The Effect of Sorbitan Monooleate and Alcohol Addition as Flow Properties Improver in Palm Oil Biodiesel

Anya Prilla Azaria, Sylvia Ayu Bethari, and Mohammad Nasikin

***Abstract*—The use of the biodiesel B-20 especially in low temperature causes a blockage in the diesel vehicle fuel filter, which in turn causes the vehicle to strike. The blockage is caused by the deposition of monoglycerides (MG) agglomeration. These MG deposits reduce the flow properties of B-20. In this study, the Sorbitan Monooleate (SMO) surfactant was used in palm oil biodiesel (B-100) with 3 variations of alcohol, which are methanol, ethanol, and octanol. For each biodiesel with 0.4% MG content, the concentration of SMO surfactant was varied by 0.1-1% by volume of biodiesel. The molar ratio of surfactant/co-surfactants used is 1:1. Samples of biodiesel were stored at room temperature (±27 ℃). The effect of SMO and three variations of alcohol was analyzed using two flow properties parameters: Cloud Point (CP), Cold Filter Plugging Point (CFPP), and also supporting data, such as flashpoint and acid number. CP and CFPP were tested every week for a month's observation. The addition of SMO and octanol to palm oil biodiesel gave the best results by reducing CP by 4.4 ℃ and CFPP by 3 ℃. The interaction between MG, oleic tails, and hydrogen bonding between them has been analyzed by Fourier-Transform Infrared Spectroscopy (FTIR) method. There are indications of intermolecular hydrogen bonding to MG after the addition of SMO and octanol at wavenumbers 3231.11 and 3289 cm^{-1}.**

***Index Terms*—Alcohol, biodiesel, flow properties, monoglycerides, sorbitan monooleate.**

I. Introduction

Energy issues play an important rule in the development of a natural scale. The existence of energy based on fossil resources has begun to thin out and increasingly scarce. The use of energy based on fossil resources in Indonesia reaches 94% of the total supply. Due to the fast fossil fuel depletion estimated for the next coming years, the necessity of developing alternative fuels became an important issue. Biodiesel from vegetable oils is seen as a solution due to the bio-renewable characteristic [1].

Following the direction of the President of the Republic of Indonesia, starting from September 2018, the B-20 mandatory was carried out massively in all sectors. The use of the B-20 turned out to cause a problem that was a breakdown experienced by diesel vehicles, especially at the low temperatures. The cause of diesel vehicle crash is the agglomeration of impurities originating from triglycerides (TG), diglycerides (DG), and monoglycerides (MG). However, the most avoided precipitate is MG, especially Saturated Monoglycerides (SMG) [2]. Components such as "cream paste" which clog the engine fuel filter using B-20 are SMG [3]. MG may also contribute to the poor low-temperature properties of biodiesel. Note that as low as 0.1% content of SMG, could lead to the increase of Pour Point (PP)/Cloud Point (CP) or even failure of the cold soak filtration test [4], [5].

Sorbitan monooleate (SMO) is a nonionic surfactant and is applied as a food emulsifier and oral medication [6]. This surfactant is soluble in oil and insoluble in water, water/oil type of emulsifier, and has HLB value 4,3. SMO with a long hydrocarbon chain and a sterically large end group was reported to be effective on the prevention of crystal growth and agglomeration [7]-[9]. The addition of SMO showed the most optimal results by lowering the CP and PP by only requiring the lowest surfactant/co-surfactant concentration to reach single phase microemulsion. Because it has an HLB 4.3 which is between the range 3-6 and also produces microemulsion, thus it has a higher interaction with biodiesel and MG [10].

For alcohol, as the co-surfactant, methanol, ethanol, 1-propanol, 1-butanol, n-butanol, and iso-propanol can reduce the crystallization temperature of biodiesel [11]. Alcohol can reduce CP and Cold Filter Plugging Point (CFPP). Biodiesel mixed with alcohol is renewable energy and can be used as alternative energy to improve biodiesel's cold flow properties and produce better emissions without affecting engine performance [10], [12].

