, octanol, cold temperatures.

1. Introduction

The world is facing a major crisis, which are fossil fuel depletion and environmental degradation. The consumption of fossil energy causes fossil fuel depletion and provide exhausting harmful emissions [1, 2]. So, it is preferred to find other alternative energy sources that can be produced from materials that available in a country [3]. Biodiesel consists of fatty acid methyl ester (FAME). It is one of alternative energy compared to the conventional diesel which is extensively produced and consumed. It is also in adaptation with governmental regulations in many different countries [4]. In Indonesia, one of the abundant materials that can be used as a raw material for renewable energy is biodiesel made from palm oil.

Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats. Biodiesel is the best candidate for diesel fuels in diesel engines because its environmental friendliness is better than gasoline and petroleum diesel [5]. Because biodiesel is one of a clean alternative energy source, biodegradable, harmless, crucially reduces the exhaust emissions and the general life cycle emission of carbon dioxide (CO₂) from the engine [6]. Biodiesel has a higher viscosity, density, pour point (PP), flash point, and cetane number than diesel fuel [7-9].

But, the usage of blending biodiesel with petroleum diesel caused problems with the low-temperatures operability performance. In some cases, precipitation above the cloud point (CP) has been detected and has led to the plugging of fuel filter [10]. Precipitation problem is caused by a “creamy paste-like” material which is
saturated monoglycerides (SMG), that was found on a
plugged fuel filter from the vehicle that used B-20 as a
fuel. It was also noted that the diglycerides (DG)
component, the saturated diglycerides (SDG), were also
present on the filter [11]. The behaviour of biodiesel at the
low temperatures is an important quality criterion. This
because partial or full solidification of the fuel may cause
blockage of the fuel lines and filters, leading to fuel
starvation, problems of starting, driving, and engine
damage due to inadequate lubrication [12].

Some of the important cold flow properties parameters
are CP and Cold Filter Plugging Point (CFPP). CP is the
temperature at which wax crystals first becomes visible
when the fuel is cooled. CFPP refers to the temperature at
which the test filter starts to plug due to the crystallization
of fuel components [13]. The cold flow properties of
biodiesel also depend on the structure of the alkyl esters.
The melting point increases with the chain length and
decreases with the increase of the double bonds. Saturated
fatty acids with ten or more carbons are solid at room
temperature and their melting point increase with chain
length, whereas unsaturated fatty acids are liquid [14].
Among the saturated acids, odd-chain acids have lower
melting points than even-chain acids [15]. Biodiesel which
produced from oil with high concentrations of fatty acids
has high melting points such as palm oil biodiesel [16].
Palm oil has higher CP than other vegetable oil. With
using palm oil biodiesel, it would be a great challenge to
be done.

The approaches for improving the low-temperature
operability of biodiesel include blending with petrodiesel,
transesterification with long- or branched-chain alcohol,
crystallization fractionation, and treatment with commercial
diesel cold flow improver additives [17]. In this research,
we will try to restore the cold flow properties of biodiesel with the additives treatment.
Several additives had been studied to improve the cold
flow properties of biodiesel. Korhonen et al., [18]
investigated four surfactants, which were Sorbitan
Monoleate (SMO), Sorbitan Monostearate (SMS),
Sorbitan Monolaurate (SML), and Sorbitan Monopalmitate
(SMP) in isopropyl palmitate and isopropyl myristate oil.
The viscosity and the droplet particle’s size were tested.
The result was the SMO and SMP formed a w/o emulsion
and had a particle droplet size <1.8 µm which was smaller
than the emulsion formed by SMP and SMS.

Then, Wang et al., [19] researched the SMO as a
surfactant on waste cooking oil biodiesel and carried out at
temperature 4°C for 60 days. As a result, the purity of
biodiesel was higher, from initially 90.2% to become
96.3%, CP and PP also decreased by 3°C. Attaphong et al.,
[20] also conducted a study using three different types of
surfactants, which were SML, SMO, and Sorbitan
Trioleate (STO) with three types of alcohols, which were
butanol, hexanol, and octanol with different molar
fractions at temperature 25°C in biodiesel B-50. The
addition of SMO showed the most optimal result by
lowering the CP and PP with the lowest surfactant/co-
surfactant concentration to reach single phase
microemulsion. Because SMO has an HLB of 4.3, which is
between range 3-6 which can produce microemulsion.
SMO is also lighter than STO and has a longer carbon
chain than SML, which provides higher interaction with
biodiesel and monoglycerides (MG). Dewang et al.,
also conducted transesterification study with mixing biodiesel
and methanol [21]. The use of alcohol as a blended fuel
with petroleum diesel has challenges due to immiscibility.
Although alcohol can be used directly in the diesel engine,
the low cetane number and lubricity values of alcohol need
to be overcome using additives. Co-surfactant can increase
the fluidity of interfacial film by penetrating the surfactant
layer. Short to medium chain length alcohols (C3-C8) are
commonly used as the co-surfactants which can reduce the
interfacial tension and increase the fluidity of the interface.

