Scientific Contributions Oil & Gas, Vol. 45. No. 3, December 2022: 143 - 152

SCIENTIFIC CONTRIBUTIONS OIL AND GAS
Testing Center for Oil and Gas
LEMIGAS

Journal Homepage:http://www.journal.lemigas.esdm.go.id
ISSN: 2089-3361, e-ISSN: 2541-0520

Enhancement of Flow Properties Biodiesel Using Sorbitan Monooleate

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Manuscript received: December 05th, 2022; Revised: December 13th, 2022
Approved: December 20th, 2022; Available online: December 22th, 2022

ABSTRACT - Depletion of fossil fuel and increased pollution caused by the burning of fossil fuel is a leading factor in to use of alternate energy especially palm oil biodiesel as a mixture of diesel oil fuel (B-XX). It was reported that the use of the B-20 caused a blockage in the vehicle's fuel filter. The blockage is caused by the presence of deposits formed from the agglomeration of monoglycerides. Three different biodiesels with monoglyceride content were used 0.40% - 0.60% by mass. The addition of monoglyceride standards (monopalmitin, monostearin, and monoolein) to biodiesel increases the volume of monoglyceride precipitates formed. The presence of these deposits decreases the flow properties of B-20. Research has been carried out to improve the flow properties of biodiesel by adding Sorbitan Monooleate (CMOST) surfactant, especially cloud points (CP) and cold filter plugging point (CFPP) parameters. The addition of 0.10%w - 1%w CMOST can reduce the CP by 4.80°C and CFPP by 2°C. This proves that the addition of SMO will improve the flow properties of B-XX as an alternative energy.

Keywords: Biodiesel, Flow Properties, Monoglycerides, CMOST.

How to cite this article:

Herlin Arina and Mohammad Nasikin, 2022, Enhancement of Flow Properties Biodiesel Using Sorbitan Monooleate, Scientific Contributions Oil and Gas, 45 (3) pp., 143-152. DOI.org/10.23327/SCOG.45.2.34232.

INTRODUCTION

The demand for producing alternative fuels has emerged as a crucial issue as a result of the predicted depletion of fossil resources in the upcoming years (Mamtani et al., 2021)(Maquirriain et al., 2021). Because they are biodegradable, biodiesel oils were thought to be the answer (Rahpeyma & Raheb, 2019). However, some challenges become a concern in the future in developing biodiesel as an alternative energy source as a substitute and mixture in petroleum (Firoz, 2017)(Vitiello et al., 2017)(Fuad et al., 2022)(Pramudito et al., 2022). The end product contains impurities including monoglycerides, diglycerides, unconverted triglycerides, free fatty acids, and glycerol, and the reaction conditions are unsuitable since the content of fatty acid methyl ester is less than 98% by weight (Monteiro et al., 2008)(Wawrzyniak et al., 2005)(Sia et al., 2020). Impurities lead to issues in the engine, including corrosion, the buildup of deposits in injection nozzles, and other issues (Alleman et al., 2016)(Amran et al., 2022)(Septiano et al., 2022) .

Due to their high fusion points and low solubility at low temperatures, monoglycerides with saturated mono glycerid chains (SMG) in particular can induce clogs in fuel filters at specified quantities (Chupka et al., 2012). The content of SMG has an enormous influence on biodiesel flow properties, especially CP (Chupka et al., 2014). To overcome the problem of flow properties in biodiesel can be solved by adding additives (Makarevičienė et al., 2015), modifying the structure (Souza et al., 2016), mixing diesel-biodiesel (Xue et al., 2016), and winterization. To improve the quality of the bio solar by preventing SMG deposits by adding additives, especially surfactants. This study used sorbitan monooleate (SMO) as a surfactant to enhance the flow characteristics of biodiesel by preventing the development of SMG deposits. Sorbitan monooleate is a sorbitan fatty acid ester (span), a nonionic surfactant w/o that can emulsify polar compounds in non-polar compounds and is effective in reducing surface tension. This SMO is oil-based and also stable at high temperatures and non-toxic. The use of SMO of 0.40% on B-20 with 5 ml water emulsions can provide good stability (Yahaya Khan et al., 2014). Surfactants with long hydrocarbon chains and sterically large end groups, such as SMO, have been shown to be effective in preventing crystal growth and agglomeration of biodiesel (Abe et al., 2017).