On the other hand, the previous research with the addition of alcohol, such as methanol by 5% and 10% could lower the flashpoint by 29.8% and 20.3%. The addition of ethanol by 5 and 10% also could lower the flashpoint by 32.8% and 25%. This may be influenced by the flashpoint of methanol and ethanol which are 11 ℃ and 12 ℃ and resulted in a drastic decrease in the flashpoint of the biodiesel and alcohol mixture. For the acid number, the addition of methanol by 5% and 10% could increase the acid number to become 0.69–0.75 mgKOH/g. The addition of ethanol by 5% and 10% also could increase the acid number to become 0.52–0.54 mgKOH/g. This probably happens since methanol and ethanol have high acidity, which can increase the acid number in the biodiesel and alcohol mixture [13].

II. Materials and Methods

A. Materials

Palm oil biodiesel (B-100) that is following the standard

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and quality (specifications) applicable in Indonesia with MG's level 0.4%, and SMO, methanol, ethanol, 1-octanol were purchased from Merck.

B. The Addition of the SMO and Alcohol in Biodiesel

The addition of SMO and alcohol as additives on biodiesel is carried out in the following stages:

Prepare biodiesels (B-100) which have MG's level 0.4% by mass, each 1 liter in a clear bottle with a lid. The addition of the SMO is 0.1, 0.5, and 1% volume and each type of alcohol with 1:1 molar fraction of surfactant/co-surfactant. Firstly, every variation of biodiesel with different types of alcohol, the flashpoints and the acid numbers are tested first to determine whether it is within the standard specifications of SNI 7182:2015 and SK Dirjen Energi Baru, Terbarukan, dan Konservasi Energi 2018. Perform an initial characterization tests such as density, viscosity, CP, and CFPP. The storage of biodiesel samples is carried out at room temperature (27 ℃). Observations and tests (CP and CFPP) are carried out every week for a month's observation.

C. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infra-Red (FTIR) analysis is carried out to determine the functional groups, hydrogen bonds, and interactions between the SMO and alcohol which gives the best results in the cold flow properties, flashpoints, and acid number. The FTIR test equipment used is the Thermo Scientific, type Nicolet IS5.

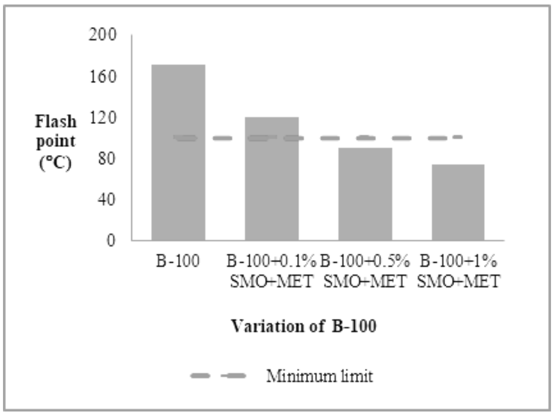
III. Results and Discussion

A. The Effect of Alcohol Addition to Biodiesel's Flashpoints

As shown in Fig.1, it could be seen that the addition of methanol, ethanol, and octanol with 1% SMO (v/v) with a ratio of 1:1 molar fraction between surfactants and co-surfactants could reduce the flashpoint by 96°C, 37.6°C, and 25°C. It could be seen that starting from the addition of methanol with only 0.5% SMO, the flashpoint was below SNI 7182:2015, which is 90°C, while the minimum standard is 100°C.

Biodiesel mixture with methanol as an additive can reduce the exhaust gas temperature due to the higher oxygen content and increase the heat of evaporation of the blended fuel, hence reduce the hydrocarbon, NO_x emission, but still, methanol is too toxic to the environment [14]. Thus, we have to consider the other effect if we want to choose methanol as the optional co-surfactant for biodiesel. For the addition of ethanol and octanol, the flashpoints were still in the range of SNI 7182: 2015 standard. However, the addition of octanol had better flashpoints than ethanol.

This happens because the initial flashpoint of methanol, ethanol, and octanol are 11 ℃, 12 ℃, and 80 ℃ respectively. So, that a drastic decrease in the flashpoints occured in the addition of methanol and ethanol compared to octanol. Biodiesel can be stored more safely if it has a higher flashpoint and also the high initial temperature is needed to do combustion in the combustion chamber [13].



