

# SOLKETAL LEVULINATE ESTER AS A POTENTIAL FUEL ADDITIVE FOR PALM BIODIESEL

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## Abstract

The use of Solketal levulinate ester (SoLE) as a potential cold flow improver (CFI) for palm biodiesel is studied. SoLE was added to palm biodiesel and several crucial palm biodiesel characteristics such as density, kinematic viscosity, pour point (PP), cloud point (CP) and cold flow plugging point (CFPP) were evaluated. SoLE was mixed with palm biodiesel at levels of 0.5%, 1.0%, 2.5%, 5.0%, 10.0%, 15.0% and 20.0%, except for CFPP, only at an additional level of 1.0%, 10.0% and 15.0%. From the study, it was observed that the best percent addition of SoLE depends on the respective parameter to be improved. The density of palm biodiesel, when blended with 0.5% to 2.5% SoLE has been shown to decrease the density of neat palm biodiesel and the density value is conformed to the EN ISO 12185 standard. Kinematic viscosity values were also enhanced with the addition of SoLE below 5.0%, and the value was also within the standard range of kinematic viscosity of palm biodiesel, which must be in the range of between 3.5-5.0 mm<sup>2</sup>s<sup>-1</sup>. The blending of palm biodiesel with SoLE at 15.0%-20.0% showed some promising effects by improving the pour point of palm biodiesel, between 2°C and 5°C, with a recommended 15.0% addition that is most economic. Similarly, the cloud point of palm biodiesel blended with SoLE at the same percentage addition showed a reduction between 3°C to 6°C. Palm biodiesel blended with SoLE at 15.0% addition showed a positive and noteworthy effect, especially on the improvement of the palm-biodiesel cold flow characteristics.

**Keywords:** biodiesel by-product, fuel additives, glycerol derivatives, palm biodiesel and solketal levulinate ester.

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## INTRODUCTION

The constant upsurge in the human population has resulted in corresponding increased energy requirements, which led to extensive use of fossil fuel resources (Verma *et al.*, 2016). As a countermeasure, there has been a significant effort in expanding biodiesel as an option to conventional petroleum-derived diesel due to its environmental conformation. Biodiesel is made from renewable

resources, for example, plant-based oils or animal lipids. The world's largest palm oil producers are Indonesia and Malaysia. Hence, the most common feedstock of biodiesel in Malaysia is palm oil (Monirul *et al.*, 2015). Palm biodiesel like many other vegetable-based biodiesels, has many advantages over fossil fuels, such as being very less toxic, biodegradable, renewable and eco-friendly (Unlu *et al.*, 2018).

However, palm biodiesel also has some performance drawbacks due to the considerable amounts of saturated fatty acid content in its chemical composition (Jadhav *et al.*, 2022). High content of saturated fatty acids will give unsatisfactory cold flow characteristics to palm biodiesel, by having extreme cloud point (CP) and pour point (PP) (Tinprabath *et al.*, 2015). These drawbacks lead to the poor operability of palm biodiesel in cold weather. Therefore, to address these issues, many researchers have reported on the enhancement of palm biodiesel

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cold flow behaviour via blending with petrodiesel (Hazrat *et al.*, 2020), transesterification reaction of biodiesel, with branched or long-chain alcohols (Edith *et al.*, 2012), winterisation (Min *et al.*, 2019) and addition of pour point depressant additives (Nie and Cao, 2020).

As opposed to other methods, adding a cold flow improver is possibly the utmost appropriate and practical method to improve the cold flow property of biodiesel, because it is more economical and convenient. Cold flow improvers (CFIs), are additives that have a low melting point, branched and non-aromatic. They can reduce the influence of wax crystals on the fuel by modifying their shape, size, growth rate and agglomeration, thus inhibiting the formation of large crystals at low temperatures. Most of the CFIs promote the formation of small (10-100 nm) needle-shaped crystals.

Cold flow properties of diesel fuel are generally determined by the following parameters *viz.* CP (cloud point), PP (pour point), and CFPP (cold filter plugging point) CP indicate the susceptibility of the fuel to plug the filters of the engine in a cold operating climate. On the other hand, PP refers to the bottom-most temperature at which the fuel becomes semi-solid and loses its flow characteristics. CFPP is the lowest temperature, expressed in degrees Celsius ( $^{\circ}\text{C}$ ), at which a given volume of diesel type of fuel still passes through a standardised filtration device in a specified time, when cooled under certain conditions (Verma *et al.*, 2016).

