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Feasibility of additive winterization of biodiesel fuel derived from various eatable oils and fat

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ABSTRACT

For simple removal of saturated fatty acid methyl esters (FAMES) from a FAME mixture, our previous research described winterization using sorbitan palmitate without agitation. However, limited information exists on additive winterization of real oil biodiesels and their separation performance. We demonstrated the additive winterization of biodiesel fuel derived from commercial eatable oils and fat (palm, lard, cottonseed, rice, and soybean). Five biodiesel fuels were prepared through a transesterification reaction under alkali conditions. The biodiesel-additive mixtures were air-cooled over 48 h at a temperature equal to or several degrees lower than the cloud point (CP) of the biodiesel without agitation. The palm biodiesel showed a marked similarity to a simulated FAME mixture, and was separated into saturated FAME-rich solid fuel and unsaturated FAME-rich liquid fuel. The CP of the recovered liquid decreased by 6–10.5 °C, and the separation factors were between 2.4 and 7.7. The kinetic viscosity of the resultant liquid increased slightly because of the oleate fraction but was in the range of the biodiesel standard. These results indicate that additive winterization is useful for the separation and purification of biodiesel. Because the separation factor of the lard biodiesel winterization using sorbitan palmitate decreased (1.3–1.9), the separation improver retains scope for improvement under high stearate conditions. The relatively lower saturated FAME biodiesels (cottonseed, rice, and soybean) were predisposed to form a slurry during the winterization. However, the CP of the recovery liquid decreased 2–5 °C from the initial biodiesels. The separation factor and liquid recovery rate will increase with the use of a proper mechanical separation method such as filtration.

1. Introduction

Biodiesel fuel is an alternative light oil that is defined as fatty acid methyl esters (FAMES). The biodiesel can be produced from various edible and inedible vegetable oils [1–3], waste oils [4,5], animal fats [1–2,6], algae oils [7], and non-eatable oils for novel feedstocks [8–11]. The low-sulfur and nitrogen content of FAMES is advantageous for fuel combustion, whereas the presence of high-melting-point saturated fatty acid methyl esters produces poor low-temperature flow properties as the high cloud point (CP) and pour point (PP) [12–13]. Therefore, CP and PP reduction is critical for applications of biodiesel in cold regions and high grounds.

A simple method for the CP and PP reduction of biodiesel is to separate saturated FAMES from the fuel. Two methods exist to do so,

namely, distillation with vaporization and winterization (or fractionation) with crystallization [14]. Although distillation is a well-established process with heating and depressurizing, a high cost and specialized skill are required for its effective operation. Larger-scale equipment demonstrates an efficient separation performance. Winterization is typically associated with crystallization during long-term storage in cold temperatures [13]. Winterization is easy and available for various scale operations [6,14–15]. The liquid FAME mixture is cooled below its cloud point whereafter the remaining liquid is separated from the generated solids. The separation performance and liquid recovery rate decrease because of liquid FAME inclusion in aggregated solid FAME particles during winterization. Therefore, a repeat of fractionation operation is applied to remove fractions of generated solid around CP [14–24].

Abbreviations: FAME, fatty acid methyl ester; CP, cloud point; PP, pour point; PM, methyl palmitate; SM, methyl stearate; OM, methyl oleate; LM, methyl linoleate; LnM, methyl linolenate; S.F., separation factor.

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For simple removal of saturated FAMES from a FAME mixture, our previous research described winterization of simulated biodiesel blended methyl palmitate (PM) and methyl oleate (OM) by additives without agitation at high methyl palmitate (PM) mass fractions (~25%–55%) [25,26]. Sorbitan monopalmitate was selected as an additive because it consisted of C, H, and O, and it assisted combustion. The additive winterization concentrated PM in the generated solid from simulated biodiesel fuels [25,27]. However, oils and fats as feedstocks contain many types of fatty acid ester groups and a small amount of naturally derived compounds other than palmitate and oleate groups. Limited information exists on additive winterization of real oil biodiesels and their separation performance.

In this work, the feasibility of additive winterization using sorbitan palmitate on real biodiesel derived from various edible commercial oils and fat was estimated. We selected various commercial oils and fat that consisted of ~10 wt%–50 wt% saturated fatty acid, especially palmitic acid (palm, lard, cottonseed, rice, and soybean), that are used extensively in Japan and globally. The composition of the selected oil-derived biodiesel is summarized in Table 1.

2. Material and methods

2.1. Biodiesel preparation

Biodiesels derived from commercial edible oils and fat were prepared through a transesterification reaction using palm (Imagine Inc., Kizugawa, Kyoto, Japan), cottonseed (Okamura Oil Mill, Ltd., Kashiwara, Osaka, Japan), rice (Tsuno Food Industrial Co., Ltd., Ito-gun, Wakayama, Japan), soybean oil (Ajinomoto Co. Inc., Tokyo, Japan), lard (Megmilk Snow Brand Co., Ltd., Sapporo, Japan), methanol (>99.8%, FUJIFILM Wako Pure Chemical Industry Co., Osaka, Japan), and KOH (>85.0%, Wako Pure Chemical Industry, Ltd.) as the alkaline catalyst. Experimental transesterification procedures have been described in detail in previous research [28]. The raw oil or fat was heated to 60 °C in a water bath, after which KOH–methanol solution was added and the mixture was agitated for 1 h. The resulting mixture was washed with KCl solution and water several times, filtered, and dried under vacuum. The sample was stored in a brown bottle under nitrogen in a dark place at room temperature before use. The selected additive, sorbitan palmitate (Span40, FUJIFILM Wako Pure Chemical Industry Co.) was combined with the biodiesels, and the resulting biodiesel-additive mixture was agitated on a hotplate stirrer at 60 °C.

2.2. Winterization

Experimental FAME winterization procedures have been described in detail in previous publications [25,27]. In summary, the biodiesel-additive mixture samples were heated to approximately 40 °C to eliminate any thermal history and allowed to cool slowly to room temperature before use. A 40–42 g sample was placed into a glass vial and allowed to stand in a low-temperature incubator (≥ 10 °C) or a 1 L beaker in a low-temperature circulator (≤ 2 °C). The samples were air-cooled to a temperature equal to or several degrees lower than the CP

of the biodiesel without agitation. This cooling step was carried out over 48 h. The sample appearance was studied. The supernatant liquid phase was separated from the solid phase (namely, the residue in the vial) by careful decantation of the supernatant out of the vial. The collected liquid was termed the liquid phase, and the residue in the vial was termed the solid phase. The winterization temperature was increased or decreased based on the appearance and liquid recovery rate at \sim (CP–2) °C.