The use of biodiesel-diesel mixed fuel has been done
before and showed the lowest emission levels which were
B-10 and B-20 [22], but in this study, we used pure palm
oil biodiesel to focus more on the cold flow properties. We
also used the SMO as a surfactant and octanol as a co-
surfactant as the highlight of the cold flow improver of
biodiesel. Thus, the use of co-surfactant octanol which is
an alcohol that has a long carbon chain can interact better
with surfactant SMO to restore biodiesel's cold flow
properties.

2. Material and Methods

2.1. Materials

Palm oil biodiesel (B-100) that is following the
standard and quality (specification) applicable in Indonesia
with MG’s level 0.4%. Distilled MG was purchased from
Rikevita (M) Sdn Bhd, Malaysia, the SMO surfactant and
1-Octanol were purchased from Merck.

2.2. The Addition of MG in Biodiesel

The addition of MG to biodiesel with an initial
biodiesel level of 0.4% which aims to vary the MG level in
biodiesel to 0.4% (B-100A), 0.5% (B-100B) and 0.6% (B-
100C). Then, samples were analyzed by Gas
Chromatography with ASTM D-6584 to adjust its MG’s
level as Arina had done in 2019.

2.3. The Addition of SMO as a Surfactant and Octanol as a
Co-surfactant in Biodiesel

The addition of SMO and octanol as the additives on
biodiesel is carried out in the following stages. First,
prepare the palm oil biodiesel (B-100) which the MG’s
level that have been varied by 0.4%, 0.5%, and 0.6% by
mass, each 1 liter in a clear bottle with lid. The addition of
SMO which are 0.1%, 0.5%, and 1% by volume and the
addition of octanol with a molar fraction 1:1 of
SMO/octanol. The storage of biodiesel samples is carried
out at the cold temperatures (+16°C). Then, analyze the
cold flow properties, which are CP with ASTM D-5773
and CFPP with ASTM D-6371. Observations and tests are
carried out every week for a month.
2.4. PSA Analysis

PSA analysis is carried out to determine the changes in MG's particle size and the distribution of MG's droplet particles before and after the addition of SMO and octanol. The PSA test equipment used is PSA Mikro CILAS 1190.

2.5. DSC Analysis

DSC analysis is carried out to determine the initial temperature of crystallization, melting temperature, and the enthalpy of biodiesel before and after the addition of SMO and octanol. The DSC test equipment used is DSC 60 Plus DSC Analyzer.

3. Results and Discussion

3.1. Analysis of Addition of MG in Biodiesel

Based on Table 1, the results of the analysis of the MG percentage in B-100A, B-100B, and B-100C correspond to the expected MG variations. It was also seen that the type of MG which is added to palm oil biodiesel, contained more monopalmitin and monoolein rather than monostearin. From this result, it can be concluded that monopalmitin which have molecular structure C_{19}H_{38}O_{4} and monostearin which have molecular structure C_{21}H_{42}O_{4}, are types of the saturated fatty acids because they do not have a double bond. Meanwhile, monoolein which has a molecular structure C_{21}H_{40}O_{4} is a type of unsaturated fatty acid. This means that the MG’s level which added in this study have more saturated fatty acids than unsaturated fatty acids. That will be the correlation between the MG’s level in biodiesel with the biodiesel’s cold flow properties.

Table 1. MG’s level in biodiesel analyzed by Gas Chromatography

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Sample</th>
<th>B-100A</th>
<th>B-100B</th>
<th>B-100C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0024</td>
<td></td>
</tr>
<tr>
<td>Monopalmitin</td>
<td>0.1888</td>
<td>0.2480</td>
<td>0.3231</td>
<td></td>
</tr>
<tr>
<td>Monostearin</td>
<td>0.1268</td>
<td>0.1298</td>
<td>0.1553</td>
<td></td>
</tr>
<tr>
<td>Monoolein</td>
<td>0.0200</td>
<td>0.0775</td>
<td>0.1477</td>
<td></td>
</tr>
<tr>
<td>Diolein</td>
<td>0.0279</td>
<td>0.0296</td>
<td>0.0313</td>
<td></td>
</tr>
<tr>
<td>Triolein</td>
<td>0.0082</td>
<td>0.0091</td>
<td>0.0092</td>
<td></td>
</tr>
<tr>
<td>Monoglycerides</td>
<td>0.445</td>
<td>0.560</td>
<td>0.667</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Analysis of Addition of MG in Biodiesel Influence as the SMO as a Surfactant and Octanol as a Co-surfactant Addition to the Biodiesel’s Cold Flow Properties