Recently, there are studies that reported the use of glycerol-based oxygenates as CFI for biodiesel, with the benefit of these compounds being renewable products derived from biomass (Muniz *et al.*, 2019). Converting glycerol to CFI also can be an alternative way to valorise glycerol to support the sustainability of the biodiesel industry. Converting glycerol to fuel additives can be made via the esterification reaction of glycerol with an organic acid such as acetic acid, levulinic acid, or the etherification and ketalization reaction of glycerol along with alcohols or ketones respectively. This will generate a range of oxygenated glycerol compounds such as alkyl and acetyl ethers of glycerol and solketals (Saengarun *et al.*, 2018; Unlu *et al.*, 2017). These potential glycerol derivatives oxygenated additives have been evaluated as biodiesel cold flow improvers. Solketal (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane) respectively has attracted more attention recently, due to its unique features in improving cold flow properties and flash point temperatures of both diesel and biodiesel as well as its blends (Aghbashlo *et al.*, 2018). It was also disclosed in a study that octane number and gum growth in gasoline decreased when oxygenated fuel additive from glycerol namely solketal was added. (Ilgen *et al.*, 2017; Saengarun *et al.*, 2017). Diesel fuel when blended with glycerol-based additives was

reported to minimise particulate emissions, improve lubricity and engine performance (Çakmak and Özcan, 2020; Neamtu *et al.*, 2019)

Glycerol-based oxygenated compound that will be discussed in this article is classified as a solketal ester. Generally, solketal ester is made from solketal and organic acid or ester. Solketal is a derivative of glycerol, which is prepared from a reaction between glycerol and acetone. Whereas compounds with carbonyl groups such as fatty acids, ketones, and anhydrides that have been studied to produce solketal esters are caprylic, lauric, palmitic and stearic acids, acetic anhydride, butyric anhydride, butanone, cyclopentanone, 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone (Perosa *et al.*, 2016). The selection of the carbonyl group from each study is arbitrary.

On the other hand, to the best of our knowledge, no study was published that described solketal levulinate ester as a cold flow improver additive, particularly in palm biodiesel. Solketal levulinate ester (SoLE) is a 100% bio-based product prepared from a reaction between solketal and methyl levulinate. Methyl levulinate is derived from biomass resources such as palm biomass including leaves, fronds and trunks (Liang *et al.*, 2020). Therefore, in this work, we present the study of SoLE as a CFI additive to enhance the palm biodiesel cold flow characteristics. Effects on density value, kinematic viscosity, acid value, cloud point, pour point and cold filter plugging point were assessed.

## MATERIALS AND METHODS

Solketal (99.8% purity), methyl levulinate, and sodium carbonate have been acquired from Sigma Aldrich, USA. Diethyl ether (99.0%) from ChemAR, Kuala Lumpur. Palm biodiesel was sourced from a local plant. All chemicals were directly used.

### Synthesis Ester of Solketal Levulinate (SoLE)

SoLE was prepared from a method reported by Mariam *et al.* (2021). In brief, the reaction was conducted in a 50 mL one-necked round bottom flask assisted with a magnetic stirrer. Solketal, methyl levulinate and sodium carbonate were put in and heated to the preset temperature of  $140^{\circ}\text{C}$  in the said flask and were heated for 4hr. Reagents were weighed up to the preferred molar ratio. The molar ratio of methyl levulinate to solketal used in this study was 1:3 where the percentage of catalyst added was 1.5% of solketal weight. An oil bath assisted by thermometer was used in monitoring the temperature of the reaction. A low vacuum was applied at the end of the condenser to capture and observe the released methanol from the

reaction. The reaction was observed using thin-layer chromatography. As the reaction completed, the product obtained was washed with distilled water to wash away sodium carbonate. This was followed by a solvent extraction step to extract SoLE using diethyl ether as solvent. These steps were repeated three times. After washing, the non-aqueous layer was collected and purified using a rotary evaporator. The product was analysed with gas chromatography (GC),  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. The yield of SoLE was determined to be about 75% and the purity of prepared SoLE was about 95%.

### Analysis and Characterisation of SoLE

**FTIR.** Determination of the SoLE functional groups was conducted *via* Fourier Transform Infra-Red analysis using Spectrum 100 FT-IR Spectrometer Perkin Elmer and the spectra were collected using 64 scans at  $4\text{ cm}^{-1}$  resolution in the range of  $650\text{--}4000\text{ cm}^{-1}$ .

**GC analysis.** GC analysis was conducted to confirm the quantitative percentage of SoLE. The GC (Agilent System 6890N Network GC System) was set up with a ZB-5HT INFERNO ( $30\text{ m} \times 250\text{ }\mu\text{m} \times 0.2\text{ }\mu\text{m}$ ) capillary column and detector of flame ionisation. The temperature was programmed at oven temperature,  $80^\circ\text{C}$ ; initial temperature,  $80^\circ\text{C}$ ; the heating rate at  $10^\circ\text{C min}^{-1}$ ; final temperature  $315^\circ\text{C}$ ; injector temperature,  $300^\circ\text{C}$ ; detector temperature,  $325^\circ\text{C}$ ; carrier gas, helium at  $40.0\text{ mL min}^{-1}$ . For sample preparation, it was diluted with dimethylformamide and dichloromethane with a ratio of one to one. The percent composition of the sample was confirmed conferring to GC chromatogram percent area.