2.3. Sample analysis

As shown in previous research [28], the CP of each sample was determined using an instrument that consisted of a low-temperature circulator and a platinum resistance thermometer. The CP was determined visually by crystallization at the bottom of a test vial at 1.0 °C intervals according to Japanese Industrial Standard JIS K2269 [29].

The density and kinetic viscosity of the prepared biodiesel were measured by a specific gravity bottle (Gay-Lussac type) and a Ubbelohde viscometer (No.1) according to Japanese Industrial Standard JIS K2249-3 [30] and JIS K2283 [31], respectively.

The FAME mass fractions of each sample were determined using gas chromatography (GC-17A, Shimadzu, Osaka, Japan) equipped with a ZB-Wax capillary column (30 m \times 0.25 mm, film thickness 0.25 μ m) and a flame ionization detector (FID), with helium as the carrier gas. The FAME mass fraction of each sample was calculated using an internal standard method like that described in European standards EN14013 and JIS K2390, using hexadecane as the internal standard. A similar analytical procedure has been reported previously [28]. Methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate were detected. The ratio of each fatty acid methyl ester was calculated.

The mass% liquid recovery rate R was determined from the mass of the recovered liquid (W_R) and the mass of the initial sample (W_i): $R = (W_R / W_i) \times 100$ [%]. The separation factor ($S.F.$) was defined as follows because the unsaturated FAMES (oleate + linoleate + linolenate) were supposed to be concentrated to liquid, and therefore, the CP and PP of the resultant liquid biodiesel were decreased [25]: $S.F. = (y_L / x_L) / (y_S / x_S)$, where x and y are the mass fractions of total saturated FAMES (palmitate + stearate) and total unsaturated FAMES (oleate + linoleate + linolenate), respectively, and subscripts L and S indicate liquid and solid phases, respectively. A separation factor > 1 indicates an increase in mass fraction of total unsaturated FAME in the liquid after winterization treatment.

3. Results and discussion

3.1. Winterization of palm biodiesel

The palm biodiesel was a light-yellow liquid at room temperature. Its density was 866.3–867.2 kg/m³ at 25 °C, which has relative errors of approximately 0.2%–0.4% compared with literature data [2]. Its kinetic viscosity was 4.34–4.37 mm²/s at 40 °C. The relative error was ~2.9%–3.5% compared with that in the literature [2] (Table 1). The FAME

Table 1

Density, kinetic viscosity, CP, and FAME fraction of biodiesel prepared from various raw oils and fat.

Raw oil	Density [kg/m ³]	Kinetic viscosity [mm ² /s]	CP [°C]	FAME mass fraction				
				Palmitate(PM)	Stearate(SM)	Oleate(OM)	Linoleate(LM)	Linolenate(LnM)
Palm	866.3–867.2	4.34–4.37	16–19.5	43.2–45.3	4.5–4.6	39.9–42.3	9.4–10.4	—*~0.5
Lard	874.1	4.69	12.0	26.5	15.8	48.9	8.2	0.5
Cottonseed	881.2	4.05	1.5	18.8	2.3	17.0	63.7	—*
Rice	881.1	4.45	1.0	16.4	1.0	44.3	37.1	1.2
Soybean	884.5	4.13	–1.5	10.4	3.8	24.3	57.2	6.3

Density at 15 °C (25 °C for palm), kinetic viscosity at 40 °C. Average of measurement at least two results. *: Not detected. Because palm biodiesel was prepared from different lots multiple times, the range of measured values was shown.

fraction of the palm biodiesel is shown in Table 1. The FAME fraction corresponds to that in the literature data [1]. The PM and total saturated FAME fractions of the palm biodiesel were higher than other biodiesels used in this research. The average CP was 16–19.5 °C in some lots. When Span 40 was mixed in the palm biodiesel, the CP of that mixed sample decreased by several degrees. Therefore, winterization was first carried out near the CP of the mixed sample, at 14 °C.

Fig. 1 shows the change in palm biodiesel sample appearance after winterization. The samples without Span40 almost solidified because the cooling temperature was lower than the CP of the biodiesel. Solid-liquid phase separation was confirmed visually in the samples with 0.5 and 1.0 wt% Span40 at all cooling temperatures. Because fine particle formation was observed at 1.5 wt% Span40, slurry particles were contaminated slightly in the recovery liquid during decantation. The change in appearance of the high PM-containing samples was nearly equal to that of the simulated FAME samples in previous research [25,26] except for the easy formation of a fine particle dispersion.

Fig. 2 shows the composition change of the recovery liquid and solid after separation by decantation, mainly in the two-phase separation samples. When the sample was separated into two phases, the PM mass fraction in the recovered liquid phase was lower than in the initial mixture, and PM was concentrated into the separated solid phase. However, little change in SM mass fraction resulted in all cases. These results indicate that Span40 concentrated PM preferably into the solid fraction well during winterization. A low cooling temperature reduced the PM fraction in the recovery liquid and the recovery solid. A high additive concentration tended to reduce the variation in PM fraction in the recovery liquid and solid because of fine particle contamination in the liquid and incomplete separation of liquid from the solid by decantation.

The recovery rate, separation factor, and CP of the recovery liquid and solid phases after winterization are summarized in Table 2. When two-phase separation was observed, the liquid recovery rate ranged from 34% to 73% and the S.F. value ranged from 3.1 to 7.6. These results are almost the same range as that in previous research using the high-PM fraction sample [26]. Vijayan et al. [22] reported that the liquid recovery of one-step winterization at (CP–3) °C was 12.6% by filtration. The CP of the liquid phase after additive winterization, CP(L), decreased by 5–10.5 °C from the CP of the initial palm biodiesel. The CP of waste cooking oil biodiesel has been reported to decrease by 5 °C from the

initial CP (14 °C) by thrice fractionation operation [24]. The CP of the solid phase, CP(S), approached the PM melting point, 29–31 °C [12,32] because of PM condensation to the solid phase and contamination of Span40 with a high melting point (40–50 °C [33]) in the solid. These results imply that additive winterization is useful for the separation of biodiesel component and improving the cold flow properties of biodiesel.