Research with SMO uses biodiesel which has different monoglyceride content, which is 0.40 (B-100 A), 0.50% (B-100 B), and 0.60% mass (B-100 C). In each biodiesel, the addition of SMO is varied by 0.10%, 0.50%, and 1% by volume. The storage of biodiesel samples is conditioned at low temperatures (16°C) and room temperature (± 27°C) (Cavalheiro et al., 2020)(Septiano et al., 2022). The effect of SMO on the initial temperature of crystal formation/wax on biodiesel was analyzed by the method of differential scanning calorimetry (DSC) ASTM D 6371(Madusanka & Manage, 2018), while the effect on flow properties was analyzed using 2 parameters: CP and CFPP . Tests are carried out every 1 week for each biodiesel sample. The use of SMO 0.10%w - 1%w improves flow properties by decreasing the cloud point by ± 1.60°C and CFPP by 2°C, which is caused by a decrease in the initial temperature of the crystal formation from 1.47°C to 6.99°C.

METHODOLOGY

Materials

Biodiesel, monoglyceride standards, SMO, beaker, pipette, volumetric pipette, magnetic stirrer, magnetic bar, automatic density meter, kinematic viscosity, CFPP tester, Differential Scanning Calorimetry (DSC), Gass Chromatography Monoglyceride (GCM).

Addition Monoglyceride standards in Biodiesel

Prepare three biodiesels (B-100A, B-100B, and B-100C) with varying monoglyceride content (0.40%, 0.50%, and 0.60%) from various raw material and producer sources, each one liter in a clear bottle with lid. Monoglyceride standards 1%w were added to each biodiesel. Storage of biodiesel samples is carried out at low temperatures (16ºC) (Cavalheiro et al., 2020). Observations and tests amount of sediment is carried out every interval from the first week to the fourth week.

Addition Sorbitan Monooleate in Biodiesel

The following stages involve the addition of SMO to improve the flow properties of biodiesel:

Prepare three biodiesels (B-100A, B-100B, and B-100C) with varying monoglyceride content from various raw material and producer sources, each one liter in a clear bottle with lid. SMO is added at 0.10%w, 0.50%w, and 1%w volume for each type of biodiesel. Perform an initial characterization test with test parameters; density, viscosity, CP and CFPP. Storage of biodiesel samples is carried out in two storage conditions; room temperature (27ºC) and low temperature (16ºC) (Cavalheiro et al., 2020). Observations and tests CFPP is carried out every interval from the first week for each type of experimental variation and all biodiesel storage conditions are carried out up to the fourth week.

RESULTS AND DISCUSSION

The Impact of Monogliserides in Biodiesel

Table.1 shows the contents of monoglyceride (monoolein, monostearyn, and monopalmitin) in biodiesel samples, analyzed using GCM ASTM D 6584 (Alleman et al., 2019).

Table 2 shows that the addition of monoglyceride standards to the biodiesel increased the levels of monopalmitin, monostearin, and monoolein, which affected the volume of monoglyceride precipitates formed. Monopalmitin is the initial trigger for crystal/wax formation when the biodiesel is at temperatures close to its haze point of 13ºC-18ºC. Monostearetes promote nucleation at low temperatures and affect crystal growth at higher temperatures, while monoolein affects the nucleation process but has no effect on crystal growth (Chupka et al., 2014) Fig.1 shows that the sediments are increasing as long as storage at a low-temperature 16ºC from the first week till the

Table 1
Monoglycerids in biodiesel

Sample	Monoolein (%mass)	Monostearin (%mass)	Monopalmitin (%mass)	In Total MG (%mass)
B-100 MG 0,40%	0,136	0,029	0,240	0,405
B-100 MG 0,50%	0,138	0,030	0,340	0,508
B-100 MG 0,60%	0,138	0,031	0,437	0,606

In this research, monoglyceride standards 1%w were added to each biodiesel.