**$^1\text{H}$  and  $^{13}\text{C}$  NMR analysis.** Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) NMR spectroscopy were recorded on JOEL JNM-ECZ600R at 600 MHz and 150 MHz, respectively at 298 K with approximately 10% w/v solutions in deuterated chloroform (Sigma, USA) NMR solvents. Chemical shifts are quoted in ppm relative to internal standard tetramethylsilane (TMS) (Sigma, USA) and reference to the residual solvent. All coupling constants are quoted in hertz (Hz). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments were routinely confirmed by  $^1\text{H}\text{--}^1\text{H}$  (COSY) and  $^1\text{H}\text{--}^{13}\text{C}$  (HMQC) data.

### Chemical Analysis

**Acid Value.** Acid value (AV) is defined as the number in milligrams of potassium hydroxide (KOH) (mg) (System, Malaysia) needed to neutralise the free fatty acid present in the unit mass (g) of a chemical

substance. MPOB Test Method c2.7: 2004 was used as the test method.

The acid value is conveyed as Equation (1):

$$\text{Acid value} = \frac{[(56.1 \times V (\text{mL}) \times M) / m] \text{ mg KOH g}^{-1}}{\quad} \quad (1)$$

where V is the KOH volume, M is concentration of KOH solution, m is the mass of the sample. AV analysis was made in duplicate and presented as mean value.

### Physicochemical Analysis

**Density.** Density was testified using DMA 5000 M (Anton Paar, UK) density meter. By using a syringe, 2 mL of product was transferred to a measuring tube until a drop emerged from the sample outlet adapter. Any presence of bubbles was circumvented. The measurement was conducted in duplicate for every product at  $25^\circ\text{C}$  and finalised as a mean value.

### Kinematic Viscosity

Measurement of kinematic viscosity (KV) was according to ASTM method D 445–12. PMT Tamson NVB Classic (Normalab, France) was used to conduct the test. The viscometer bath was set between  $40^\circ\text{C}$  and  $100^\circ\text{C}$  (Constant temperature bath, Cannon Instruments, State College, PA). The test was duplicated for every product and the final reading was recorded in average value. ASTM method D446 was used as a standard to select types of viscometry capillary (Ubbelohde capillary viscometer, Cannon Instruments, USA).

### Cloud Point

Cloud point (CP) of SoLE was tested via the PP Classic purchased from Norma lab (Belgium) following the official ASTM method D 2500–09. The product (50 mL) was put in a test container and examined at  $1^\circ\text{C}$  decrement.

### Pour point

Pour point (PP) was evaluated in reference to ASTM method D 97–12 using PP Classic (Normalab, Belgium) with an efficiency of  $3^\circ\text{C}$ . The analysis was conducted by putting a test container containing 50 mL of sample into a cylinder immersed in ethanol (95%) as the cooling media. The analysis container was clutched horizontally for 5 s in every  $3^\circ\text{C}$  reductions and ceased when samples were no longer flowing. The temperature where the product is not flowing would be added to  $3^\circ\text{C}$  and denoted as the pour point.

## Cold Filter Plugging Point

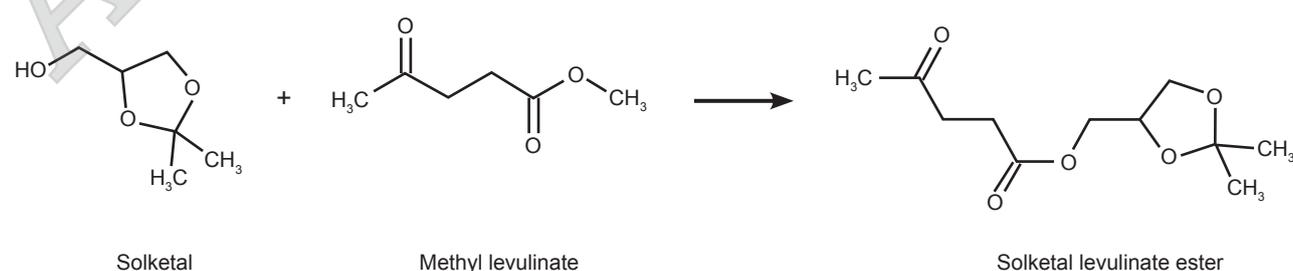
Cold filter plugging point were determined based on EN 116. The CFPP is the highest temperature at which a given volume of fuel fails to pass through a standard filtration device in a specific time, when cooled under standard conditions.

## RESULTS AND DISCUSSION

Synthesis of levulinate ester via an esterification reaction between levulinic acid and short chain alcohol has been previously reported using different homogeneous acid catalysts, for example, sulphuric acid ( $H_2SO_4$ ), hydrochloric acid (HCl) and phosphoric acid ( $H_3PO_4$ ) (Pileidis and Titirici, 2016) and various heterogeneous acid catalysts, such as sulphonic acid functionalised materials (Song *et al.*, 2015). However, we observed that the esterification of solketal with levulinic acid in the existence of an acid catalyst gave sub-standard yields of SoLE. This might be due to hydrolysis of solketal that might occur under an acidic state developing unwanted by-products. This corresponds to the result described by Noor Armylisas *et al.* (2021) where utilisation of acid catalyst will accommodate more side reactions, for example, fatty acid degradation (oxidation, dimerisation) or from polymerisation or dehydration of glycerol that turns into a higher polymer of glycerol or acrolein. Therefore, in this study, SoLE was synthesised using a base-catalysed transesterification reaction as we previously established in our lab. The properties of SoLE with 95% purity were reported previously (Mariam *et al.*, 2021). *Figure 1* showed the chemical reaction equation for transesterification of solketal with methyl levulinate to obtain solketal levulinate ester.

