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Winterization of biodiesel through progressive freezing for cold flow properties improvement

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Abstract. In cold environment, pure biodiesel cannot be used directly as an alternative fuel as it crystalizes easily at low temperature due to its saturated fatty acid (SFA) content. Thus, the winterization method is used to reduce the SFA content that gives high melting point to biodiesel. However, the conventional winterization method was reported to be complicated and ineffective in separating the liquid and solid content formed. Progressive freezing (PF) is introduced to improve the separation efficiency in the winterization process by removing the solid SFA layer formed on the wall of the crystallizer without the use of complicated equipment. In this study, the initial value of cloud point (CP) and pour point (PP) of the biodiesel were measured and compared with the values obtained after the PF process. The effect of coolant temperature, freezing time and stirring rate towards the efficiency of the PF process were also determined. The obtained results showed that the best performance of winterization was observed at coolant temperature of 6 °C, freezing time of 20 minutes and stirring rate of 50 rpm. At this condition, the recovery of biodiesel is 65.46% while CP, PP and SFA content were reduced by 2.65 %, 14.29 % and 3.96%, respectively.

1. Introduction

Exploration and drilling of fossil fuels due to rapid industrialization have resulted in various effects such as toxins release, waste disposal problems and oil spills. Besides, the petroleum reserves were reported to deplete rapidly due to big scale fossil fuels extraction [1]. This phenomenon also causes troubles to the countries which are relying on the import of crude petroleum oil especially in dealing with foreign exchange crisis. Furthermore, usage of fossil fuels had resulted in pollution and it is connected to other environmental issues like global warming, climate change and critical human diseases. Therefore, extensive researches have been done in recent years to search for an alternative fuel, where the findings have led to the discovery of biodiesel as one of the significant choices to replace the conventional non-renewable fossil fuels, as it is safe, non-toxic, biodegradable, contains no sulphur, having lower emission profiles and acts as a desirable lubricant [2, 3]. Besides, the use of biodiesel gives various social benefits to rural revitalization, creation of new jobs, and reduced global warming [4].

However, biodiesel has higher cloud point (CP) and pour point (PP) than petroleum diesel because of its saturated fatty acid (SFA) content, which gives high melting point to biodiesel [5, 6]. Thus, it tends to crystallize easily in cold environment. The low CP and PP make the biodiesel completely impossible to be used in the winter countries like United States where their environment temperatures range from 0°C to 49°C [7]. As the fuel particles condense and gelling formation starts at low temperature, the crystal nuclei are formed and cloudy appearance can be observed. This is known as the cloud point and it shows the possibility of fuel to clog the pipes or filters at low operating temperatures. Pour point is



observed when the temperature of biodiesel is further reduced to the point where the flow stops. Crystallization causes blockage and prevent fuel flow in the engine which leads to fuel starvation, clogging of filters and incomplete combustion of fuel to start up an engine during cold climate [8].

Cold flow properties of biodiesel can be improved by reducing parts of its SFA via winterization [9]. Winterization method is a thermomechanical separation process where some parts of triglycerides of fats are crystallized from biodiesel [10, 11]. Conventionally in this process, biodiesel is stored in a cold room or refrigerator for a period of time. At this stage, nuclei and crystals are allowed to grow under a controlled cold temperature until the crystals of different sizes and characteristics are formed. Then, the slurry will be separated into solid and liquid fractions through vacuum filtration [6]. The winterized biodiesel is now with lower SFA content and thus has lower tendency to crystallize due to its lower melting point as compared to the one with more SFA content [12, 13]. However, the current method of winterization is considered as complicated as the solid-liquid mixture must be transferred into a sintered glass funnel for the filtration step, while maintaining the cold temperature [6]. Furthermore, the separation of solid and liquid biodiesel was found to be ineffective as slushy and small solid biodiesel can bypass the filtration process.

Therefore, in this study, a new method namely progressive freezing (PF) is introduced to replace the conventional winterization method. Technically and theoretically, PF offers a simpler process and could possibly improve the separation efficiency of biodiesel winterization process. In this process, the components of biodiesel are separated based on differences in crystallization temperatures [14]. During the process, crystals are formed layer by layer on a cooled surface until a large and single crystal block is formed [15, 16]. The distinguishable boundary between the crystal layer and the unfrozen liquid facilitates the separation of the two phases. In this study, a cylindrical crystallizer was filled with liquid biodiesel before being immersed in a refrigerated waterbath containing a coolant. During the process, a digital stirrer was used to mix the liquid biodiesel to further improve the mass and heat transfer between the coolant and the biodiesel. Besides, the coolant also helps in maintaining the cold temperature throughout the winterization process. This study aimed to improve the winterization process by reducing the percentage of SFA content which give a better cold flow properties of biodiesel. The practicability of implementing PF in biodiesel winterization process was examined through various analysis.