Table 2
Monoglyceride content of biodiesel after adding standard monoglyceride

Sample	Monoolein (%mass)	Monostearin (%mass)	Monopalmitin (%mass)	In Total MG (%mass)
B-100 MG 0,45%	0,120	0,049	0,245	0,450
B-100 MG 0,55%	0,162	0,098	0,293	0,552
B-100 MG 0,65%	0,164	0,143	0,355	0,653

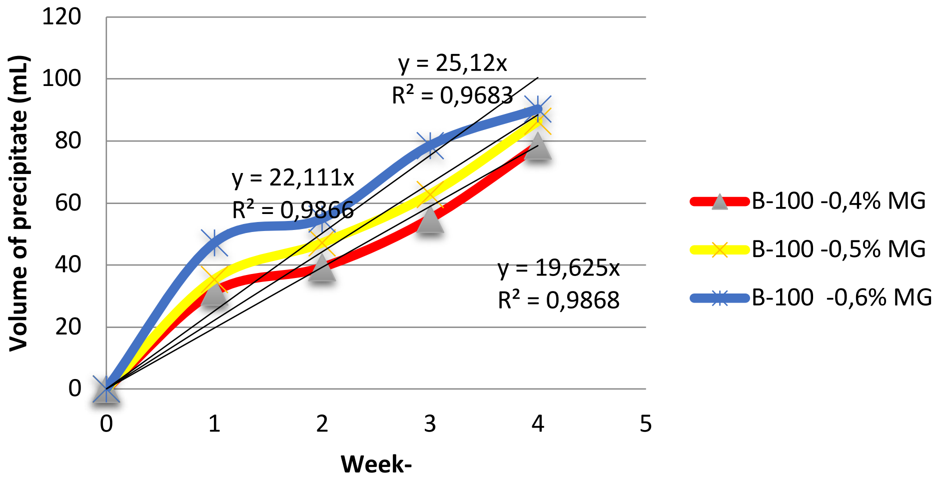
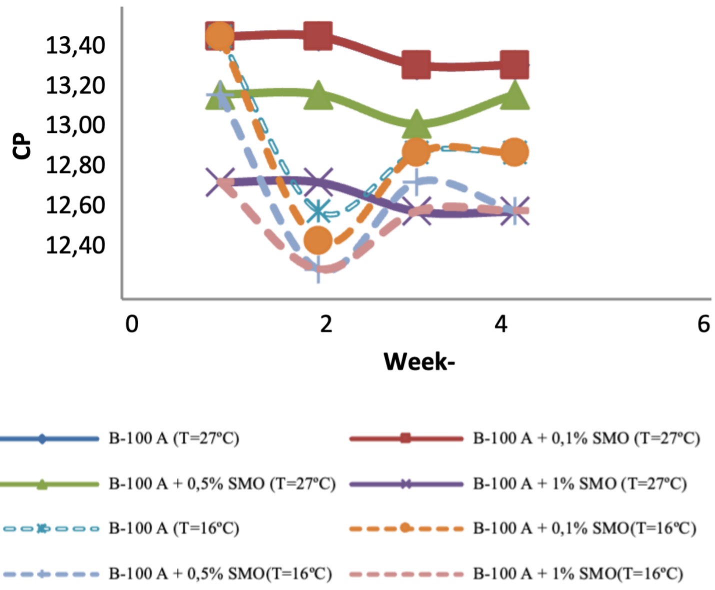


