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Effect of nonionic surfactants on the low temperature winterization separation of fatty acid methyl ester mixtures

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HIGHLIGHTS

- The separation of a FAME mixture by additive winterization was examined.
- Sorbitan mono fatty acid esters were selected as additives.
- Effects of additives were examined near the cloud points of FAME mixtures.
- The additive changed crystal appearance and improved phase separation performance.
- The optimum additive concentration was in the range of 0.25–0.50 wt%.

ARTICLE INFO

ABSTRACT

This work investigated the removal of saturated fatty acid methyl esters (FAMEs) from FAME mixtures by winterization, employing additives as solid–liquid phase separation improvers during the cooling process. Model mixtures were prepared by blending saturated FAMEs (methyl palmitate and methyl stearate) and an unsaturated FAME (methyl oleate). Sorbitan monopalmitate (Span40) and Sorbitan monostearate (Span60) were selected as separation improvers because their molecular structures were close to those of the saturated FAME in the model mixture. These additives were found to improve the solid–liquid phase separation of FAME mixtures. Four different solid phases were observed during winterization, depending on the additive concentration: a solid wax, a solid incorporating small amounts of liquid, a large crystal agglomeration, and a slurry of fine particles. The formation of the large crystal agglomeration made it easier to perform solid–liquid separation via decantation, such that the saturated FAME was readily removed from the liquid phase when employing the optimum additive concentration. When the additive had an equal or longer carbon chain length compared with the saturated FAME, a greater extent of low temperature separation was obtained. These results will be helpful to the future development of the additive winterization process.

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1. Introduction

Biodiesel has received much attention as an alternative to petroleum-based diesel fuels. Fatty acid methyl esters (FAMEs) are the main component of biodiesel, and are derived from plant oils, animal fats, or waste cooking oils via esterification with methanol [1,2,11–13]. Biodiesel must conform to the fuel properties stated in the American Society of Testing and Materials standards D6751 and D7467 or the European Committee for Standardization standards EN14214 and EN590. A major disadvantage of biodiesel is poor flow at low temperatures, a direct consequence of the high melting points of saturated FAMEs. For

example, the melting point of methyl palmitate (the primary saturated FAME in biodiesel) is approximately 303 K. This property can lead to operating problems, such as the plugging of engine filters during cold weather, so many researchers have tried to improve the low temperature flow properties of FAME mixtures [3–13]. If saturated FAMEs could be easily removed from biodiesel, the low temperature flow properties of the fuel would improve dramatically. One means of doing so is to separate saturated FAMEs through winterization. In this method, the FAME mixture is cooled so that a saturated FAME-rich solid phase forms [13–21]. Ideally, the unsaturated FAME-rich liquid phase is then separated from the saturated FAME-rich solid phase, and this unsaturated material will exhibit higher fluidity at low temperatures, even though the saturated FAME-rich solid phase typically has a higher cetane number and greater oxidative stability, both of which are

important in a diesel fuel. In practice, the recovery of the liquid phase is typically very low and solid–liquid phase separation and associated compositional changes in the liquid phase are not observed [14] because the unsaturated FAMEs can be trapped in crystals of the saturated FAMEs. Notably, this phenomenon is different from the process that generates peritectic and eutectic mixtures. To prevent this type of inclusion, mechanical agitation is typically applied during winterization [15–18]. Another means of improving the winterization yield is using chemical additives acting as cold flow improvers that prevent crystal growth and modify crystallization behavior. Winterization with cold flow improvers, also known as additive winterization, can potentially be used to inhibit the crystallization of saturated FAMEs and thus would assist in overcoming low temperature flow. Dunn et al. [17,18] tested commercial additives as cold flow improvers for petroleum diesel fuel when employing the winterization method. They reported that the solid–liquid separation of soybean oil biodiesel was improved by cold flow additives. However, to data there have been few reports concerning the mechanism by which winterization additives function. Also little information on the effects of the structures and physical properties of additives exists.

Traditional winterization and the additive winterization by Dunn et al. [17,18] require several mechanical operation stages, such as agitation and filtration, for saturated FAME removal. In addition, traditional winterization [14–19] has poor separation efficiency of saturated FAME in single step. Because these additional and multiple processes increase the overall energy requirements, equipment costs and material losses, it would be beneficial to simplify the previous winterization process. Thus, a need exists to investigate additives that are not only low temperature flow improvers but also promoters of phase separation.