Several objectives had been set up to emphasize the purpose of this project. The objectives are to determine the cold flow properties of biodiesel through cloud point (CP) and pour point (PP), to study the effectiveness of winterization process through PF under different operating parameters such as coolant temperature, freezing time and stirring rate and finally to analyze the performance of winterization of biodiesel through PF based on the recovery of winterized biodiesel, percentage reduction of SFA and cold flow properties of the biodiesel.

2. Materials and Methods

2.1. Materials

The raw materials used were biodiesel and ethylene glycol. The biodiesel served as the main solution to be winterized while ethylene glycol was used as a coolant in refrigerated water bath. Ethylene glycol was selected due to its low temperature range in the heat transfer process. The biodiesel was self-made using sodium hydroxide, methanol and vegetable oil (palm based cooking oil).

2.2. Preparation of Biodiesel

Biodiesel was prepared by adding 12.75 g of sodium hydroxide into 225 mL of methanol in a beaker, where the mixture then was slowly stirred until all sodium hydroxide completely dissolved. Then, 1 kg of vegetable oil was added into the mixture and blended for 30 minutes. The mixture was then transferred into a container for settlement. The top layer of biodiesel was then obtained for experiment. Sample of prepared biodiesel was then analysed for SFA content, initial CP and initial PP.

2.3. Progressive Freezing Process

The experimental setup of the PF process consisted of a cylindrical freeze crystallizer, a refrigerated waterbath, a digital stirrer and two retort stands. The main apparatus of the system is cylindrical freeze crystallizer as it provided the place for crystallization to occur. A refrigerated waterbath was used to store the coolant, at which the desired readings of coolant temperature were controlled. On the other hand, two retort stands with clamp were used to hold the crystallizer while it is immersed into the waterbath. In order to provide a well-mixed liquid mixture, a digital stirrer was used to stir the diluted ethanol at the desired stirring rate. Figure 1 shows the experimental setup for the progressive freezing process.

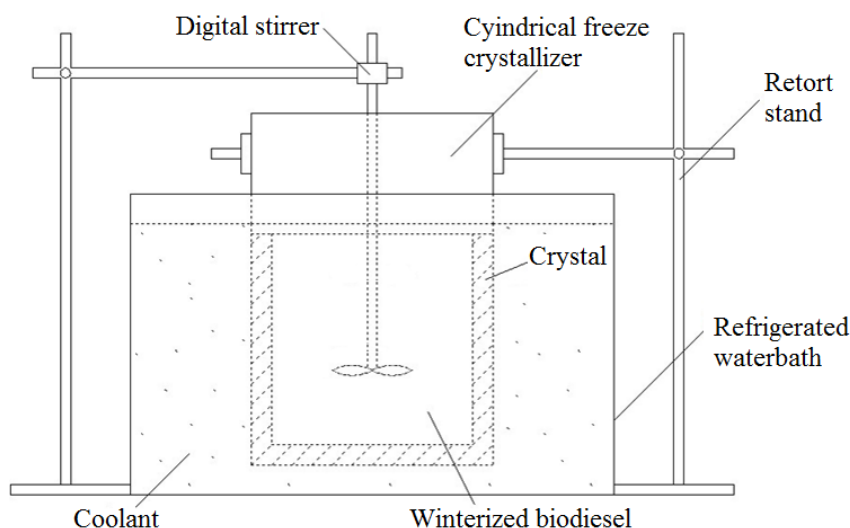


Figure 1. Experimental setup for the progressive freezing (PF) process.

During the experimental run, the refrigerated waterbath was filled with ethylene glycol and distilled water at a ratio of 1:1 before it was switched on. The waterbath was cooled until the desired coolant temperature is achieved. Next, the cylindrical freeze crystallizer was immersed into the refrigerated waterbath while being supported by two retort stands to give a stable position. As the coolant temperature reached the desired reading, 300 mL of biodiesel was fed into the crystallizer. At this time, the digital stirrer was switched on to stir the biodiesel. The solution was left in the crystallizer for the freezing process to occur.