The kinetic viscosities of the resultant liquid and solid at 40 °C were measured under representative conditions, 0.5 wt% and 1.0 wt% Span40 at 13 °C, because of a higher *R* and lower CP(L). Huang et al. reported for the biodiesel viscosity that a high OM content increased the kinetic viscosity of a FAME mixture [34]. Because the resultant liquid after winterization contains a higher OM than the original biodiesel, we can predict the increase in kinetic viscosity of the resultant liquid. In contrast, the kinetic viscosity of the solid decreases because of a reduction in OM content. The liquid kinetic viscosity increased slightly and was 1.1%–1.4% higher than that of the original (Table 3). The kinetic viscosity of the resultant solid also increased slightly by 2.0%–3.7% because the kinetic viscosity of the resultant solid will be affected by Span 40 dissolution rather than the FAME content change. However, these kinetic viscosities were in the range of the biodiesel standard (<5.0 mm²/s).

In summary, we demonstrated that winterization using Span40 reduces the PM efficiently from palm biodiesel by one-step operation. These experiments showed that the proper concentration of Span 40 was 0.5 wt%–1.0 wt% in terms of the recovery rate and the separation factor, which replicates the experimental results using the FAME mixture that simulated palm in our previous research [26].

3.2. Winterization of lard biodiesel

The lard biodiesel was a yellow liquid at room temperature. Its density was 874.1 kg/m³ at 15 °C, and its kinetic viscosity was 4.69 mm²/s at 40 °C (Table 1), which corresponded approximately by relative errors of 0.1% and 4.1%, respectively, to that in the literature [1]. The FAME fraction of the lard biodiesel is shown in Table 1. The FAME fraction was like that in the literature [1]. The PM and total saturated FAME fractions of the lard biodiesel were second-highest in this research. A high SM fraction features the lard biodiesel. The average CP was 12.0 °C. When Span 40 was mixed in the lard biodiesel, the CP of

Cooling temperature [°C]	Additive concentration [wt%]			
	0	0.5	1	1.5
14	S	T	T	D
13	S	T	T	T
12	S	T	T	T

S, Solidification; ST, Solidification-partially two phase separation; T, Two phase separation; TD, Two phase separation-partially particle dispersion; D, Particle dispersion;

Fig. 1. Appearance of phase separation in palm biodiesel-Span40 systems at various additive concentrations and temperatures.

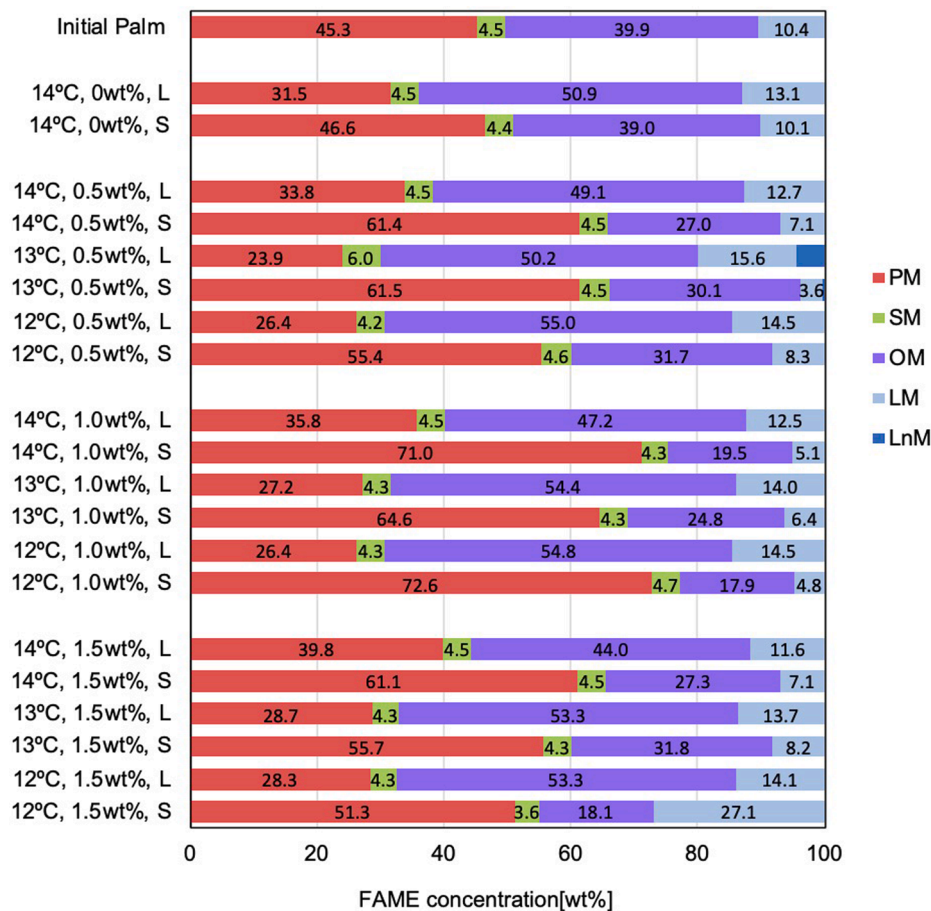


Fig. 2. Composition of palm biodiesel after additive winterization. L: liquid phase, S: solid phase.

Table 2

Liquid recovery, separation factor, CP of liquid and solid phase for winterization of palm biodiesel.

Span conc./Temp.	R [%]	S.F. [-]	CP(L) [°C]	CP(S) [°C]
0 wt%				
14 °C	10.5	1.85	14.5	22.5
0.5 wt%				
14 °C	59.4	3.12	9.5	22.5
13 °C	43.2	3.94	8.5	26.0
12 °C	34.4	3.41	9.0	22.0
1.0 wt%				
14 °C	73.0	4.52	13.5	28.0
13 °C	50.3	4.17	9.0	27.5
12 °C	58.9	7.68	12.5	29.0
1.5 wt%				
14 °C	74.1	2.40	13.5	28.5
13 °C	37.9	3.05	9.0	28.0
12 °C	53.5	2.51	11.0	29.0

Table 3

Kinetic viscosities of liquid and solid phase.

Span 40 conc.	Kinetic viscosity [mm ² /s] (percent change from neat)			
	liquid		solid	
0.5 wt%	4.43	(+1.37%)	4.46	(+2.06%)
1.0 wt%	4.42	(+1.14%)	4.53	(+3.66%)

Neat biodiesel with kinetic viscosity of 4.37 mm²/s was used.

that sample mixture increased 1.0–2.0 °C because of Span 40.

Fig. 3 shows the change in lard biodiesel samples after winterization. The neat lard biodiesel solidified completely at (CP–2) °C. Solid–liquid phase separation was confirmed visually in the samples with lower concentrations of Span40 at 11 °C and higher concentrations of Span40 at 10 °C. Although the total saturated FAME fraction of lard biodiesel was approximately that of palm biodiesel, the appearance change was different from both. The higher SM fraction influences the sample appearance at a low temperature.