Figure 1
Volume of sediment during storage time

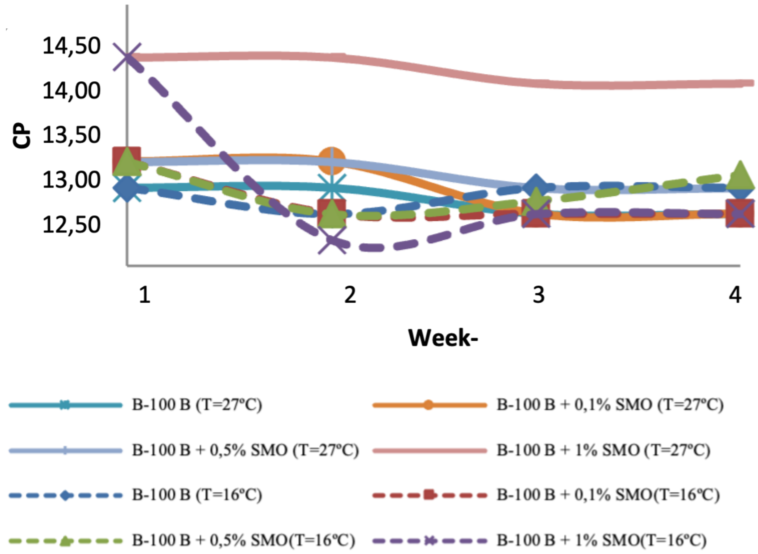
fourth week. The amount of sediment is increasing along with the intensified monoglyceride content in biodiesel (Paryanto et al., 2019). From the total sediment volume data during the storage period, the slope value of biodiesel with 0.45% monoglyceride content is 19.63, biodiesel with 0.55% monoglyceride is 22.11, and biodiesel with 0.65% monoglyceride is 25.12. From the slope data obtained, it is known that biodiesel with the largest monoglyceride content has the largest slope value (Paryanto et al., 2019). This indicates that the largest sediment volume is found in biodiesel with the largest monoglyceride content. From the data above, it can be seen that the monoglyceride content affects the amount of biodiesel deposition at low temperatures (Aisyah et al., 2018). Therefore, there is a standard limitation of monoglyceride content in biodiesel according to SNI 7182: 2015 (Nasional, 2015).

The Effect of Addition Sorbitan Monooleate in Biodiesel

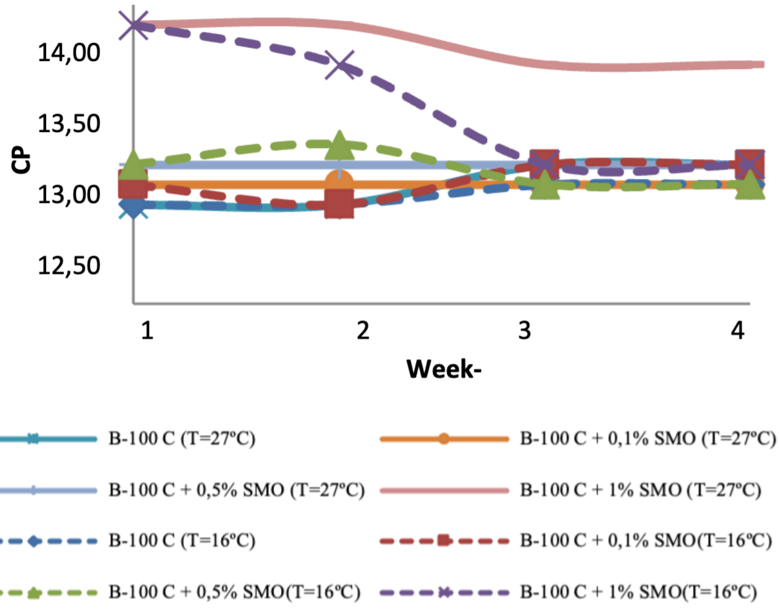
Values change in CP on B-100 A with variations of SMO (0.10%w, 0.50%w, and 1%w) at room temperature indicate a stable CP value from the first week to the fourth week, with a range of values between 12.80 - 13.20 °C. While B-100 A with a mixture of SMO variations (0.10%, 0.50%, and 1%) at low temperatures decreased the cloud point value in second week and this value was stable until fourth week , with a range of values between 12.50 - 12.80ºC, this is because biodiesel undergoes a phase change (crystal formation) when low-temperature conditioning for the first week formed deposits at the bottom of the storage container after being conditioned at room temperature. The data can be seen in fig 2(a). Samples of B-100 B with variations of SMO (0.10%,w 0.50%w, and 1%w) stored at room temperature and low temperatures decreased the value of the CP on observation of the second week and this value was stable until the fourth week (Fig 2(b)). The same results also apply to B-100 C samples with variations of SMO both stored at room temperature and low temperature (Fig 2(c)). CFPP values of B-100 A with SMO variations at room temperature and low temperatures show stable CFPP values from the first week to the fourth week, with a range of CFPP values between 13-11 ºC. The data can be seen in fig 3(a). Samples of B-100 B