At certain designated time, the stirring process was stopped and the crystallizer was removed from the refrigerated waterbath. The winterized liquid biodiesel was first collected before thawing the crystal layer formed. The volume of both portions were measured and recorded. In this study, three operating parameters which are coolant temperature, stirring speed and freezing time were varied at five different readings.

2.4. Cloud Point (CP), Pour Point (PP) and SFA Analyses

The samples of initial and winterized biodiesel were analysed for CP and PP values by a Cloud point/Pour point Analyser. The analyses were conducted based on the light sensitivity of 3% while the tilt out tests were performed for each 1°C drop. The percentage of SFA reduction was obtained by comparing the initial and final value of SFA in the samples. The results given by the analyser were conformed to ASTM D2500, ISO 3015, IP 219, Gost 5066 and Gost 20287 standards.

On the other hand, gas chromatography-mass spectrometry (GCMS) method was used to determine the reduction in the total amount of SFA content in the winterized biodiesel. The step was conducted using flame ionization detector with temperature of 300 °C with its column temperature increased from 100 - 240 °C using ramp rate of 15 °C/minutes.

3. Results and Discussion

3.1. Characterization of Biodiesel

The results obtained from the GCMS analyses shown that the prepared biodiesel contains 37.63% of saturated fatty acid (SFA), comprising of decanoic acid, docosanoic acid, eicosanoic acid, heptadecanoic acid, hexadecanoic acid, pentadecanoic acid and tetracosanoic acid. The other components found were unsaturated fatty acid (UFA) and impurities. Next, the result from CP/PP Analyser shown that the biodiesel had an initial CP of 7.54 °C and initial PP of 7 °C.

3.2. Effect of Coolant Temperature

Coolant temperature is the most significant parameter in affecting the performance of PF process. Theoretically, the process of nucleation and crystal growth depends on the temperature of the coolant, at which lower coolant temperature may enhance the crystallization process [17]. In this experiment, stirring rate and freezing time of the PF process were kept constant at 50 rpm and 20 minutes, respectively. Meanwhile, the coolant temperature was varied from -4°C to 8°C. Figure 2 shows the changes in biodiesel recovery at different coolant temperature.

Based on the figure, the percentage of biodiesel recovery increases proportionally as the coolant temperature increased from 4 °C to 8 °C. It was also found that lower amount of solid crystals was formed as the temperature increases. Theoretically, lower coolant temperature could provide initial supercooling conditions that is needed for the ice nucleation process. However, further lowering the coolant temperature will result in even higher ice crystal growth rate that would trap unsaturated fatty acid in the solid formed, thus reducing the biodiesel recovery [18-21]. In actual situation, it is always encouraged to keep the production of the solid crystals as low as possible, as the solid crystals obtained can only be sold as the low grade fuel at cheap price after they are melted into liquid again. Moreover, high amount of low grade fuel produced from progressive freezing will cause low profitability or economic loss in a more serious case. Based on the experiment, the biodiesel undergone progressive freezing at the coolant temperature of 6 to 8 °C had resulted in biodiesel recovery of more than 60% while any coolant temperature lower than 6 °C had resulted in low biodiesel recovery.

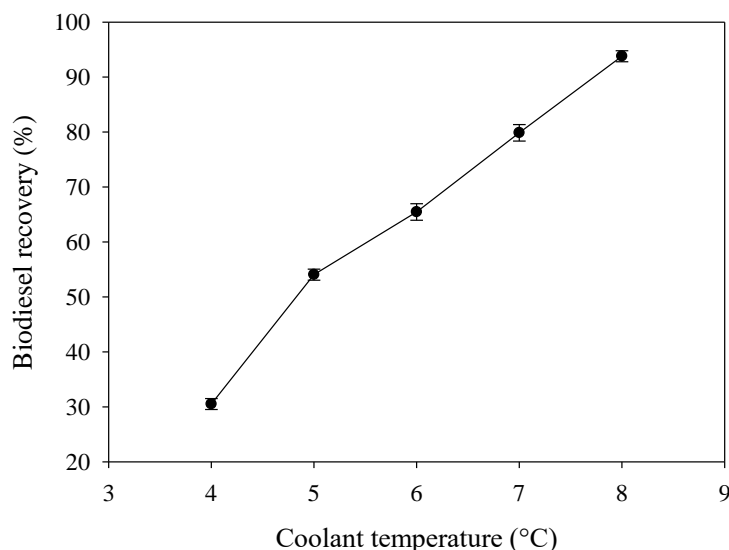


Figure 2. Changes in biodiesel recovery at different coolant temperature.