### Fuel Properties of Biodiesel Blended with SoLE as Cold Flow Improver Additive

The properties of the palm biodiesel with the addition of v/v SoLE were investigated as a CFI additive. Addition of SoLE was at 0.5%, 1.0%,



*Figure 1.* Reaction scheme of transesterification of solketal with methyl levulinate to obtain solketal levulinate ester.

2.5%, 5.0%, 10.0%, 15.0% and 20.0% respectively. The fuel properties, for example, density (25°C) (EN ISO 12185), viscosity (40°C) (EN ISO 3104), acid value (EN 14104), pour point (ISO 3016), and cloud point (ASTM D2386) were measured and concluded in agreement with the established methods. The biodiesel parameters were established according to EN 14214 and ASTM D6751 standards. Fuel property tests and measurements were repeated two times and they were reported as a mean value.

### Density

Density is a crucial fuel characteristic for biodiesel. Biodiesel has been deliberated as renewable fuel with both benefits and disadvantages. However, the disadvantage of biodiesel such as high density at low temperature affects diesel engines and fuel systems destructively. Thus, the reduction of the density of biodiesel fuel in unmodified diesel engines is crucial (Pham *et al.*, 2018). Consistent with the standard implemented (EN ISO 12185), the density value of biodiesel must be in the range of between 860-900  $kg\ m^{-3}$ . The density of SoLE and neat palm biodiesel use in this study are 1097.6  $kg\ m^{-3}$  and 877  $kg\ m^{-3}$  respectively. The density of palm biodiesel with the incorporation of different amounts of SoLE was between 870-908  $kg\ m^{-3}$  except for biodiesel with the addition of 20% SoLE (*Figure 2*). However best performance was observed with addition of SoLE at 0.5%, that gave density value of 869.5  $kg\ m^{-3}$ . The addition of SoLE has reduced the density of neat palm biodiesel by 7  $kg\ m^{-3}$ . As described by Alptekin and Canakci (2008), density of the material (oil) should be very low (860-900  $kg\ m^{-3}$ ) to avoid engine failure. High density can affect the process of atomisation during biodiesel combustion, resulting in lower engine performance and increased NOx emissions.

Properties of palm biodiesel when added with SoLE has showed to comply with the international standards, even with high density of SoLE (1096.6  $kg\ m^{-3}$ ), proving its compatibility to be used in a diesel engine.

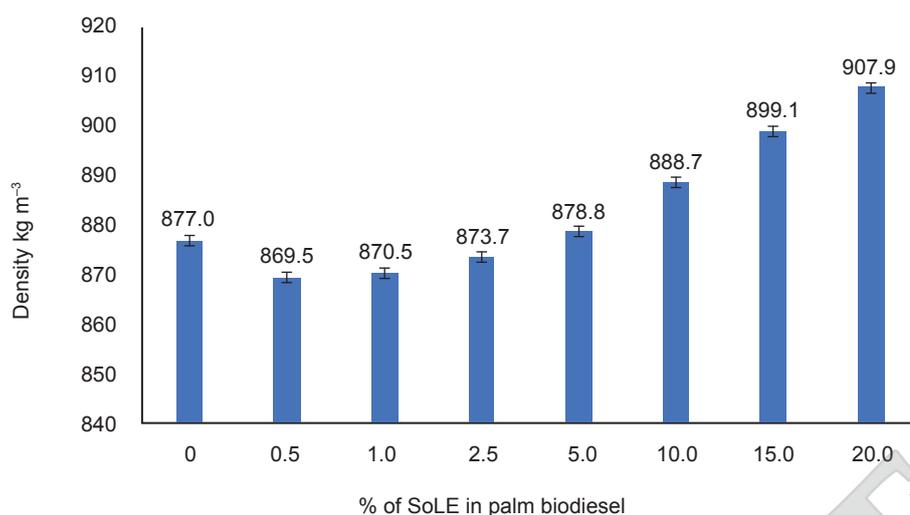


Figure 2. Effect of SoLE amount on the density of palm biodiesel.

Therefore, the results showed that palm biodiesel blended with 0.5% to 2.5% of SoLE have improved the density of palm biodiesel to the minimum limit of the standard specification value. Addition of SoLE has showed to improve the characteristic that contribute to the engine performance. This indicated the noteworthy potential of using SoLE as an effective CFI additive for palm biodiesel.