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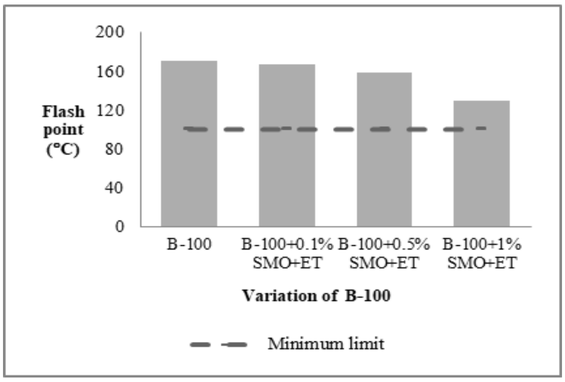

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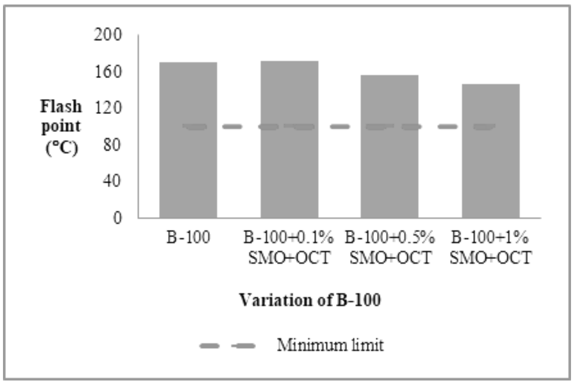

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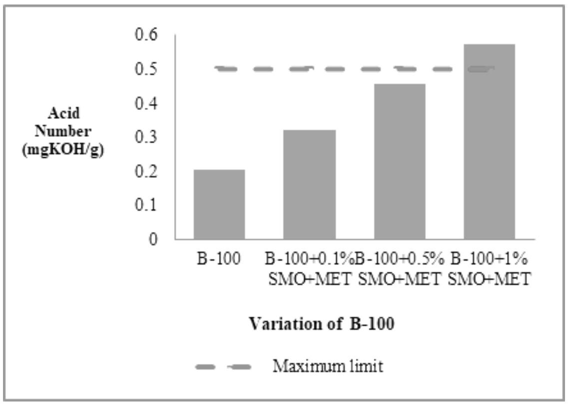
Fig. 1. The effect of flashpoints in biodiesel : (a) with the addition of SMO and methanol (b) with the addition of SMO and ethanol (c) with the addition of SMO and octanol.

B. The Effect of Alcohol Addition to Biodiesel's Acid Number

As shown in Fig. 2, it could be seen that the addition of methanol, ethanol, and octanol with 1% SMO (v/v) with a ratio of 1:1 molar fraction between surfactant and co-surfactants could increase the acid number by 1.8, 0.4, and 0.5 mgKOH/g. It was seen that, with the addition of methanol, the acid number increased dramatically compared to the addition of ethanol and octanol. In fact, with the addition of methanol at 1% SMO, the acid number had exceeded the maximum limit of SNI 7182:2015, which is 0.5 mgKOH/g. Meanwhile, ethanol and octanol have the acid number that are not so much different and still in the SNI 7182:2015 standard.

The alcohol acidity order is affected by the electron affinity of the alkoxyl radicals which in general increases with the size of the alkyl group. This order is consistent with the electron affinity values [15]. Carbon atoms have the electron affinities of -154 kJ/mol. The more carbon atoms in alcohol, the electron affinity value will be more negative, so the acidity value also tends to decrease. Methanol with a smaller number of carbon atoms compared to ethanol and octanol tends to have a greater electron affinity. Thus, the acidity value will also be greater.



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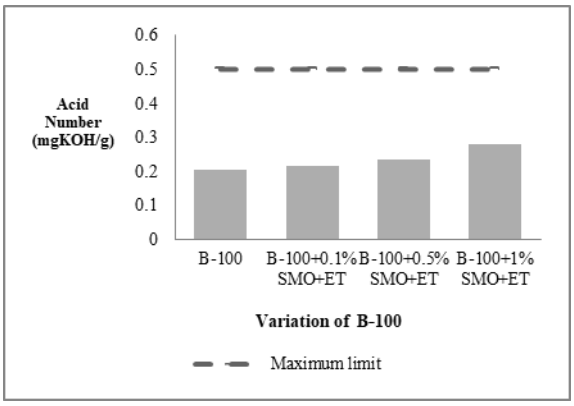