Fig. 4 shows the composition change of the recovery liquid and solid after separation by decantation, mainly in the two-phase separation samples. The SM fractions in the recovery liquid and solid varied significantly from the initial lard biodiesel compared with the PM fraction. These results suggest that the SM first crystallizes in the samples and results in complete solidification because the SM fraction is high in the lard biodiesel. In previous research using the SM–OM mixture [25], Span 40 had a low inhibition of crystal growth of SM in the SM–OM mixture. Therefore, a mixed additive (for example, Span 40 and Span 60) may be an efficient solution to form two-phase separation. This is a subject for future investigation.

Table 4 summarizes the recovery rate, separation factor, and CP of the recovery liquid and solid phases after winterization of the lard biodiesel. The liquid recovery rate ranged from 14% to 85%. The high recovery rate was observed at lower Span40 concentrations and higher cooling temperatures. The S.F. value ranged from 1.3 to 1.9, which is lower than that of palm biodiesel winterization. The CP(L) decreased 1.0–5.0 °C from the CP of the neat lard biodiesel because of the decrease in SM fraction. However, the CP(S) remained close to the CP of the neat lard biodiesel because of insufficient condensation of saturated FAMES to the solid phase and the contamination of recovery liquid. It should be

Cooling temperature [°C]	Additive concentration [wt%]				
	0	0.3	0.5	1	1.5
12					
11					
10					

S, Solidification; ST, Solidification-partially two phase separation; T, Two phase separation; TD, Two phase separation-partially particle dispersion; D, Particle dispersion

Fig. 3. Appearance of phase separation in lard biodiesel-Span40 systems at various additive concentrations and temperatures.

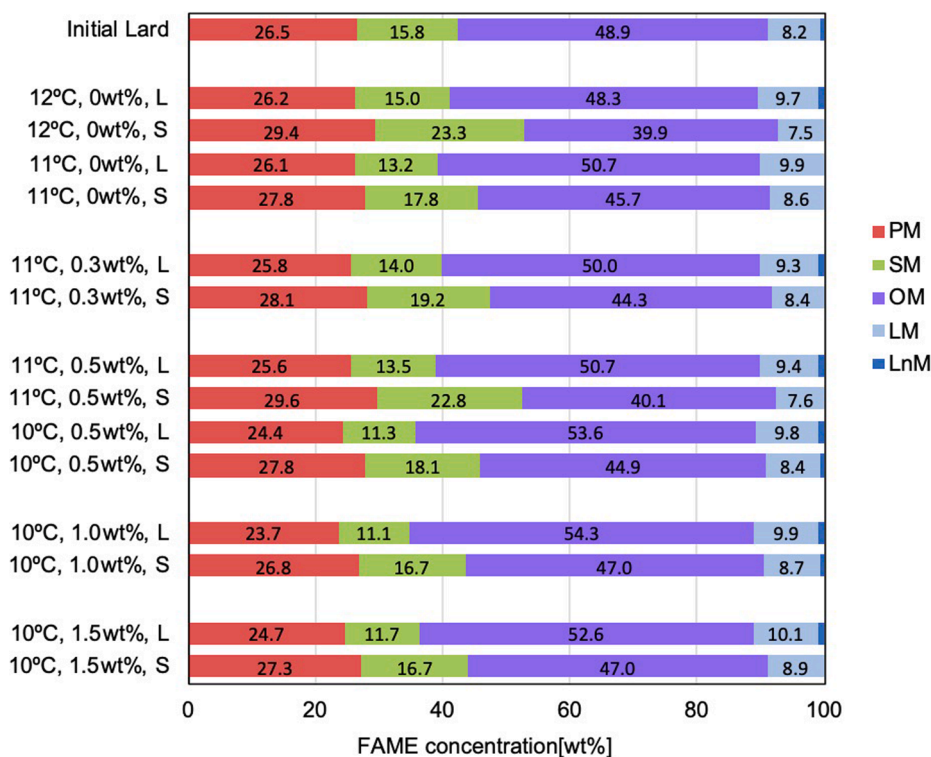


Fig. 4. Composition of lard biodiesel after additive winterization. L: liquid phase, S: solid phase.

considered for improving separation efficiency to select a proper condition and to increase the liquid recovery by filtration.

In summary, the CP of the liquid lard biodiesel recovered by additive winterization decreased ~ 5 °C from neat biodiesel. However, the separation factor was low, and the CP variation was small because of the high SM fraction and insufficient solid separation. Further investigation will be required to perform a more efficient winterization for the high SM content-biodiesel as lard biodiesel.

3.3. Winterization of cottonseed biodiesel

The cottonseed biodiesel was a light-yellow liquid at room temperature. The density was 881.2 kg/m^3 and the kinetic viscosity was 4.05

mm^2/s (Table 1). The relative errors of these data to the literature data [2] were approximately 0.7% and 0.5%, respectively. The FAME fractions of these biodiesels are shown in Table 1. The FAME fraction was consistent with the literature data [1]. The PM fraction of cottonseed biodiesel was 18.8%, and the linoleate fraction was relatively higher than other biodiesels. The average CP was 1.5 °C.

Fig. 5 shows the change in appearance in the cottonseed biodiesel samples after winterization. The neat cottonseed biodiesel solidified incompletely around CP, but the liquid recovery was impossible. Coarse particles were confirmed visually in the mixed biodiesels with 0.5 wt% Span40, but the slurry coexisted slightly in these samples. A higher concentration of Span40 formed the cottonseed biodiesel slurry easily. This result indicates that it is difficult for the PM-rich particles to grow

Table 4

Liquid recovery, separation factor, CP of liquid and solid phase for winterization of lard biodiesel.

Span conc./Temp.	R [%]	S.F. [-]	CP(L) [°C]	CP(S) [°C]
0 wt%				
12 °C	85.6	1.59	11.0	17.0
11 °C	36.2	1.29	9.0	12.5
0.3 wt%				
11 °C	63.9	1.36	9.0	13.0
0.5 wt%				
11 °C	74.4	1.71	8.5	14.0
10 °C	34.5	1.53	7.0	14.5
1.0 wt%				
10 °C	15.2	1.44	7.0	12.5
1.5 wt%				
10 °C	14.4	1.38	8.5	11.5

large at lower PM fractions and higher methyl linolenate fractions. The liquid recovered by decantation involved part of the slurry. Other mechanical separation is required to recover the purer liquid fraction.