(a)



(b)

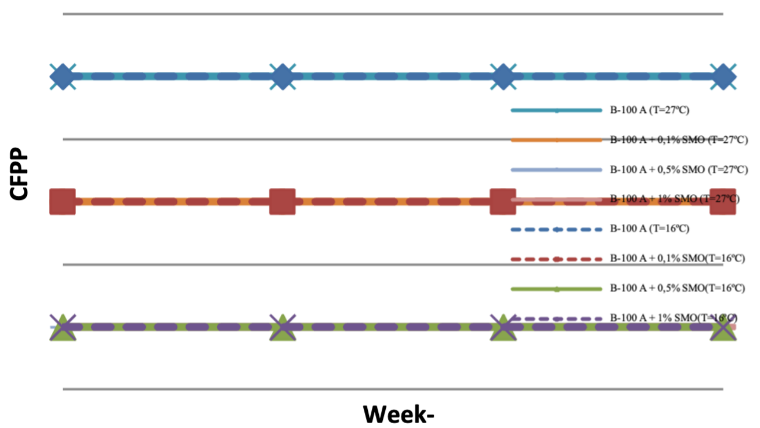


(c)

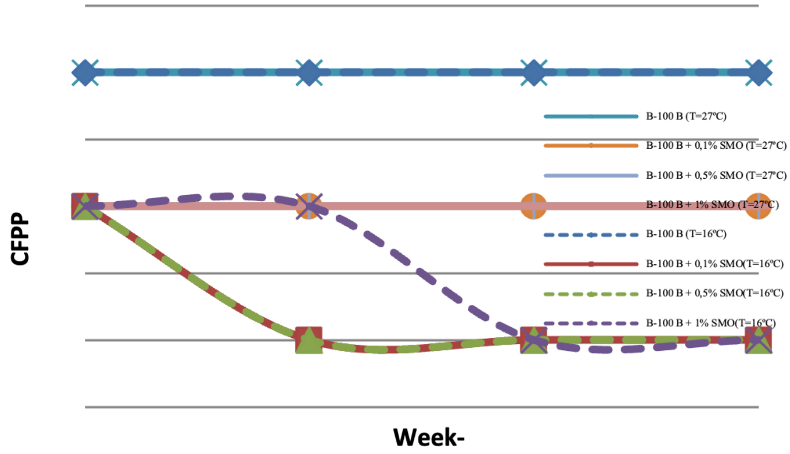
Figure 2
Comparison of values in CP at room temperature and low temperature
(a) B-100 A, (b) B-100 B, (c) B-100 C

and B-100 C with variations of SMO stored at room temperature showed stable CFPP values from the first week to the fourth week, with the range of CFPP values is between 15 - 13 ºC (Fig 3(b)). Whereas B-100 B and B-100 C, with variations of SMO at low temperatures, experienced a decrease in CFPP values at the observation of the second week and this value was stable until the fourth week with the range of CFPP values is between 15 - 13ºC, this is because after biodiesel undergoes a phase change (crystal formation) at low temperature for the first week, then the biodiesel formed deposits at the bottom of the storage container after being conditioned at room temperature. Overall, the addition of SMO by 0.10%w, 0.50%,w, and 1%w in B-100 A, B, and C samples caused a decrease in CFPP in the first to fourth week. Similar to the CP, SMO inhibits aggregation of crystal wax/biodiesel at low temperatures thereby reducing cloud points and CFPP biodiesel (Wang et al., 2014).