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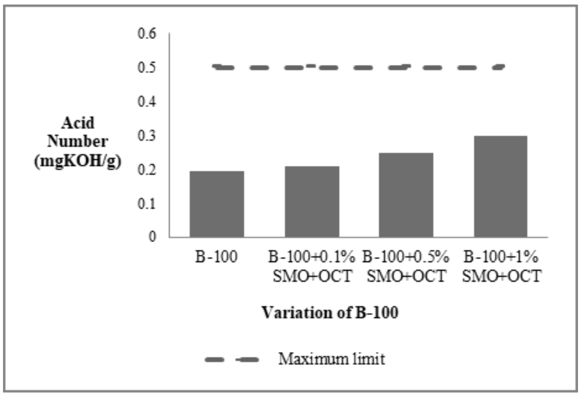

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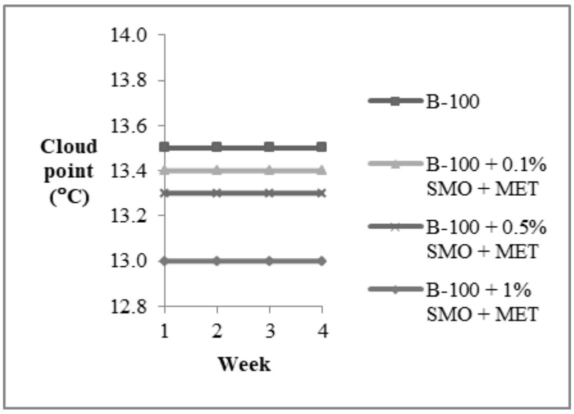
Fig. 2. The effect of the acid number in biodiesel : (a) with the addition of SMO and methanol (b) with the addition of SMO and ethanol (c) with the addition of SMO and octanol.

C. The Effect of SMO and Alcohol Addition to Biodiesel's Cold Flow Properties

CP is the temperature in which crystallization begins when small, solid crystals become visible the fuel cools [8]. For the low-temperatures applications of biodiesel, CP is a decisive parameter [16]. Based on Fig. 3(a), during four weeks of observation, with the addition of methanol, CP had a range between 13-13.4 ℃. In Fig. 3(b), with the addition of ethanol, CP had a range between 12.8-13.4 ℃. In Fig. 3(c) with the addition of octanol, CP had a range between 9-12.5 ℃. The temperature range tended to be stable from the first to the fourth week.



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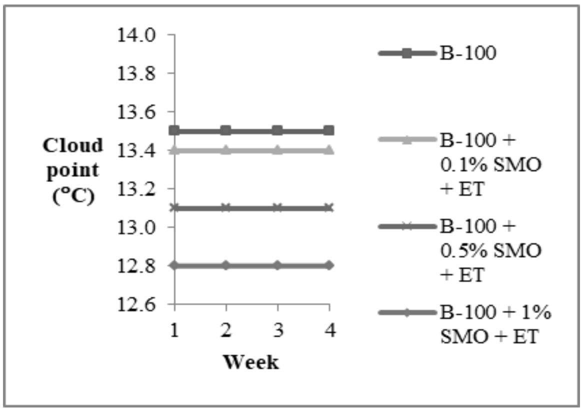

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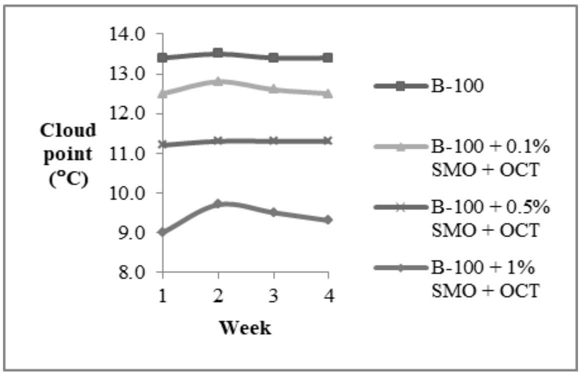

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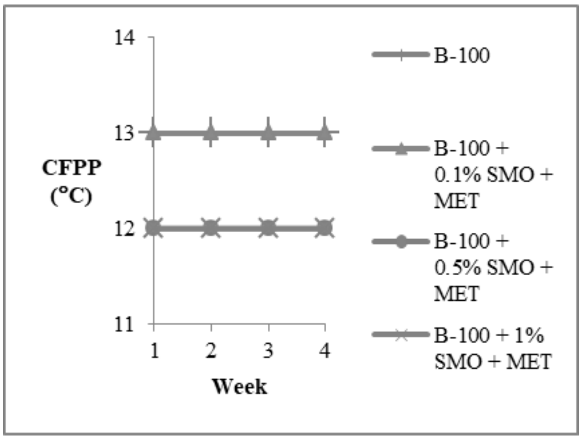
Fig. 3. The effect of CP in biodiesel at cold temperature : (a) with the addition of SMO and methanol (b) with the addition of SMO and ethanol (c) with the addition of SMO and octanol.