Fig. 6 shows the composition change of the recovery liquid and solid after separation by decantation when the liquid fraction is recovered smoothly. As in the case of palm biodiesel, the PM mass fraction in the recovered liquid phase was lower than in the initial biodiesel, and PM was concentrated into the separated solid phase. The temperature-dependence and additive concentration-dependence of the PM fraction in the recovery liquid were like those of palm biodiesel.

Table 5 summarizes the recovery rate, separation factor, and CP of the recovery liquid and solid phases after winterization of cottonseed biodiesel at 0.5 wt% Span40. The maximum liquid recovery rate by decantation was 46% because of the avoidance of fine particle contamination. The separation economy needs to be considered but, a proper mechanical separation will enhance the recovery rate. The S.F.

value was ~ 2.6 , which is higher than lard biodiesel winterization but lower than palm biodiesel winterization. In the winterization of the waste cooking oil biodiesel whose total saturated FAME fraction is close to the cotton biodiesel, the liquid recovery and S.F. have been reported to be 10–30 % and 1.0–1.7 through a filtration operation [15]. Although the PM fraction of the recovery liquid was close to the initial soybean biodiesel (Table 1), the CP(L) of the liquid was lower than that of the initial soybean biodiesel. The difference in SM and LM fractions will influence the CP. Because the PP is a function of the CP [13] and the CP (L) decreased 5.0–6.5 °C from the CP of the neat cottonseed biodiesel, the PP quality of the recovered liquid will satisfy the requirement of grade 1 (PP = < -2.5 °C) and grade 2 (PP = < -7.5 °C) light oils in the Japanese Industrial Standard [35]. The CP(S) increased 2.5–3.5 °C with 0.5 wt% additive because of PM condensation to the solid phase. Although the PM fraction in the recovered solid in cottonseed biodiesel winterization was like the recovery liquid in palm biodiesel winterization, the CP(S) of cottonseed biodiesel was lower than the CP(L) of palm biodiesel. The high fraction of LM with a low melting point affects the appearance change and CP by interaction between FAMES and between FAME and natural compounds.

3.4. Winterization of rice biodiesel

The rice biodiesel was a yellow liquid at room temperature. Its density was 881.1 kg/m³, and its kinetic viscosity was 4.45 mm²/s (Table 1). These data were like those in the literature data with relative errors of approximately 0.3% and 5.3%, respectively [1]. The FAME fractions in Table 1 were consistent with the literature data [1]. The PM fraction was like that of cottonseed but with the ratio of unsaturated FAMES. The average CP was 1.0 °C, which approached that of the cottonseed biodiesel. With Span 40 addition, the CP of rice increased by several degrees.

Fig. 7 shows the change in the appearance of the rice biodiesel samples after winterization. The neat rice biodiesel solidified easily

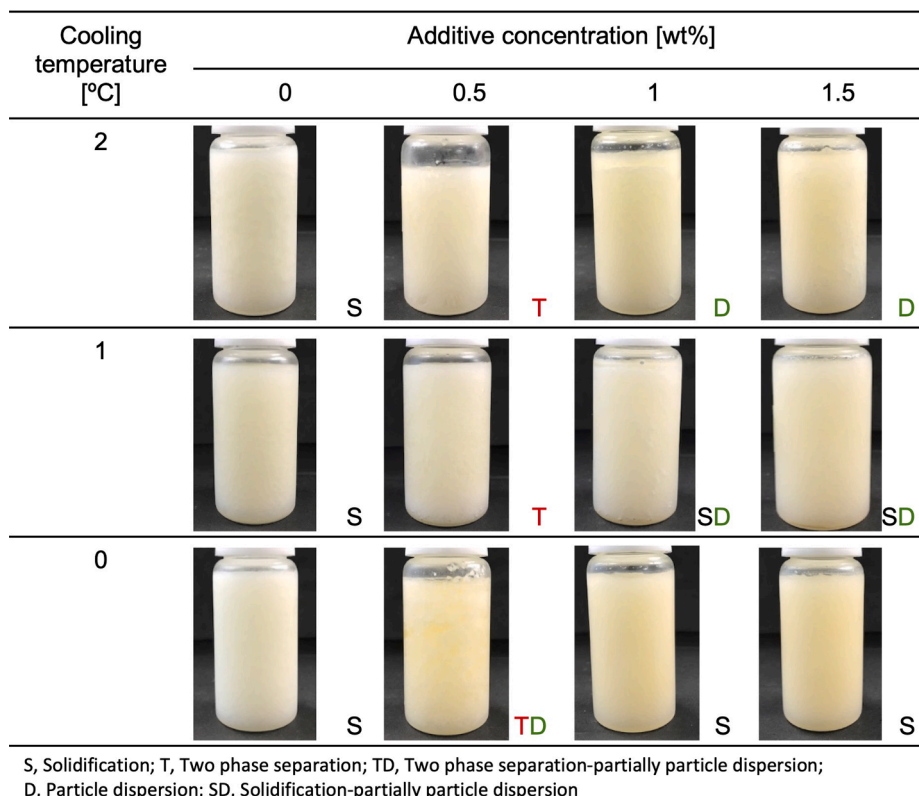


Fig. 5. Appearance of phase separation in cottonseed biodiesel-Span40 systems at various additive concentrations and temperatures.

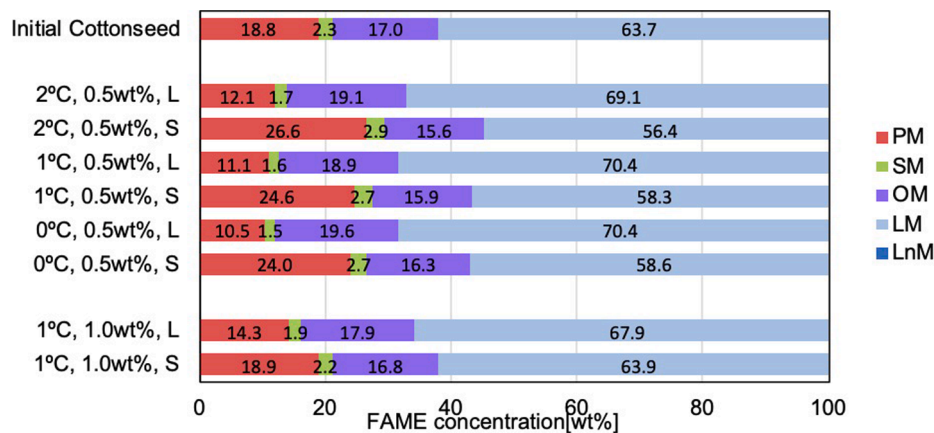


Fig. 6. Composition of cottonseed biodiesel after additive winterization. L: liquid phase, S: solid phase.

