The use of non-ionic surfactants with different Hydrophilic-Lipophilic Balance (HLB) and their effect on flow properties in palm oil biodiesel

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Abstract. The use of surfactants has been known to reduce the interfacial tension between the two fluids. Surfactants have Hydrophilic-Lipophilic Balance (HLB) values that vary depending on their function. Previously, the addition of the Sorbitan Monooleate (SMO) had succeeded in reducing the Cloud Point (CP) by 4.2°C and the Cold Filter Plugging Point (CFPP) by 2°C. In this research, two different types of nonionic surfactants were tried, named the Sorbitan Monolaurate (SML) and the Sorbitan Trioleate (STO), which have HLB values of 8.6 and 1.8, respectively. This research aims to prove whether these surfactants can improve the flow properties of palm oil biodiesel by reducing the interfacial tension. Each surfactant was varied in palm oil biodiesel with a content of 1 and 2% at room temperature (±27°C) for a month with every week observation. Then, it was tested using the flow properties parameters, which are the CP, Pour Point (PP), and CFPP. The FTIR analysis is also carried out to determine the interactions between MG and these surfactants. The addition of 1% SML caused escalation in the CP, PP, and CFPP by 3.2, 3.5, and 6°C, respectively. Meanwhile, the addition of 2% STO caused a reduction in the CP and PP by 0.5 and 1°C, respectively but the CFPP tended to be constant.

1. Introduction

Biodiesel is an alternative form of energy that can be produced from oils from plants or animal fats. One of the main problems caused by the use of biodiesel is its poor flow properties. The parameters of the flow properties include cloud point (CP), pour point (PP), and cold filter plugging point (CFPP). Biodiesel tends to have high CP, PP, and CFPP [1]. The CP, which usually occurs at a higher temperature than the PP, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Meanwhile, PP is the lowest temperature in which a liquid fatty material will still flow. Solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems. This crystal agglomeration is caused by Saturated Monoglyceride (SMG). This is what can cause the use of biodiesel can cause a breakdown in diesel vehicle [2]. Monoglycerides (MG) is one of the impurities in the biodiesel caused by the reversible reaction from triglycerides (TG) into glycerol which one of the steps including the forming of diglycerides (DG) and MG [3]. In previous studies, the effect of SMG and other impurities on the
precipitant formation on the cold temperature of biodiesel and concluded that SMG is the main component affecting CP and the final melting temperature (FMT) [4].

In this research, palm oil biodiesel is used. The previous studies showed that the composition of fatty acids is a major factor affecting the parameters of biodiesel, especially the low-temperatures properties. It revealed that biodiesel from palm oil produces the highest CP and PP among other eleven biodiesel samples from various feedstock (including; camelina, canola, coconut, corn, jatropha, rapeseed, safflower, soy, sunflower, tallow and grease) [5]. One way to overcome the poor flow properties of palm oil biodiesel is to add surfactant additives. Surfactants are reported to reduce PP or even CP. This additive aims to reduce the size, modify the shape of the wax crystal, and prevent the crystal from growing until it closes the fuel filter [6-9]. The surfactant molecules migrate toward the oil-water interface whereby, by inhibiting coalescence and decreasing interfacial tension, they exert their role of interface stabilizers [10,11]. Moreover, if the surfactant concentration exceeds its corresponding critical micellar concentration (CMC) value, the surfactant molecules spontaneously self-assemble into micelles, thus plummeting the interfacial tension to a minimum [12].

In this study, two types of sorbitan esters surfactants were used with different Hydrophilic-Lipophilic Balance (HLB) values [13]. The Sorbitan Monolaurate (SML) and the Sorbitan Trioleate (STO) each have HLBs of 8.6 and 1.8. At 25°C molecules of SML and STO are in the disordered liquid-crystalline state. The lower the HLB is the smaller the initial size of the vesicles [14]. Based on the previous research, using surfactants with HLB range between 8-11, which is SML, the efficiency of encapsulation decreases. With the decrease in the encapsulation efficiency of the surfactant, it results in increased permeability of the surfactant. The higher the permeability of the surfactant, the surfactant can be easier to pass some particles that penetrate it [15]. The STO surfactant is the most hydrophobic type of surfactant among other sorbitan ester surfactants [13]. So, the performance of these two surfactants will be compared to the palm oil biodiesel’s flow properties.

2. 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%, the SML surfactant was purchased from Sigma Aldrich, and the STO surfactant was purchased from Shanghai Terppon Chemical.

2.2. The addition of the SML and STO in biodiesel
The addition of the SML and STO as additives on biodiesel is carried out in the following steps. Prepare biodiesel (B-100) which has MG’s level 0.4% by mass, each 1 litter in a clear bottle with a lid. The addition of the SML and STO are 1 and 2% (v/v). Perform the flow properties test which is CP, PP, and CFPP [16]. The storage of biodiesel samples is carried out at room temperature (±27°C). Observations and tests (CP, PP, and CFPP) are carried out every week until a month.

2.3. Fourier-Transform Infrared Spectroscopy (FTIR) analysis
Fourier Transform Infra-Red (FTIR) analysis is carried out to determine functional groups, hydrogen bonds, and interactions between MG with surfactant SML and STO. The FTIR test equipment used is the Thermo Scientific, type Nicolet IS5.
3. Results and discussion

3.1. The effect of SML addition to biodiesel’s cold flow properties

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Figure 1. The effect of biodiesel’s cold flow properties with the addition of SML: (a) CP (b) PP (c) CFPP.
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Based on Figure 1a, the addition of 1% SML to biodiesel increased the CP by 3.2°C in the fourth week. And with the addition of 2% SML, the CP increased drastically by 6.7°C in the fourth week of observation. Based on Figure 1b, the same thing happened as CP, with the addition of 1 and 2% SML respectively increased the PP by 3.5 and 4.4°C in the fourth week of observation. Based on Figure 1c, with the addition of 1 and 2% SML respectively increased the CFPP by 5 and 6°C even in the first week of observations.