Besides, CP and PP were found lowest at 6 °C, as shown in figure 3. The final obtained CP and PP were also reduced by 1 °C (13.26 %) and 1.47 °C (21 %), respectively. The reduction in CP and PP are due to the removal of SFA from the winterized biodiesel. However, it was found that CP and PP of winterized biodiesel were higher than the original sample (7.54 °C) as the PF process was run at coolant temperature below 6 °C. This is mainly due to high viscosity of biodiesel that happened at low temperature, which reduced the crystal growth rate. Thick slurry was formed by the fine crystals in the liquid biodiesel containing high amount of unsaturated fatty acid (UFA). Due to inability in separating

UFA from thick slurry, the loss of these acids had resulted in low overall UFA content in liquid winterized biodiesel, which led to high CP and PP.

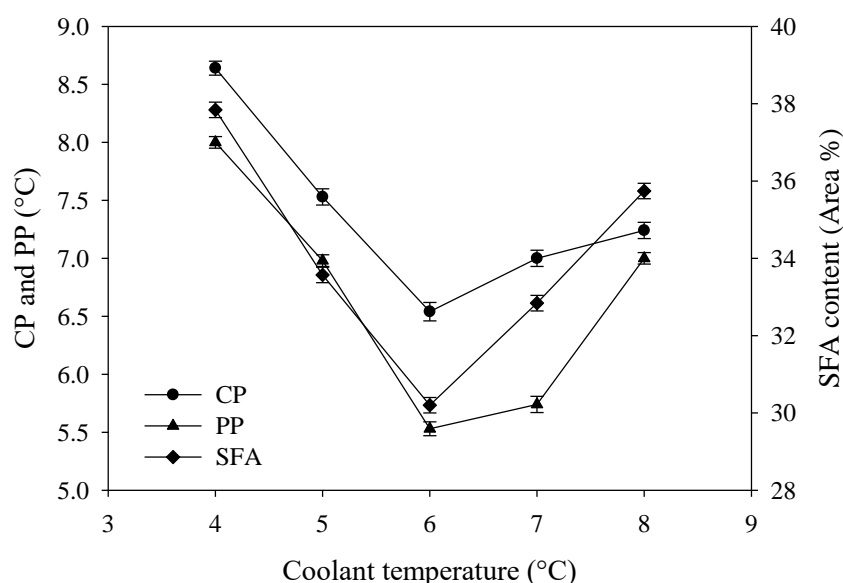


Figure 3. Changes in CP, PP and SFA content at different coolant temperature.

Similarly, the SFA content was also found lowest at 6 °C, as also shown in Fig. 3. The highest total reduction of this fat was found to be 19.74%. SFA content increased when the coolant temperature was set below 6 °C due to the high viscosity of liquid biodiesel caused by the high amount of suspended solid. Contrary, the SFA content was found 0.56% higher than the initial value as it cooled at 4 °C. Again, this is mainly due to the formation of thick slurry containing fine crystals which resulted in the reduction of the overall percentage of UFA in liquid winterized biodiesel. Therefore, intermediate coolant temperature in the selected range was favoured in the progressive freezing process as it significantly improved the cold flow properties of the biodiesel.

3.3. Effect of Freezing Time

In order to study the effect of freezing time towards the percentage of biodiesel recovery, CP, PP, SFA content and percentage of SFA reduction, the experiment was conducted by varying the freezing time from 20 to 50 minutes. The other parameters such as coolant temperature and stirring rate were kept constant at 6 °C and 50 rpm, respectively. Figure 4 shows the changes in biodiesel recovery at different freezing time.

From the figure, the biodiesel recovery decreases as the freezing time increased, indicating that more biodiesel was crystallized and deposited on the wall of the crystallizer. The highest biodiesel recovery was observed at the freezing time of 20 minutes as the loss of solid crystals was only 34.54 %. Contrary, low biodiesel recovery was observed when the liquid was frozen for more than 20 minutes, which could also result in higher operating cost and lower profitability.