Table 5

Liquid recovery, separation factor, CP of liquid and solid phase for winterization of cottonseed biodiesel.

Span conc./Temp.	R [%]	S.F. [-]	CP(L) [°C]	CP(S) [°C]
0.5 wt%				
2 °C	46.0	2.61	−4.0	5.0
1 °C	37.0	2.58	−5.0	4.0
0 °C	32.6	2.66	−3.5	4.0

below the CP of the biodiesel, and liquid recovery was impossible in this case. Another research [22] has also shown no liquid fraction at (CP − 1) °C. When a few additives were mixed in the biodiesel, large quantities of small particles formed, but an overall suspended appearance was observed. Even though the winterization temperature decreased to −4 °C, the appearance kept the solidification particles in a partially dispersed state. Therefore, the liquid phase was not recovered rapidly by decantation, and the liquid recovery was low. The maximum liquid recovery rate by decantation was 23% because of the avoidance of small particle contamination (Table 6). The low recovery rates can increase cost, followed by lower economic competition. Another mechanical

separation filtration method is required for liquid recovery rate enhancement in the rice biodiesel case. The cost is the next challenge of additive winterization.

Fig. 8 shows the composition change of the recovery liquid and solid. Unlike for cottonseed biodiesel, the changes in PM fraction in the liquid and solid phases were small. The solid-phase composition was like that of the initial rice biodiesel. The result indicates that liquid remained in the vial for the solid phase. When the winterization temperature was 0 °C, ~3%–5% of the PM fraction decreased in the liquid phase. Although the ratio of unsaturated FAMES differed from that of the cottonseed biodiesel, the effect of the unsaturated FAME ratio remained unclear. Table 6 summarizes the separation factor and CP of the recovery liquid and solid phases. The S.F. value was like lard rather than cottonseed biodiesel winterization, but the liquid recovery and CP reduction were small.

3.5. Winterization of soybean biodiesel

The soybean biodiesel was also a light-yellow liquid at room temperature. Its density was 884.5 kg/m³, and its kinetic viscosity was 4.13 mm²/s (Table 1). The relative errors of these data to the literature data

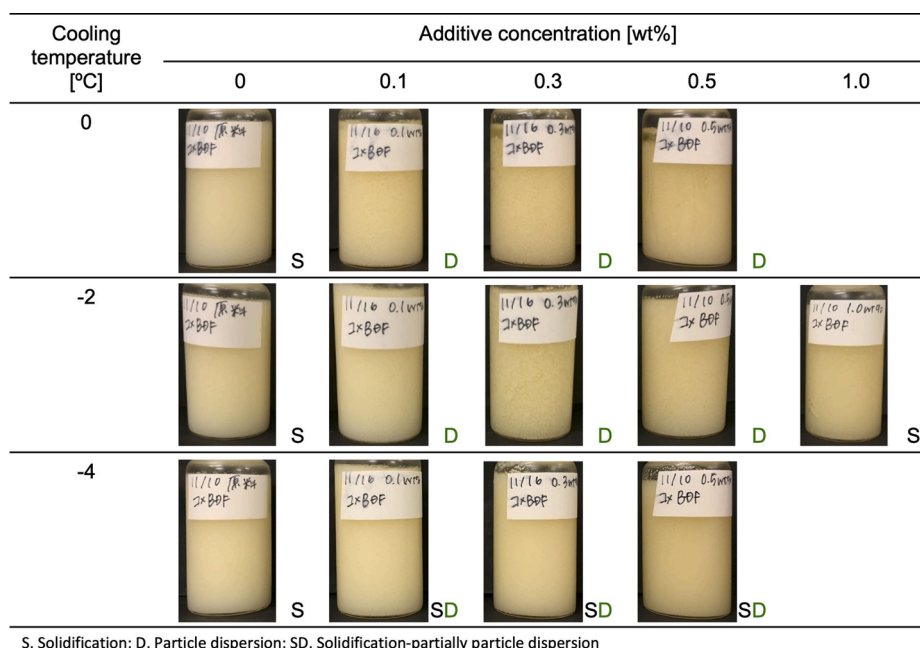


Fig. 7. Appearance of phase separation in rice biodiesel-Span40 systems at various additive concentrations and temperatures.

Table 6

Liquid recovery, separation factor, CP of liquid and solid phase for winterization of rice biodiesel.

Span conc./Temp.	R [%]	S.F. [-]	CP(L) [°C]	CP(S) [°C]
0.1 wt% -2 °C	18.1	1.09	1.5	1.5
0.3 wt% 0 °C	13.1	1.66	-2.5	3.5
-2 °C	8.6	1.35	—*	3.0
0.5 wt% 0 °C	11.3	1.38	-2.5	1.0
-2 °C	23.1	1.06	0.0	3.5

*Insufficient liquid recovered to measure CP.

[1] were ~ 0.2% and 3.7%, respectively. The FAME fractions of the biodiesels in Table 1 were consistent with the literature data [1]. The soybean biodiesel has the lowest PM fraction (10.4%) among the used biodiesels in this research. The linoleate fraction of cottonseed and soybean biodiesels was higher than other biodiesels. Although the average CP was -1.5 °C, the CP of the soybean-Span40 mixture decreased by 1.0–2.0°.

Fig. 9 shows the change in appearance in the soybean biodiesel samples after winterization. The neat soybean biodiesel separated the liquid phase slightly near the CP (-2 °C), but the liquid recovery was low. With Span40 addition, finer particles than those in the cottonseed and rice biodiesels formed and settled at the bottom of the experimental vial. Although the sediment layers may appear to be suspended in liquid biodiesel, the two-phase separation was confirmed visually in samples with 0.5 and 1.0 wt% Span40. Much of the supernatant liquid was recovered. As a result, the recovery rate ranged from 25% to 83% (Table 7). Because the PM fraction change of the liquid from the initial soybean biodiesel was ~ 2% (Fig. 10), the S.F. value ranged from 1.3 to 1.9, which is like that of lard biodiesel winterization. However, the CP (L) decreased 2.5–5.0 °C from the CP of the neat soybean biodiesel

because the PM fraction has a high impact on the CP under the lower PM fraction condition [28,36]. Therefore, the PP quality of the recovered liquid approaches the grade 1 and grade 2 light oils also for soybean biodiesel winterization. It was reported for soybean biodiesel that the CP of the resultant liquid in 11-step dry fraction was -7.1 °C and the liquid yield was 33% [13]. The additive winterization can achieve the same separation as multiple-step dry fractions in one-step operation.