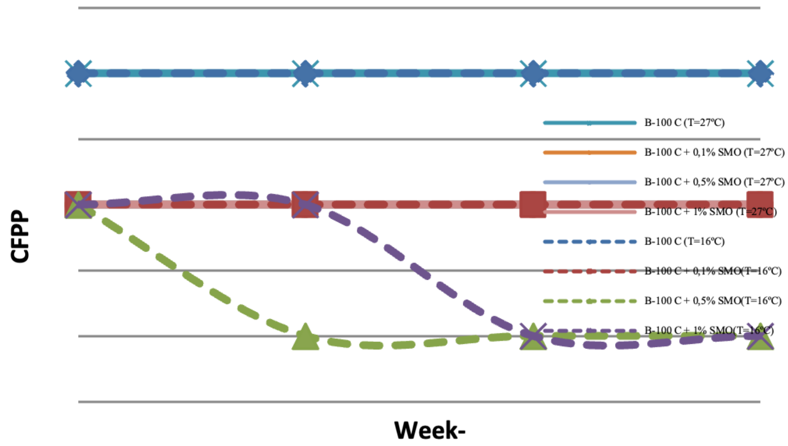
Based on all the experimental data above, the addition of SMO to three types of palm oil biodiesel with additional variations of volume SMO, gave a positive influence on biodiesel flow properties parameters. The addition of SMO to biodiesel can reduce cloud points and CFPP, as can be seen in Fig



(a)



(b)



(c)

Figure 3
Comparison of CFPP values at room temperature and low temperature, a.) B-100 A, b.) B-100 B, c.) B-100 C

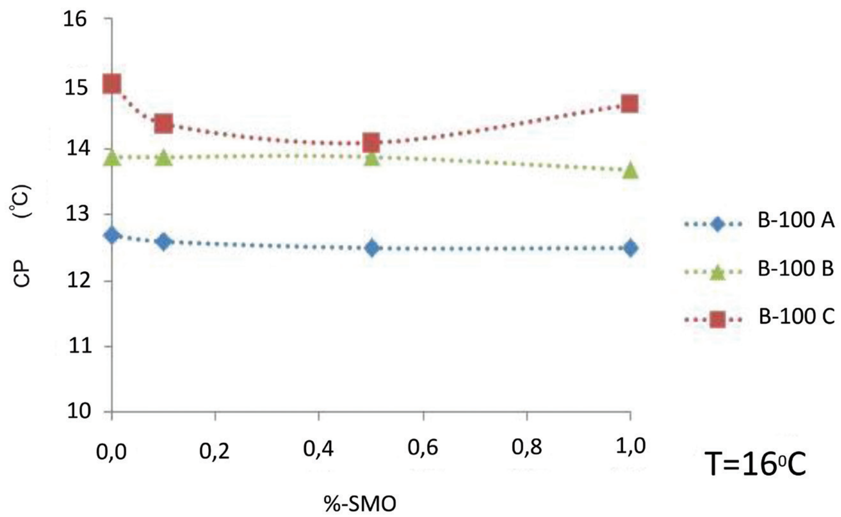


Figure 4
CP values of biodiesel after the addition of SMO

4. and Fig 5. The biggest decrease in CP and CFPP occurs in B-100 A from 13ºC to 11ºC, along with the increasing addition of SMO.

Decreasing the CP value, will prevent the formation of nucleation of the crystals that trigger the agglomeration of biodiesel. If this crystallization continues until a continuous crystal network is formed, the fuel flow is disrupted, resulting in lean conditions (poor fuel) in the engine, which eventually causes incomplete combustion, which is responsible for vehicle starting problems in the winter (Monirul et al., 2015).