The aim of the present study was to examine the effects of an additive as a separation improver regarding the phase separation of a FAME mixture during the cooling process, and its efficiency at removing saturated FAMEs from the mixture in single step. The results of this work could be helpful in improving the additive winterization method. Span40 (sorbitan monopalmitate) and Span60 (sorbitan monostearate) of were selected as the additives because these compounds have fatty acid ester chains similar to those of the saturated FAMEs used. As well, it has been reported that additives with a long hydrocarbon chain and a sterically large end group tend to effectively prevent crystal growth and agglomeration [6–10].

2. Material and methods

2.1. Sample preparation

Methyl oleate (>60.0%, but the concentration in the COA by supplier is 72.4–73.9 wt%), methyl palmitate (>95.0%) and methyl stearate (>90.0%) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without further purification. A model FAME mixture was prepared by blending methyl oleate with methyl palmitate or methyl stearate, employing a saturated FAME to unsaturated FAME mass ratio of 1:3. The proportion of saturated FAME was selected because it allowed ready observation of crystallization near room temperature. The FAME ratios of samples were determined from the ratio of saturated FAME to unsaturated FAME in rice bran and Jatropha curcas oils [11–13] and determined from waste cooking oil containing many feedstock oils blends (mainly plant oils contain in animal fats). The saturated FAME reagent was brought to approximately 333 K using a heating mantle, after which the molten saturated FAME and the unsaturated FAME were quickly blended. The actual mass fractions in the FAME mixtures were determined by gas chromatography (GC), and these mass

fractions were taken as the initial FAME concentrations. The initial FAME concentrations are summarized in Table 1. Span40 and Span60 (>95.0%, Wako Pure Chemical Industries, Ltd.) were chosen as separation improvers because they have similar side chains to those in the FAMEs (that is, fatty acid ester chains) and sterically large functional groups (the sorbitan unit). These compounds will prevent crystal growth and agglomeration of FAME crystals like "Tailored additive" [22]. This is a compound have both similar structure to interact and different one to repel. These compounds were added to the FAME mixtures at 0.25–4.0% by weight, using magnetic stirring and with heating at approximately 333 K.

2.2. Winterization process

Prior to implementing the winterization process, the FAME samples were heated to approximately 313 K to eliminate any thermal history, after which they were allowed to slowly cool to room temperature.

In the winterization procedure, each sample was cooled to a temperature equal to or less than the cloud point (CP) of the saturated/unsaturated FAME mixture without agitation. This cooling step was carried out over 48 h in a low temperature incubator LTE-1200W (TOKYO RIKAKIKAI CO, Ltd., Japan). After cooling, the extent of phase separation was assessed by visual inspection and the saturated FAME mass fraction in the separated liquid phase was determined by GC. The change in the saturated FAME mass fraction [%] in the liquid phase was calculated as $((x_{L,i} - x_L)/x_{L,i}) \times 100$, here $x_{L,i}$ is the initial mass fraction of the saturated FAME in the sample and x_L is the mass fraction of the saturated FAME in the liquid phase obtained following winterization.

The solid and liquid phases were readily separated by decantation and the recovery [%] of the liquid phase was calculated as $(W_R/W_i) \times 100$, here W_R is the weight of the recovered liquid and W_i is the weight of the initial sample. Because methyl oleate was concentrated in the liquid phase, a factor reflecting the separation of methyl oleate into the liquid phase upon winterization was defined as $(y_L/x_L)/(y_S/x_S)$, here x and y are the mass fractions of the saturated FAME and of methyl oleate, respectively, and subscripts L and S indicate liquid and solid phases. If the separation factor is more than unity, methyl oleate tends to concentration in liquid more than solid.

2.3. Sample analysis

The CP of the FAME mixture before processing was determined with the same test apparatus referred to in Ref. [25]. This instrument included a low temperature circulator and a platinum resistance temperature detector, thus closely matched the test requirements included in Japanese Industrial Standard JIS K2269 [26]. The CP of each sample was determined by visually inspecting for crystallization at 1-K temperature intervals. Thus, the CP values of the methyl palmitate-methyl oleate and methyl stearate-methyl oleate mixtures were found to be 282 and 292 K, respectively. The FAME mass fractions of each sample were determined using a gas chromatograph (GC-17A, Shimadzu Japan) equipped with an Rtx-Wax capillary column (length 30 m, film thickness 0.25 μm, internal diameter 0.25 mm) and a flame ionization detector (FID), with helium as the carrier gas. The FAME mass fraction of each sample was calculated based on the internal standard method in a manner similar to the methodology provided in European standards EN14013 and JIS K2390 [27], using hexadecane as the internal standard. A similar analysis also employing hexadecane as the internal standard has been reported in detail in previous research [25]. The accuracy of the correction factor was confirmed by analyzing a standard FAME mixture (RM-6, Sigma-Aldrich Co., LLC).