3.6. Feasibility of additive winterization using sorbitan palmitate

Winterization using 0.3–1.0 wt% Span40 is a feasible method for various biodiesels. The additive winterization can reduce PM in the palm biodiesel significantly. Because the PM fraction decreased in the original biodiesel in the order of cottonseed, rice, and soybean, the biodiesel sample is predisposed to slurry formation during winterization because PM solid particles cannot grow fully. Because of insufficient separation by decantation, changes in the FAME fraction, S.F., and liquid recovery rate were low. They lead to increase costs, and as a result, reduce the economic efficiency of the additive winterization method. Another mechanical separation method, such as filtration, should be introduced to increase the changes in the FAME fraction and the liquid recovery. For example, previous research [27] has shown that the recovery rate with vacuum filtration was 81.3% for a single stage in additive-agitation winterization. In this case, the authors have made a slurry forcibly with mechanical agitation. The recovery rate was approximately 14% higher than that of additive winterization. The addition of mechanical separation will enhance the feasibility of additive winterization for these biodiesels. It is also necessary for economic efficiency to consider the reuse of additives and the control of crystal particle shape. The economic and the cost are the next challenges of additive winterization.

Biodiesel with a higher SM fraction as lard had a different appearance of solid phase to PM-rich biodiesels. The appearance change is attributed to the higher melting point of SM and the difference

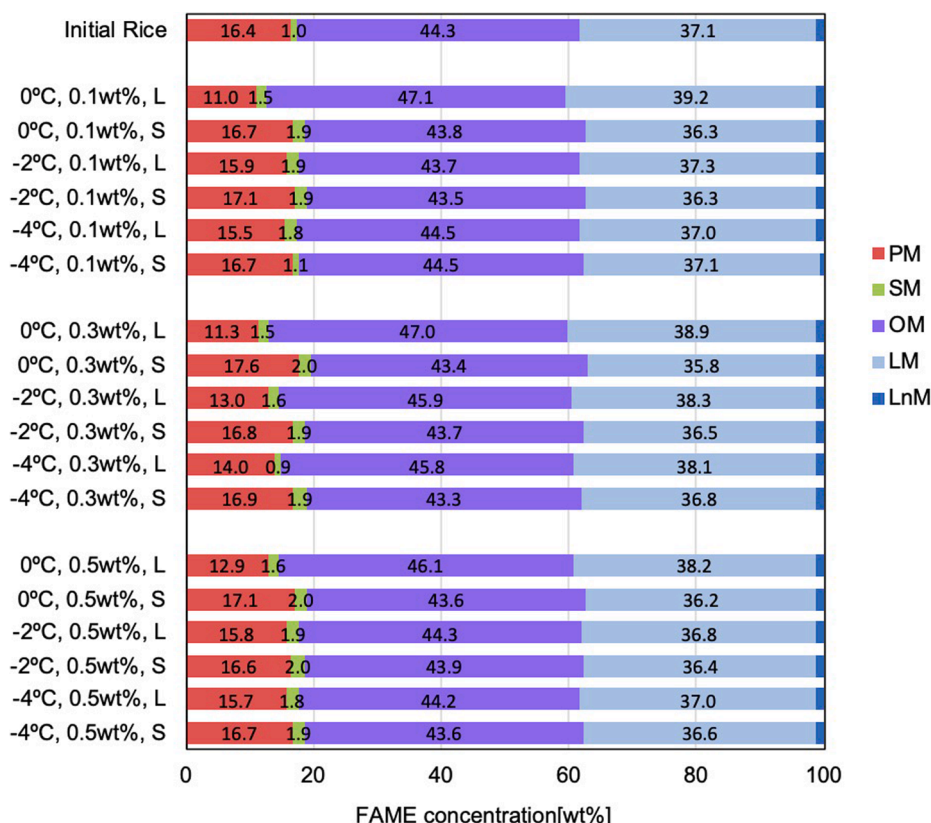


Fig. 8. Composition of rice biodiesel after additive winterization. L: liquid phase, S: solid phase.

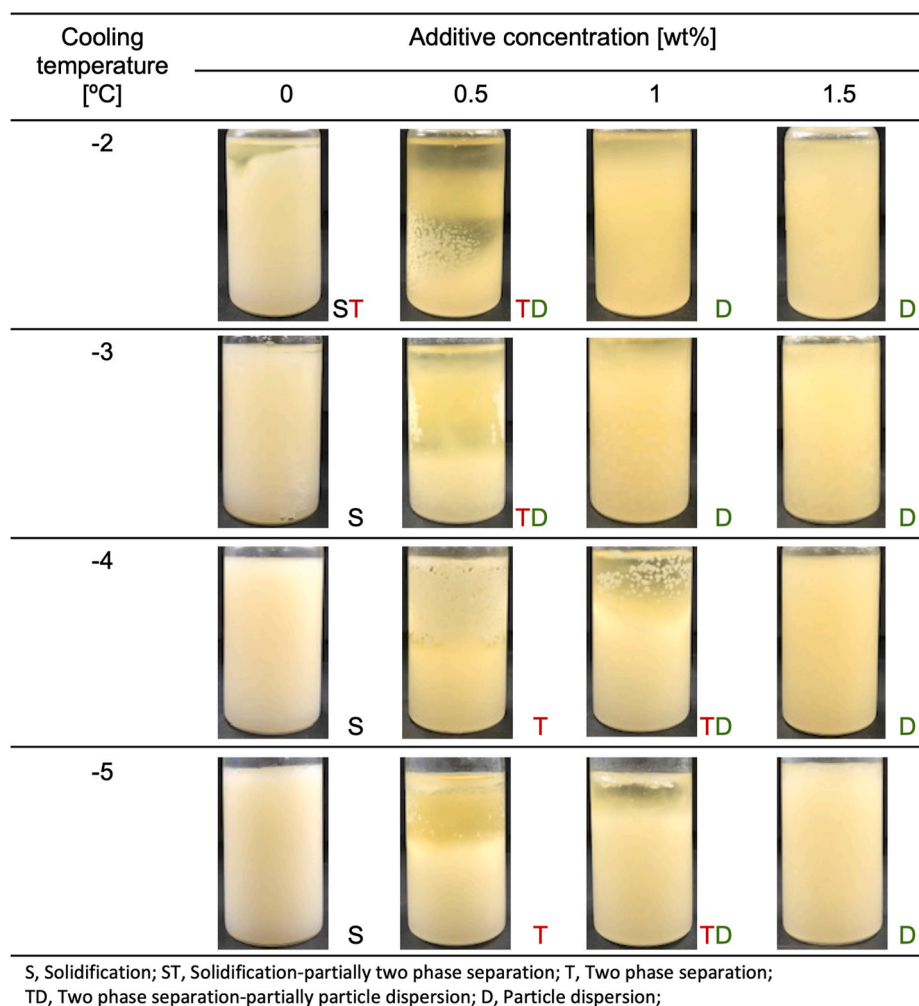


Fig. 9. Appearance of phase separation in soybean biodiesel-Span40 systems at various additive concentrations and temperatures.