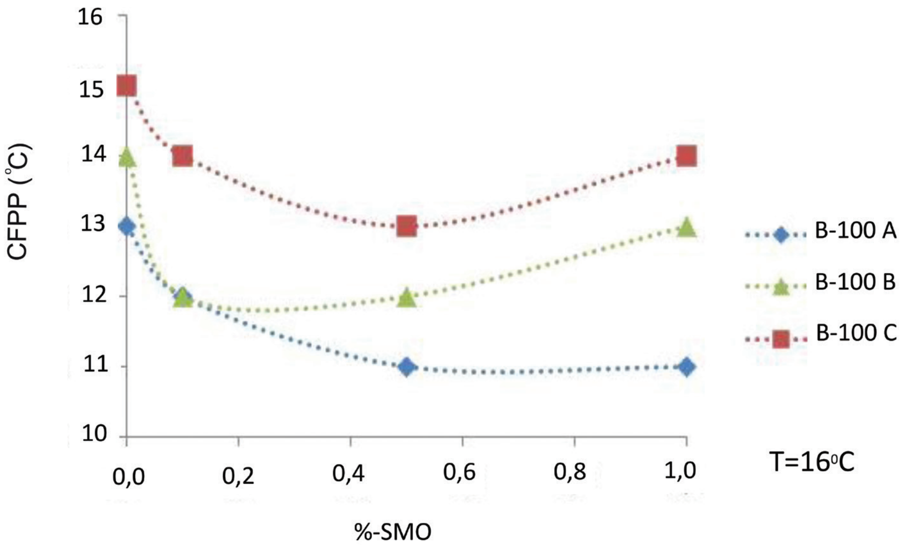


Figure 5
CFPP values of biodiesel after the addition of SMO

Differential Scanning Calorimetry (DSC) analysis

The vertical axis in Fig 6. represents the heat flow rate, and the horizontal axis represents the temperature of the DSC test, where the peak initial temperature (onset) in the curve reflects the initial temperature of crystal precipitation/wax in biodiesel. The peak slope reflects the rate of crystal precipitation/wax on biodiesel, and the liquid-solid phase change energy (ΔH) reflects dispersion stability.

Table. 3 shows the initial temperature of the peak B-100 A + 1% SMO (onset) at 6.99°C, which is lower than B-100 A which is 10.47°C. The peak temperature (peak) decreases from 19.98ºC to 18.73ºC. The absolute value ΔH decreases from 1200 mJ to 987.38 mJ. These results indicate that the addition of 1% SMO to biodiesel B-100 A reduces the temperature at which crystals are formed. When SMO is added to biodiesel, the absolute value of H decreases significantly, indicating that dispersion is more stable.

The peak area of biodiesel added with SMO is much smaller than pure biodiesel, indicating that the number of crystals is greatly reduced. Basically, adding SMO to biodiesel tends to slow the aggregation of crystals/wax at low temperatures, changing crystallization behavior by modifying crystal shape.

However, it also prevents the formation of larger crystals. All of the aforementioned factors contribute to a decrease in CP and CFPP biodiesel (Wang et al., 2014)(Sierra-Cantor & Guerrero-Fajardo, 2017). With a lower freezing point than pure biodiesel (B-100 A), the addition of 1% SMO alters the crystallization process, holding back the agglomeration of crystals, and thus slowing the growth of crystals and reducing the amount of crystals at low temperatures. The flow properties such as viscosity and shear stress known to have negative effect on buildup of wax which can be monoglyceride (Septiano et al., 2022)a machine learning algorithm using unifi ed model approach from Huang (2008. The smaller size, quantity, and distribution of crystals make B-100 A + 1% SMO have better cold flow properties (Lian et al., 2017).