In Fig. 1(a), the initial CP of B-100A was 13.4°C and with the addition of 1% SMO and octanol, the CP decreased by 4.6°C in the first week. With the addition of 1% SMO and octanol, CP tended to experience a slight increase for about 0.8°C from the first to fourth week. In Fig. 1(b), the initial CP of B-100B was the same as B-100A, which is 13.4°C. With the addition of 1% SMO and octanol, CP decreased by 1.4°C in the first week. From the first to the fourth week, CP tended to be unstable. In Fig. 1(c), the initial CP of B-100C was 13.8°C. With the addition of 1% SMO and octanol, CP decreased by 1.3°C in the first week also. From the first to the fourth week, CP tended to be unstable as well as Figure 1(b). It is seen that the CP’s most optimum decrease at the cold temperatures was when the addition of 1% SMO and octanol to the B-100A. This may occur because the MG’s level tends to be low in biodiesel, thus making the surfactant and co-surfactant work better. The cold temperatures cause the formation of solid wax crystal nuclei that have submicron in scale and invisible to the human eye. Further decreases in temperature cause the crystal nuclei to grow. These crystal nuclei of biodiesel probably caused by the amount of saturated fatty acids in biodiesel [23]. It may be possible that the hydrophilic head in SMO, which has similar polarity to MG and also great solubility at the cold temperatures, can be interacting with the polar head groups of the MG to inhibit nucleation and reduce the CP. The most effective additives for inhibiting nucleation, generally have a similar structure to the nucleating species [24,25].
Fig. 1. The influence of CP at the cold temperatures in biodiesel: (a) B-100A (b) B-100B (c) B-100C

In Fig. 2(a), the initial CFPP of B-100A was 13°C, then decreased by 3°C with the addition of 1% SMO and octanol. For the B-100A, CFPP increased by 1°C from the second to the fourth week. Whereas with the addition of 0.1-1% SMO and octanol, CFPP tended to be stable. In Fig. 2(b), the initial CFPP B-100B was 14°C, then decreased by 3°C with the addition of 1% SMO and octanol. For the B-100B, CFPP increased by 1°C from the second to the fourth week, the same with the B-100A. Whereas with the addition of 0.1-1% SMO and octanol, CFPP tended to be stable. In Fig. 2(c), the initial CFPP B-100C was 15°C, then decreased by 3°C with the addition of 0.5% SMO and octanol. For the B-100C, CFPP increased by 1°C from the second to the fourth week, the same with the B-100A and B-100B. For the B-100C with the addition of 0.1% SMO and octanol, CFPP decreased by 1°C from the second to the fourth week. Whereas the addition of 0.5-1% SMO with octanol tended to be stable.

This shows that, at B-100C, the most optimum decrease in CFPP occurs with the addition of 0.5% SMO and octanol. CFPP of biodiesel increases as the increasing content of saturated esters and also as the decreasing content of unsaturated esters [14, 26-28]. This statement supports the CFPP of biodiesel B-100C which is greater than the B-100A and B-100B. Because, with the addition of MG, especially the increasing of saturated ester content in biodiesel make the CFPP will be increasing too.

Fig. 2. The influence of CFPP at the cold temperatures in biodiesel: (a) B-100A (b) B-100B (c) B-100C

3.3. PSA Analysis

The most common method for dispersing powder test materials into dispersing media and particle’s chemical characteristics measurement is PSA [29]. Fig. 3(a) showed that on the histogram, the MG’s particle diameter is between 1-100 µm. Fig. 3(b) showed that the MG’S particle diameter that had been dissolved into SMO and octanol was between 1-20 µm. The visual observations on MG’s histogram also showed that the diameter of MG particles in SMO and octanol was much smaller than MG without the addition of SMO and octanol. Fig. 3(b) showed that the distribution of MG’s particle size after the addition of SMO and octanol was not evenly distributed. It is caused by the aggregates in granules and also the particles do not spread evenly because some are centered on several angles. It also caused by the grains which are not well dispersed or uneven. Thus, the particle size distribution tended to have more than one particle distribution peak.
Fig. 3. The particle size analyzer histogram of: (a) MG (b) MG after the addition of SMO and octanol