Next, figure 5 shows the changes in CP, PP and SFA content at different freezing time. From the trends, all CP, PP and SFA increase as the freezing time increased. Even though more crystals were formed at longer freezing time, these crystals were found to be too fine and not stable enough to form bigger crystals layers. These fine crystals were found suspending in the liquid biodiesel and formed thin slurry instead of layer of crystal on the wall of the crystallizer. The slurry became thicker as the freezing time increases as more fine crystals were formed and being suspended in the liquid biodiesel. More UFA remained in the slurry of crystals formed in the crystallizer instead of layered crystal, thus increasing the SFA content of the winterized biodiesel. Thus, increasing the freezing time would not lower down the overall SFA content of the winterized liquid biodiesel. Consequently, the value of CP and PP of the

winterized biodiesel increased as the UFA remained in the slurry at the end of the experiment. Therefore, the shortest freezing time in the selected range was favoured in the progressive freezing process as it gave a better readings of cold flow properties of the biodiesel.

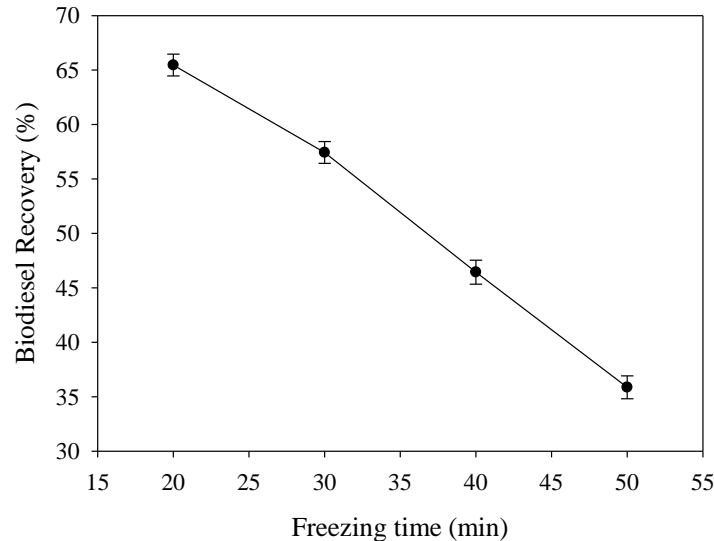


Figure 4. Changes in biodiesel recovery at different freezing time.

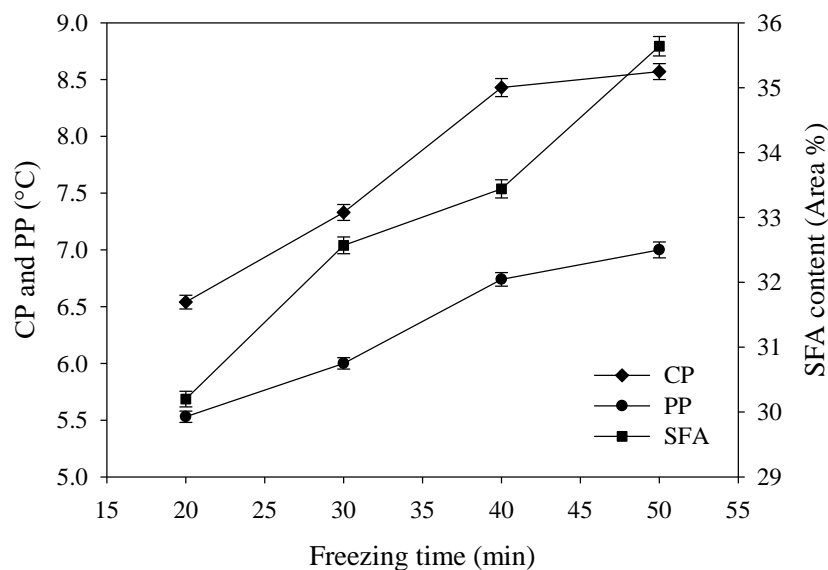


Figure 5. Changes in CP, PP and SFA content at different freezing time.

3.4. Effect of Stirring Rate

In this analysis, the stirring rate had been manipulated from 50 rpm to 300 rpm while the other parameters were kept constant at coolant temperature of 6 °C and freezing time of 20 minutes. The changes of biodiesel recovery and SFA content at different stirring rate are shown in Figure 6. From the figure, highest biodiesel recovery (65.46%) was obtained at 50 rpm while 300 rpm gives the lowest recovery. Less amount of solid crystals was observed as the stirring rate is increased. This is mainly caused by the high agitation rate that had fragmented the crystals during the growing stage, thus crystals were found suspended in the liquid biodiesel instead of layered crystal on the wall of crystallizer.