Study by Garcia *et al.* (2008) has reported that addition of pure solketal at 5% to neat biodiesel has showed to increase the density of the neat biodiesel. They also extent their study on the addition of solketal acetate and triacetin mixture at 2/3 ratio and similar result was observed where the density of the neat biodiesel increased. In terms of density characteristics, they concluded that the addition of acetyl group to solketal does not help in improving the biodiesel density. In contrast with our study, the addition of levulinate group to solketal had improved the density of neat biodiesel. Nevertheless, our finding is coherent with the study by Ali *et al.* (2014), that reported the density decreased with the addition of oxygenates additive such as alcohol and ether to palm oil methyl ester. Venkatesan *et al.* (2017) in their study also revealed that, the density of biodiesel blends from *Jatropha* oil were gradually reduced with the addition of oxygenates. Generally, addition of suitable oxygenates additives, such as glycerol based oxygenates compound to palm biodiesel, can potentially reduce its density. The basic factors that affect the liquid density are atomic weight of the element or the molecular weight of the compound and the distance between atoms (Inter-atomic distances) or molecules (Inter-molecular spaces). Therefore, the differences of the effect given by respective oxygenates additives are reported might be due to the basic factors as stated above.

### Kinematic Viscosity

Kinematic viscosity is the crucial key feature of biodiesel which measures the resistance of the biodiesel to flow (Kassem and Çamur, 2016). High kinematic viscosity of fuel has a detrimental effect in low-temperature weather, where viscosity escalates when the temperature is low (Liu, 2015). According to the kinematic viscosity standard for biodiesel, the kinematic viscosity values must be in the range of 3.50 and 5.00 mm<sup>2</sup> s<sup>-1</sup>. The kinematic viscosity of SoLE and palm biodiesel used in this study were 7.32 mm<sup>2</sup> s<sup>-1</sup> and 4.64 mm<sup>2</sup> s<sup>-1</sup> respectively. Figure 3 showed the deviations in the kinematic viscosity value of palm biodiesel versus the SoLE amount. It was observed that the addition of SoLE at all percentages tested (0.5 to 20.0% v/v) resulted in kinematic viscosity of between 4.51-4.73 mm<sup>2</sup> s<sup>-1</sup>. These values are within the standard specification for kinematic viscosity of biodiesel. However, it was also discovered that at lower percentage addition of SoLE (0.5 to 5.0%), the viscosity of palm biodiesel had slightly enhanced.

Palm biodiesel blended with SoLE has showed to slightly improve the viscosity values that is also within the standard limits of the kinematic viscosity standards for biodiesel. This result demonstrates that, the process of improving cold flow property by SoLE addition would not give an adverse effect on other fuel properties such as kinematic viscosity and density.

Our findings supported the previous study from Garcia *et al.* (2008) where they have reported that introduction of an acetyl group in the free OH of solketal has been an effective solution to improve the viscosity of palm biodiesel. The viscosity also complies with ASTM D6751 and EN 14214 Standards.

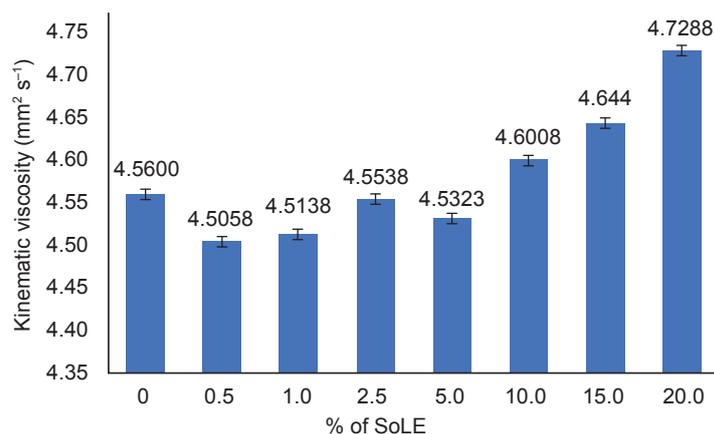


Figure 3. Effect of SoLE amount on the kinematic viscosity of palm biodiesel.

To the best of our knowledge, no previous reports had discussed on how the addition of CFI additive had affected the kinematic viscosity of palm biodiesel. This might be due to the raw materials having the greatest influence on the biodiesel viscosity. Fatty acid composition determines the degree of saturation while the composition determines the degree of saturation. Viscosity increases with increasing degree of saturation (Ayetor *et al.*, 2015).

#### Acid Value

The acid value measurements were conducted following EN 14104 analysis method. The maximum acid value of palm biodiesel, as stated in the above analysis method is 0.5mg KOH g<sup>-1</sup>. Typically for biodiesel, the acid number derives almost exclusively from the fatty acid content due to the hydrolysis (depend on the amount of water that may likely be present in the biodiesel) of ester linkages in both the triglyceride feedstock and the biodiesel during its manufacturing (Mahajan *et al.*, 2006). Figure 4 demonstrates the variations of

acid value with the addition of various amounts of SoLE in the fuel mixture. The addition of 0.5% to 20.0% of SoLE into palm biodiesel resulted in acid values of blends to be approximately 0.6 mg KOH g<sup>-1</sup>. The result shows a marginal difference in the acid number of biodiesel blends in comparison with the maximum limit allowed in EN 14104 standard. This might be due to the contribution of acid value from levulinic acid which may originate from the hydrolysis of SoLE that produce solketal. Palm biodiesel blended with SoLE only showed a marginal deviation from the standard specification for the acid value. This can be improved by maximum stripping off any compound that may contribute to the higher acid value of palm biodiesel.