Then, the data that we had, was made into Fig.4 which showed a comparison between MG's particle diameter and MG's particle diameter after the addition of SMO and octanol. The size of the particles is divided into small, medium, and large particles [30]. Fig. 4 showed that for the MG, small particle size (diameter at 10%), medium (diameter at 50%), and large (diameter at 90%) successively had an average diameter of 8.18, 38.17, and 68.30 µm. For the MG after the addition of SMO and octanol, the particle size diameter successively became 0.29, 3.62, and 8.88 µm. With the addition of SMO as a surfactant and octanol as a co-surfactant, makes the diameter of the MG particles are much smaller. Thus, that is possible to reduce the MG agglomeration. If the Van Der Waals force that causing the attractive force between MG particles is reduced, then agglomeration can also be avoided. Thus, the MG particles will also be dispersed evenly in SMO and octanol [31].

Fig. 4. The average particle size diameter of MG and MG with the addition of the SMO and octanol

3.4. DSC Analysis

The DSC method is a technique that is useful for measuring the physical characteristics of a petroleum product and the phase change of a material. They have conducted a DSC analysis of petroleum products, such as paraffin waxes, petrolatum, lube oils, fuel oils, and bitumens [32]. In this research, we used the DSC method to analyze the phase change of palm oil biodiesel. DSC analysis can also be used to determine the thermophysical property value of a material such as melting point, latent heat, and specific heat [33, 34].

Fig. 5 showed the endothermic curve associated with the melting process. The curve began with the onset temperature and then went to the peak temperature. The onset temperature is taken as the melting point temperature and the latent heat is calculated based on the total area below the peak of the solid transition to liquid [35]. Fig. 5 also showed that the latent heat shifted to a higher value when the biodiesel was added with 1% SMO and octanol. With the addition of the SMO as a surfactant and octanol as a co-surfactant, the sample temperature gradient increased, and the heat flux peak during the melting process increased with increasing gradient [36]. Melting temperature is the temperature at which the solid phase changes to a liquid phase. High melting points and polarity can caused by MG, especially SMG and DG can also cause the crystallization problems in fuel [11].

Fig. 5. The DSC curve of B-100A and B-100A after the addition of 1% SMO and octanol

Table 2 showed that the onset temperature which is the melting temperature. This is the temperature when the MG's form is solid (agglomerated) and gradually changes to the liquid phase (evenly dispersed on biodiesel). In Table 2, the onset temperature of B-100A was 9.79°C, while for B-100A which had been added by 1% SMO and octanol was 4.97°C. This means that the onset temperature after the addition of 1% SMO and octanol decreased by 4.82°C. The latent heat of B-100A was -1250 mJ, while the latent heat of B-100A which had been added by 1% SMO and octanol was -920.46 mJ. The latent heat of B-100A which had been added by 1% SMO and octanol, was smaller than the pure biodiesel (B-100A), which indicates that the dispersion was more stable after the addition of SMO and octanol into biodiesel. The SMO and octanol with a lower freezing point, change the crystallization process, inhibit the agglomeration of crystals, retard crystal growth and therefore reduce the crystals’ amount at the low temperatures [37].
Table 2. The melting temperature in biodiesel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak (°C)</th>
<th>Onset (°C)</th>
<th>Endset (°C)</th>
<th>Heat (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-100A</td>
<td>24.06</td>
<td>9.79</td>
<td>31.55</td>
<td>-1250</td>
</tr>
<tr>
<td>B-100A after the addition of 1% SMO and octanol</td>
<td>21.83</td>
<td>4.97</td>
<td>27.56</td>
<td>-920.46</td>
</tr>
</tbody>
</table>

4. Conclusion

In this work, the addition of SMO as a surfactant and octanol as a co-surfactant at the cold temperatures to restore the flow properties of palm oil biodiesel was conducted. It is concluded that the addition of SMO and octanol can improve the flow properties parameters, which are CP and CFPP. The addition of 0.1-1% SMO with octanol at the cold temperatures reduced the CP by 4.6°C and CFPP by 3°C. The changes in MG’s particle diameter before and after the addition of SMO and octanol was observed. For the small, medium, and large particle size respectively from 8.18, 38.17, and 68.30 μm to 0.29, 3.62, and 8.88 μm. Also, the onset temperature decreased from 9.79 to 4.97°C, indicates that SMO as a surfactant and octanol as a co-surfactant have a role in restoring the biodiesel’s cold flow properties. Thus, with the addition of SMO and octanol, palm oil biodiesel can be used over a wider temperature ranges.

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1180