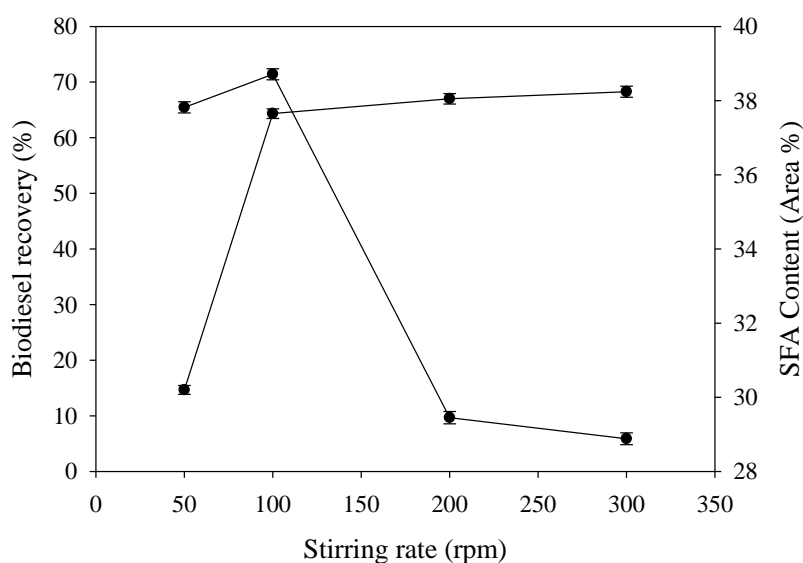






Figure 6. Changes in biodiesel recovery and SFA content at different stirring rate.

Alternatively, the trend shows that higher stirring rate resulted in higher SFA content in the winterized biodiesel. The lowest SFA content of 30.2% was obtained at 50 rpm. As the speed increased, more fine crystals were formed because the growth was disturbed by the strong motion. These crystals were remained in the liquid biodiesel and a very thick crystal slurry was formed. As the fine crystals could not be separated from the thick slurry, huge loss of UFA from the winterized biodiesel was expected, thus increasing the SFA content of the liquid.

In addition, Table 1 shows the image of winterized biodiesel in the crystallizer. The stirring rate of 50 rpm was considered as the best speed as the mild motion has enhanced crystals growth and deposition of big sized crystals on the wall of crystallizer. Meanwhile, most of the crystals remained suspended in liquid biodiesel as the stirring speed is increased above 50 rpm. Higher stirring rate could provide disturbance to the growth of crystals and resulted in lower percentage of SFA removal by the process. In conclusion, the lowest stirring rate in the selected range (50 rpm) was favoured for an efficient winterization process.

Table 1 Image of winterized biodiesel at different stirring rate

Stirring Rate (rpm)	50	100	200	300
Crystallization Image				

4. Conclusion

The main aims of the project were to determine the cold flow properties of biodiesel, study the effectiveness of winterization process through progressive freezing under different operating parameters and analyse the performance of winterization of biodiesel through progressive freezing. The experiment was done by using the palm based biodiesel and ethylene glycol and the circulating coolant. The samples collected were analysed using Cloud Point and Pour Point Analyser and Gas chromatography–mass spectrometry (GCMS) to determine the improvement made by the progressive freezing process.

Based on the findings, the initial biodiesel sample had CP and PP values of 7.54 °C and 7 °C, respectively, while SFA content was 37.63 %. Lower coolant temperature yielded lower biodiesel recovery, and high viscous biodiesel which later resulted in less efficient cold flow properties improvement of the biodiesel. As expected, longer freezing time has resulted in lower biodiesel recovery as high portion of the biodiesel were frozen. In addition, too long freezing time produced fine and unstable solids suspended in the liquid biodiesel hence lowering the efficiency of improving the CP and PP of the biodiesel. On the other hand, higher stirring rate yielded a lower biodiesel recovery and efficiency of cold flow properties improvement as more fine crystals were formed at higher stirring rate. The best performance of winterization could be observed at coolant temperature of 6°C, freezing time of 20 minutes and stirring rate of 50 rpm as it significantly improved the cold flow properties of biodiesel (CP and PP reduction of 13.26 % and 21 %, respectively. Besides, the highest biodiesel recovery of 65.46% and the highest SFA reduction of 19.74% were also obtained at these conditions.

In conclusion, progressive freezing method showed good potential for the winterization of biodiesel and further study can be done to improve this technology for the biodiesel commercialization in the future.

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