#### Pour Point

The pour points of biodiesel were tested according to the ISO 3016:2019(E) analysis method. The pour point of a fuel is defined as the lowest temperature at which it becomes semi-solid and

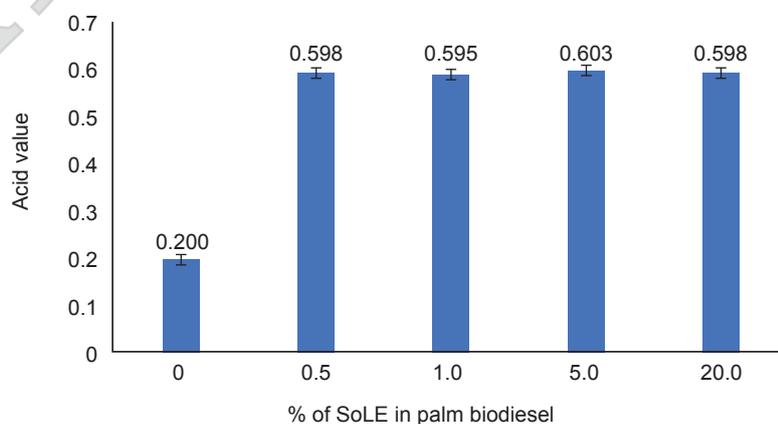


Figure 4. Effect of SoLE amount on the acid value of palm biodiesel.

loses its flow characteristics. When the temperature is further reduced, the crystal nuclei aggrandise and inhibit the free-flowing of fuel (Verma *et al.*, 2016). From our lab analysis, palm biodiesel pour point was 19°C and this value was similar as reported by Verma *et al.* (2016), which was 19.7°C. Figure 5 shows the pour points of palm biodiesel blended with SoLE at levels of 0.5% to 20.0%. The results showed reductions of pour point values between 2°C to 5°C, in comparison with the neat palm biodiesel. The lowest pour point was observed when 15.0% and 20.0% of SoLE was added. The results observed in our study are in accordance with the observation conveyed by Cornejo *et al.* (2017) that evaluated different glycerol-based oxygenated compounds such as solketal, triacetin and mixtures of esters mono-, di- and tri-acetylated glycerol (MAG, DAG, and TAG) and a mixture of ethers such as mono-, di and tri-*tert*-butyl glycerol (MTBG, DTBG, and TTBG). Their study conveyed that glycerol-based oxygenated compounds stated above (Figure 6) have been proven as pour point and cloud point improvers, especially in biodiesel and their blends. Another study by Silva *et al.* (2010) indicated that the addition of butanal/glycerol acetal (one of the glycerol-based oxygenated compound family) had reduced the pour point of animal fat biodiesel in 5°C.

It should be highlighted that as the palm biodiesel temperature was reduced, polar groups of oxygen-bearing functional groups, be it esters, alcohols, ketones, and ethers from the glycerol-based oxygenates class, would come in contact with the polar methyl ester groups to reduce and arrange the cluster size of the hydrocarbon crystals. Thus, pour and cloud point of biodiesel were reduced when the crystal size of the saturated fatty methyl ester was lessened (Saengarun *et al.*, 2017).

Glycerol-based oxygenated additive generally has been reported to improve the pour point of biodiesel. However, the advantage of SoLE over other glycerol-based oxygenated additive as raw material to produce SoLE both can be obtained from palm derivatives, which is glycerol from palm oil and levulinic acid from palm biomass respectively. This can be a sustainable approach to improve palm biodiesel industry directly and palm oil industry at whole.

### Cloud Point

Cloud point is the evaluation of the critically low temperature at which fuel develops the first particles of wax crystals and cloudiness is observed, as the temperature of the fuel gradually decreased under standard conditions (Saeedi Dehaghani and Rahimi, 2019). The best cloud point should be obtained in the range of -3 to -12 according to standard. Palm biodiesel contains high content of palmitic acid that contributes to the high cloud point of palm biodiesel at 21°C (Verma *et al.*, 2016). Figure 7 presents the cloud point values of palm biodiesel, blended with various amounts of SoLE. It was observed that, as the amount of SoLE elevated, the cloud point of palm biodiesel depreciated from 21°C to as low as 15°C. Lowest cloud point was observed when palm biodiesel was blended with 15% and 20% of SoLE. From this result, we reckon that, it is likely that SoLE had depresses the palm biodiesel cloud point. SoLE played a role in delaying the agglomeration of the wax crystals in palm biodiesel, or in other words, it alters the crystal shape and size which will inhibit lateral crystal growth. This effect is of utmost interest showed by SoLE. In this study, the cloud point measurements were performed according to the ASTM D 2386 analysis method. According to this