In general, for the four-week observation, the addition of methanol, ethanol, and octanol respectively decreased the CP by 0.5 ℃, 0.7 ℃, and 4.4 ℃. This showed that the most significant decrease in CP resulted from the addition of SMO with octanol. This happens because SMO inhibits aggregation of crystal wax/biodiesel at the low temperatures while reducing the CP of biodiesel [8] and also octanol has a carbon chain that is longer than methanol and ethanol. Thus, it can increase the hydrophobicity of the biodiesel's emulsion system [10].

CFPP is the lowest temperature, which is indicated by a decrease in temperature every 1 ℃, in which a given volume of diesel type of fuel, still passes through a standardized filtration device in a specified time when cooled under certain conditions. This gives an estimate for the lowest temperature that fuel will give trouble-free flow in certain flow systems [17].



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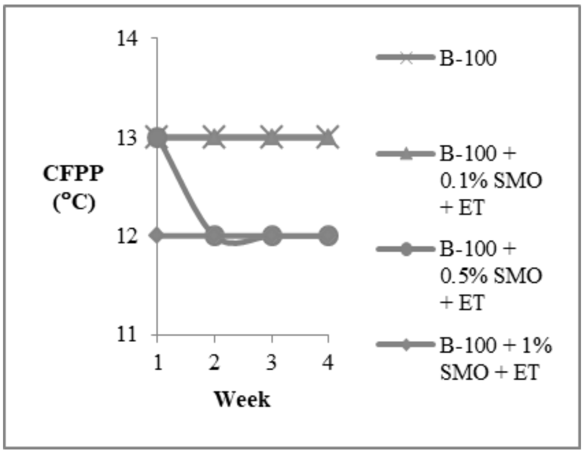

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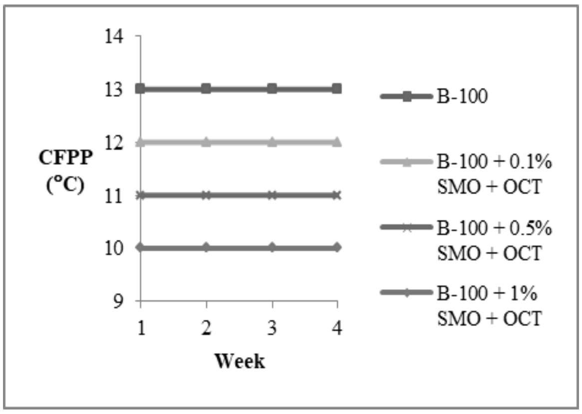

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Fig. 4. The effect of CFPP in biodiesel at cold temperature : (a) with the addition of SMO and methanol (b) with the addition of SMO and ethanol (c) with the addition of SMO and octanol.

Based on Fig. 4 (a), the addition of SMO with methanol decreased the CFPP by 1°C. In Fig. 4 (b) with the addition of ethanol, decreased the CFPP by 1°C also. Meanwhile, in Fig. 4 (c) with the addition of octanol at the highest levels could decrease the CFPP by 3°C. CFPP value tended to be stable from the first to the fourth week. From these results, the addition of SMO with octanol has the most significant effect in reducing the CFPP in palm oil biodiesel.

The addition of SMO to palm oil biodiesel can improve flow properties parameters, especially the CP and CFPP [18]. By decreasing CP, SMO and alcohol will prevent the formation of crystal's nucleation that triggers the agglomeration of MG in biodiesel. If this crystallization continues, which results in a disruption of fuel flow that causes lean conditions (poor fuel) in the engine, which responsible for starting problems in vehicles during winter [19].