The significantly increased CP, PP, and CFPP values during a month observation indicate that the SML surfactant is not effective in increasing the flow properties of biodiesel. HLB is used as a criterion for surfactant selection and was found to work well for many surfactants of different structures [17].

Based on the previous research conducted by Wang, et al., the content of fatty acids in the SML, including lauric acid (50%), myristic acid (19%), palmitic acid (9%), caprylic acid (7%), and capric acid (6%) [18]. With the most lauric acid content in it, where lauric acid is a type of saturated fatty acid and has a melting point of 44°C, which tends to be high. Thus, it tends to be rather difficult to interact with MG so that visually agglomerate will form under the bottle.

Based on the research conducted by Tsai, et.al., the SML can only convert large macrovoids into straight finger type channels [19]. The phenomenon of the formation of finger-like macrovoids indicates that a substance that has high viscosity is replaced by a substance that has a low viscosity, thus forming a finger-like macrovoids cavity. The SML cannot inhibit the huge macrovoids completely, so the mechanical strength of biodiesel will also decrease and its stability will also decrease [20].

3.2. The effect of STO addition to biodiesel’s cold flow properties

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Figure 2. The effect of biodiesel’s cold flow properties with the addition of STO: (a) CP (b) PP (c) CFPP.
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Based on Figure 2a, the addition of 1% STO to biodiesel decreased the CP by 0.3°C in the first week. The addition of 2% STO to biodiesel decreased the CP by 0.5°C also in the first week. Based on Figure 2b, with the addition of 1% STO, the PP was constant from the first until the fourth week. With the addition of 2% STO, the PP decreased by 1°C in the fourth week of observation. Based on Figure 2c, with the addition of 1% STO, the CFPP increased by 1°C until the second week and back to initial CFPP again until the fourth week, which was 13°C. With the addition of 2% STO, it also increased by 5°C until the fourth week. This probably indicates that the addition of 2% STO is sufficiently saturated and causes flow properties to increase. When viewed from the HLB, the STO has an HLB value of 1.8 and is a very hydrophobic nonionic surfactant. Surfactant STO, which was previously found to mediate a rise in the electric conductivity of nonpolar solutions, can also lead to large electric surface potentials on suspended colloidal particles and efficient electrostatic stabilization of nonpolar dispersions [21].

This shows that theoretically, the STO surfactant can stabilize dispersions in nonpolar media. However, this research can indeed reduce the value of CP and PP when applied to palm oil biodiesel. Its influence on the CFPP is less visible because the value of the CFPP has not decreased.

3.3. Fourier-Transform Infrared Spectroscopy (FTIR) analysis

Figure 3 shows the chemical structure of the SML and STO surfactants. That can be seen that in the figures, the SML has three OH groups, whereas the STO has only a hydroxyl group. The SML carbon chain is also shorter than the STO. This is also an indication that, with more hydroxyl groups and shorter carbon chains in the SML, the surfactant SML is more polar than the STO. Thus, the possibility of SML to not dissolve in biodiesel will also be higher than STO.

Figure 4 shows the interaction between the SML and MG using the FTIR method. It is seen that there is no significant shift in the wavenumber in the C-H group and the C=O group. The hydroxyl group has been seen by a slight shift in the wavenumber from 3396.22 to 3393.76 cm\(^{-1}\) with only a slight increase in intensity from 92.745 to 92.888%. The shift of the wavenumber shows that there is a slight molecular hydrogen bond between the SML and MG [22]. However, the value of the shift is not significant because its intensity also does not change significantly. This is also supported by the non-improved flow properties of biodiesel that have been added by the SML. Figure 5 also shows the interaction between the STO and MG using the FTIR method. It is seen that there is no significant shift in the wavenumber in the C-H group and the C=O group. The hydroxyl group has been seen by a slight shift in the wavenumber from 3470.37 to 3472.47 cm\(^{-1}\) with only a slight decrease in their intensity from 98.844 to 98.703%.

Figure 4. The FTIR Spectrum of: (a) the SML (b) the SML with the addition of MG.
The FTIR spectrum between the SML and MG along with the STO and MG cannot explain in detail why the STO could reduce CP and PP more significantly than SML. This because in general, there are not very significant differences in the FTIR spectrum of only the SML and the STO with the SML and the STO that have been mixed with MG. Although in previous studies, FTIR analysis has been carried out on the interaction of surfactants to decrease the surface tension of a binary mixture. The stronger the hydrogen bond occurs, the resulting interfacial tension in a binary mixture will also decrease [23]. Therefore, further research must be done about the interactions that occur.

![Figure 5](image_url)  
**Figure 5.** The FTIR Spectrum of: (a) the STO (b) the STO with the addition of MG.

4. Conclusion

The addition of the SML in palm oil biodiesel couldn’t improve the cold flow properties parameters, which are CP, PP, and CFPP. The addition of 1-2% SML, raised the CP, PP, and CFPP by 3.2, 3.5, and 6°C. The addition of the STO in palm oil biodiesel slightly could improve the cold flow properties parameters, which are CP and PP. The addition of 1-2% STO decreased the CP and PP by 0.5 and 1°C. But, the CFPP remained constant.

For future work, it is recommended to conduct experiments with different types of surfactants. Thus, the most effective surfactants are obtained to improve the cold flow properties in palm oil biodiesel.

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