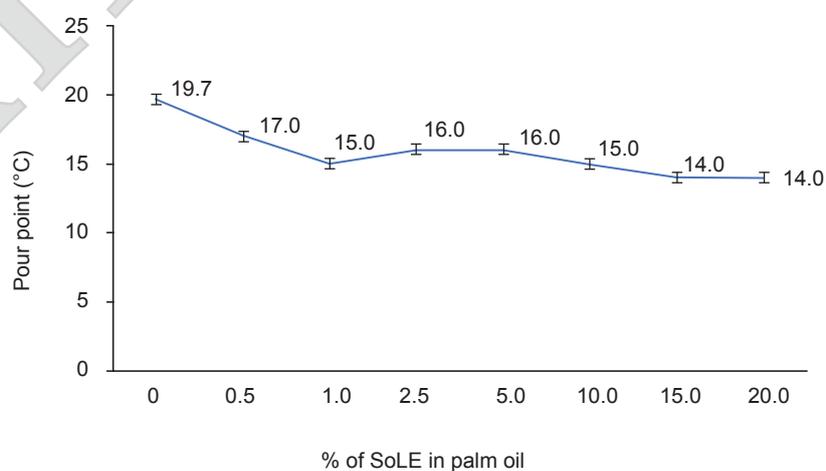


Figure 4. Effect of SoLE amount on the acid value of palm biodiesel.

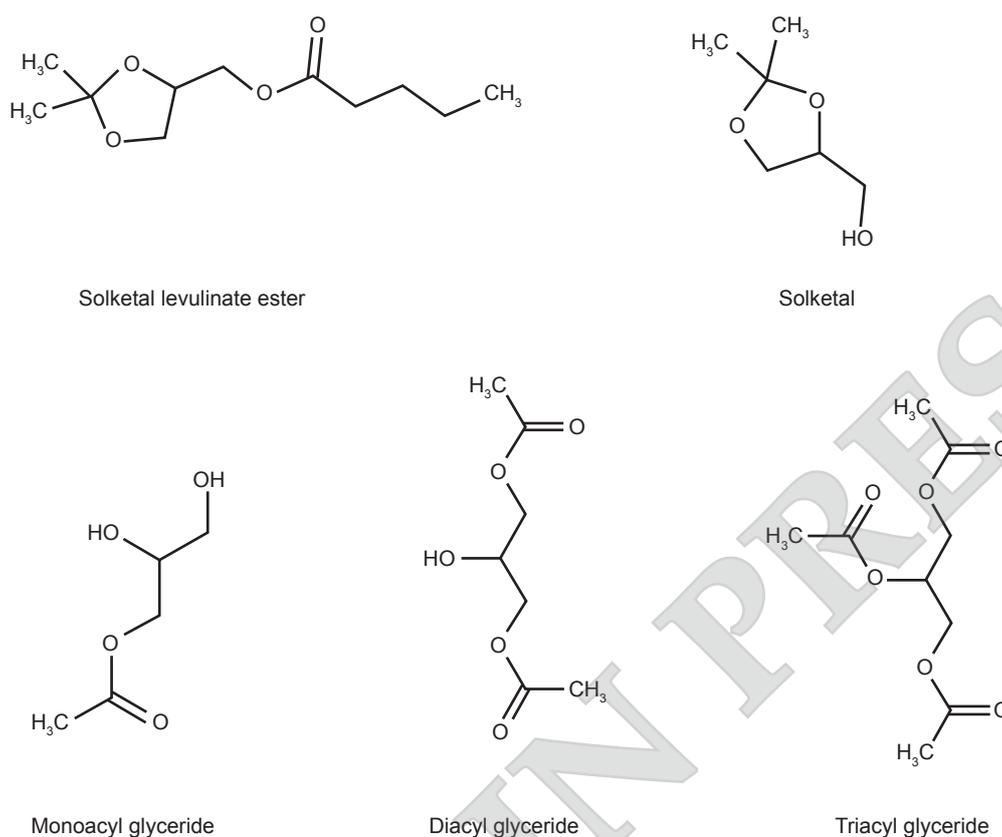


Figure 6. Chemical structure of glycerol-based oxygenated compounds.

standard, the cloud point value of biodiesel should be between 5°C and -65°C. From the results obtained, the addition of SoLE has improved palm biodiesel cloud point even though it has slightly diverged from standard. This result showed the potential of SoLE as a cold flow improver of palm biodiesel. This finding is in accordance with Klepáčová, *et al.* (2003) whereby their study stated that the glycerol alkyl ethers (glycerol oxygenates with ether functional group) had reduced the cloud point when added to biodiesel with 5°C reduction while SoLE at 6°C. From this study, to improve the cloud point of palm biodiesel, the optimum suggested addition of SoLE is 15%. As described earlier, the advantage of SoLE is the raw material from palm based origin, which can reduce the dependency on imported chemical additive to improve the CFI of palm biodiesel.