CONCLUSIONS

The addition of 0.1%w - 1%w SMO to palm oil biodiesel improved the flow properties parameters, reducing CP by 1.6°C and CFPP by 2°C.

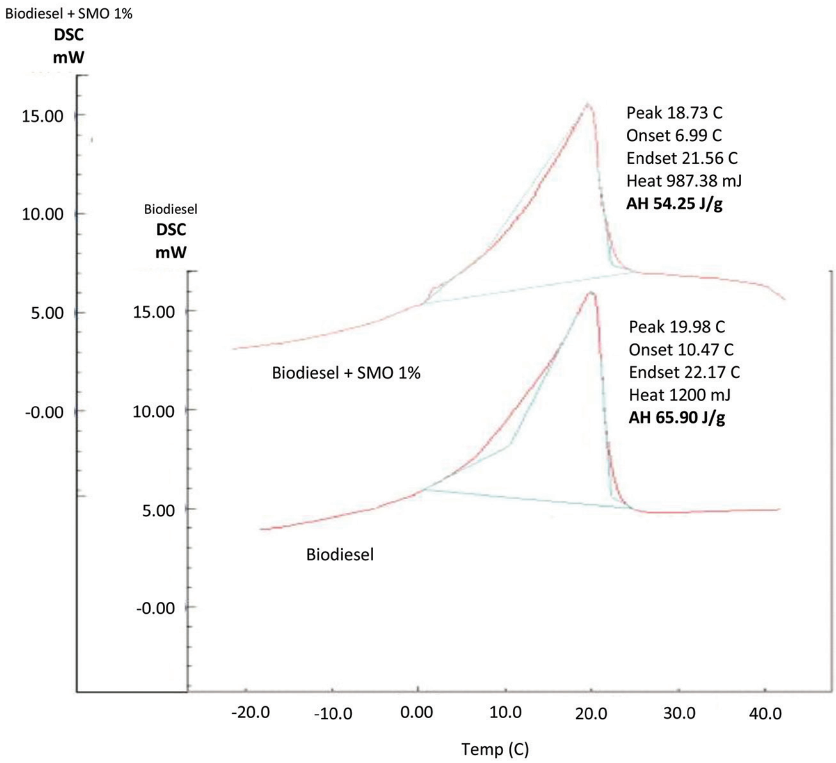


Figure 6
Values change in crystal formation temperature/wax on biodiesel and biodiesel + 1% SMO

Table 3
Temperature changes in biodiesel's wax

Sample	Onset	Peak	Endset	∆H	Heat
B-100 A	10,47	19,98	22,17	65,90	12000
B-100 A +1%SMO	6,99	18,73	21,56	54,25	987,38

These results were also supported by a decrease in the onset temperature of crystal/wax formation. The initial peak temperature in B-100 A was 10.47°C to 6.99°C in B-100 A + 1%. The peak temperature decreased from 19.98°C to 18.73°C. The absolute value of ∆H decreased from 1200 mJ to 987.38 mJ that indicated the addition of SMO to biodiesel slows down the aggregation of crystals/wax at low temperatures, modifies the crystallization behavior of crystals by changing the crystal shape and also inhibits the formation of larger crystals because SMO is able to interact with monoglycerides.

ACKNOWLEDGMENT

We acknowledge the support received from PPPTMGB Lemigas for the facilities. In addition, Lies Aisyah, Dziki Ufidian Alwi, and colleagues in Lemigas and University of Indonesia want to thank for their patience, care and support.

GLOSSARY OF TERMS

Symbol	Definition	Unit
%w	% massa	
B-XX	%w of palm oil biodiesel as a mixture of diesel oil fuel	

GCM	Gass Chromatography Monoglyceride
SMO	Sorbitan Monooleate
MG	Monoglyceride
CP	Cloud Point
CFPP	Cold filter plugging point
B-100 A	Biodiesel with monoglyceride content 0.45 %
B-100 B	Biodiesel with monoglyceride content 0.55%
B-100 C	Biodiesel with monoglyceride content 0.65%

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