Table 7

Liquid recovery, separation factor, CP of liquid and solid phase for winterization of soybean biodiesel.

Span conc./Temp.	R [%]	S.F. [-]	CP(L) [°C]	CP(S) [°C]
0.5 wt%				
-2 °C	83.2	1.11	-4.0	0.0
-3 °C	76.6	1.72	-4.5	2.0
-4 °C	50.3	1.76	-5.0	1.0
-5 °C	48.3	1.94	-7.5	0.5
1.0 wt%				
-4 °C	34.5	1.37	-5.0	0.0
-5 °C	25.4	1.55	-6.5	-1.5

interaction of SM-OM compared with PM-OM. Because the fraction of SM that was first crystallized was low, the particle size tended to be small. Because of the same carbon chain length of SM to OM and LM, the SM interaction to OM and LM is large. Span 60 (sorbitan monostearate) was an efficient additive to the SM-OM mixture [25]. Therefore, it is necessary to investigate the use of mixed additives in winterization of the SM-rich biodiesel.

Although biodiesels of higher LM fractions in unsaturated FAMES as cottonseed and soybean forms slurry, the generated particles separated easily from the resultant liquid. The CP(L) of the recovered liquid shifted significantly. These results imply that the PM-rich solid is easy to separate from the LM-rich liquid. The difference between PM-OM and PM-LM interactions will influence the separation performance greatly.

For example, the interaction difference may be explained by an interaction parameter, which is the energy difference between the energy of a different molecule pair and the average of the same molecule pairs [37]. In the fatty acid cases [37], the interaction parameter of stearic acid-oleic acid tends to be more negative than that of palmitic acid-oleic acid in the liquid phase. The interaction parameter of palmitic acid-oleic acid tends to be more negative than that of palmitic acid-linoleic acid in the liquid phase. Further investigation is required to provide a valid explanation for a relationship between the interaction parameter and FAME separation.

The kinetic viscosity of the resultant liquid at 40 °C was slightly higher than the original palm-biodiesel because of the oleate concentration, but it was in the range of the biodiesel standard. The kinetic viscosity of the solid at 40 °C increased slightly because of the increase in additive content. OM composition change of palm biodiesel is the highest among the biodiesels used in this study. Therefore, the kinetic viscosity of other biodiesels after winterization will also be within an acceptable range. The recovery of the additive from the solid and its reuse are future issues for a high-efficiency and economic winterization.

The real oils include a small number of natural ingredients (such as tocopherol and cholesterol). These materials may act as an aggregation inhibitor. The effect of natural compounds on winterization will require further investigation.

4. Conclusions

We demonstrated the separation of saturated fatty acid methyl esters

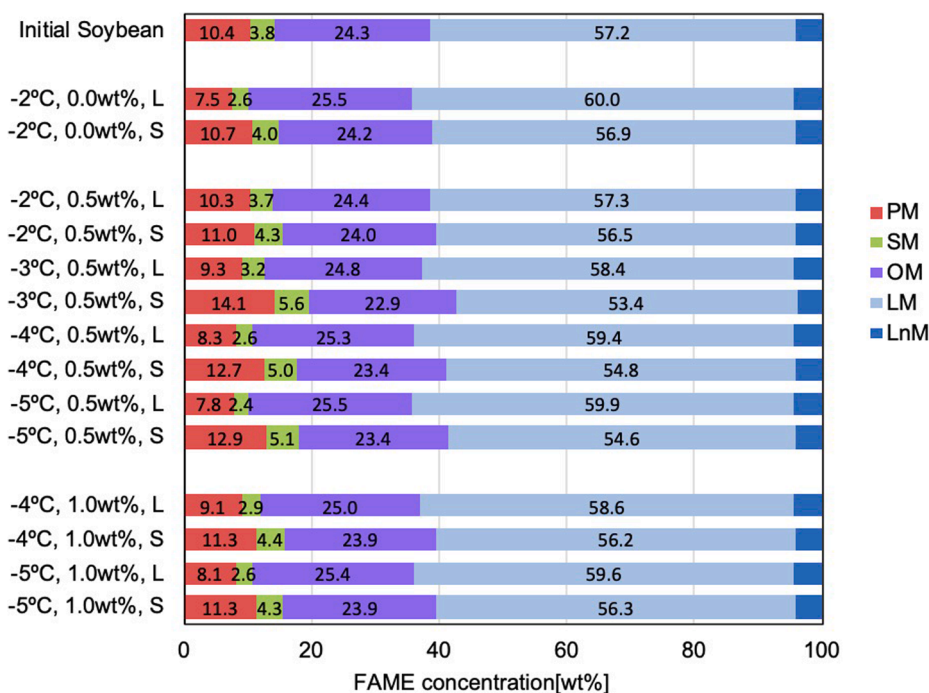


Fig. 10. Composition of soybean biodiesel after additive winterization. L: liquid phase, S: solid phase.

(FAMES) from biodiesel fuel derived from commercial eatable oils and fat (palm, lard, cottonseed, rice, and soybean) by winterization. Additive winterization using sorbitan palmitate was a feasible method for CP reduction of liquid biodiesels derived from the real oils. The CP of palm biodiesel decreased by 6–10.5 °C with a high liquid recovery after the winterization. The separation factors were between 2.4 and 7.7. The low-PM content biodiesel (cottonseed, rice, and soybean) formed a slurry. However, the CP of the recovery liquid decreased 2–5 °C from the initial biodiesels. The liquid recovery and CP variation will increase with mechanical separation. Because additive winterization is effective over a wide range of PM fraction in biodiesel, multiple operation can be also acceptable to decrease the CP(L). For a further upgrade of additive winterization, it is necessary to investigate the effect of the use of mixed additives and the impacts of the PM/SM ratio and OM/LM ratio.

CRediT authorship contribution statement

Hideo Tajima: Conceptualization, Methodology, Visualization, Writing - original draft. **Masahiro Abe:** Investigation, Writing - review & editing. **Hiroiyuki Komatsu:** Validation. **Kazuaki Yamagiwa:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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