### Cold Filter Plugging Point

Cold filter plugging (CFPP) point is described as the minimum temperature at which 20 mL of

sample passes through the filter in 60 or less (Leng *et al.*, 2020). According to the standards CFPP value, it should be +5°C or as low as -20°C when compared with the neat biodiesel CFPP value. *Table 1* shows CFPP value of neat biodiesel and CFPP value of neat biodiesel when added with 1%, 10% and 15%. The result conveyed that no significant improvement of CFPP value were observed at any percentage of SoLE added. With these results, SoLE can be considered as not an effective additive to improve CFPP of neat biodiesel.

Besides that, Garcia *et al.* (2008) also reported that the mixture of solketal acetate and triacetin that they synthesised from solketal and acetic anhydride also showed no significant effect in improving CFPP of neat biodiesel.

Edith *et al.* (2012) reported that CFPP reducing additives, called "CFPP depressants", act during nucleation by altering the structure of the crystals formed from an orthorhombic shape to a needle-like shape, hence no blocking to fuel filters. Thus, they inhibit the growth of the crystals formed, to ensure that they remain in a fine suspension rather

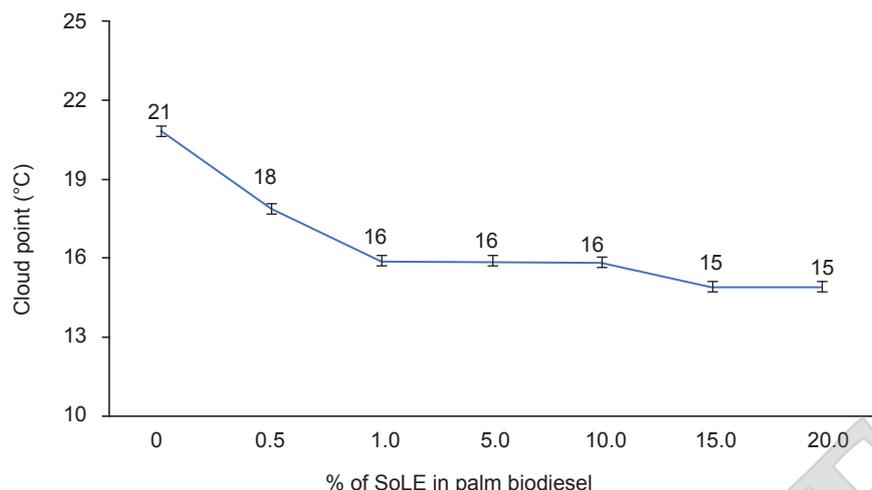


Figure 7. Effect of SoLE amount on the cloud point of palm biodiesel.

than gelling up. They are usually used with wax anti settling agents. From this we can conclude that SoLE does not act as how CFPP depressant works.

Although SoLE does not improve CFPP very well, SoLE works quite well as PP additive, and as CP additive. This might be because SoLE does not alter the shape of the crystals formed; instead, they collect on the surface of the crystals formed to hinder their growth and prevent gel network formation.

TABLE 1. EFFECT OF SOLE ADDITION ON COLD FILTER PLUGGING POINT OF NEAT PALM BIODIESEL

Sample	Cold filter plugging point (°C)		
	Test 1	Test 2	Test 3
Biodiesel 100%	11	11	11
SoLE 1%	10	10	10
SoLE 10%	9	9	9
SoLE 15%	9	10	9

## CONCLUSION

This study has shown that SoLE can be added to palm biodiesel as CFI additive, with best percent addition suggested at 0.5% to 5.0% for improvement of density and kinetic viscosity, and 15.0% for improvement of pour point and cloud point. Addition of SoLE does not give any prominent effect on CFPP value. Density of palm biodiesel when blended with 0.5% SoLE gave density value of  $869.5 \text{ kg m}^{-3}$  and the value showed to conform to the EN ISO 12185 standard with the reading obtained at  $899.1 \text{ kg m}^{-3}$ . Kinematic viscosity had slightly enhanced at lower percentage addition of SoLE (0.5% to 5.0%), and the values also conformed with the standard which must be in the range of  $3.5$  to  $5.0 \text{ mm}^2 \text{ s}^{-1}$ . The blending of palm biodiesel with SoLE at

15%-20% percentages also showed promising effects by improving the pour point of palm biodiesel between  $2^\circ\text{C}$  and  $5^\circ\text{C}$ , and 15% is considered to be the most economic and recommended. Similarly, the cloud point of palm biodiesel blended with SoLE at same percentage addition also showed a reduction of between  $3^\circ\text{C}$  to  $6^\circ\text{C}$ .

SoLE can improve the low temperature properties of biodiesel, which will probably promote biodiesel utilisation in cold weather. In addition, SoLE was able to improve the cloud point and pour point of palm biodiesel. Density and kinematic viscosity conform to the standard specifications measured in this study, nonetheless, acid value showed marginal deviation value from the specification. In summary, SoLE could be regarded as a potential bio-based cold flow properties improver to improve the cold flow properties of palm biodiesel.

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