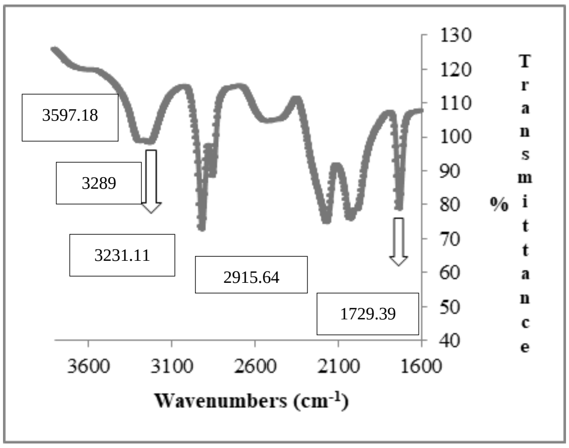
According to the flashpoints, acid number, CP, and CFPP, octanol showed the best results, thus it was tested using FTIR to illustrate the interaction between MG with the SMO as a surfactant and octanol as a co-surfactant.

D. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

Based on Fig. 5 (a), for the MG, there was a peak at wavenumber 3597.18 cm^{-1} which is a free OH group. According to Fig. 5 (b), for the MG with the addition of SMO and octanol, the peak of free OH groups in the range 3600-3650 cm^{-1} was lost. This is due to the formation of OH-O bonds and weakens the free OH group bonds. It can be estimated the type of hydrogen bonding that occurs. In Fig. 5 (b), the C-H group didn't change significantly, which was at wavenumber 2915.64 cm^{-1} to 2922.4 cm^{-1}.

In Fig. 5 (b), there was a broad peak at wavenumber 3384,57 cm^{-1} which indicated the intermolecular hydrogen bonding, whereas in Fig. 5 (a), there were 2 types of hydrogen bonds, which were the intramolecular hydrogen bond at wavenumber 3597.18 cm^{-1} and the intermolecular hydrogen bonds at wavenumbers 3231.11 cm^{-1} and 3289 cm^{-1}. This indicates that the intermolecular hydrogen in the MG bond after the addition of SMO and octanol is stronger than MG itself.

When the carbonyl group participates in the hydrogen bonding, the C=O stretching shifts to a lower frequency or a higher wavenumber. In Fig. 5 (a), the C=O stretching was at wavenumber 1729.39 cm^{-1}, whereas in Fig. 5 (b), the C=O stretching shifted to a higher wavenumber to 1740.80 cm^{-1} and its intensity also increased from 78.768% to 83.409% which indicates the occurrence of the intermolecular hydrogen bonds between C=O and OH groups in SMO and octanol [20].



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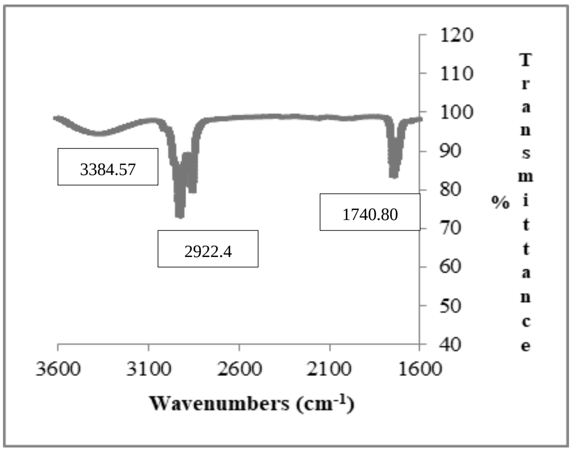

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Fig. 5. FTIR spectra of : (a) MG (b) MG with the addition of SMO and octanol.

IV. Conclusion

In this work, the addition of the SMO and alcohol to improve the flow properties of palm oil biodiesel was conducted. It can be concluded that:

1. The addition of the SMO and alcohol in palm oil biodiesel could improve the cold flow properties parameters, especially the CP and CFPP. The addition of 0.1-1% SMO with octanol gave the best results with reducing the CP by 4.4 ℃, CFPP by 3 ℃, and also the flashpoints and acid number parameters are in sync with SNI 7182: 2015 and SK Dirjen Energi Baru, Terbarukan, dan Konservasi Energi 2018 standards.
2. Based on the FTIR spectra analysis, the interaction that occured between MG, SMO, and octanol is assumed to be the intermolecular hydrogen bond.

For future work, it is recommended to conduct experiments with different types of biodiesel, surfactants, and co-surfactants. Thus, the most optimum results are obtained to prevent the MG's agglomeration in biodiesel.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Anya Prilla Azaria designed and performed the experiments, analyzed data, and wrote the paper; Sylvia Ayu Bethari and Mohammad Nasikin supervised the research and revised the paper; all authors had approved the final version.

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