



Full Length Article

Evaluation of the separation of saturated fatty acid methyl esters obtained from additive winterization using a nonionic surfactant

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ARTICLE INFO

Keywords:

Biodiesel fuel
Fatty acid methyl ester
Winterization
Phase separation improver
Sorbitan mono fatty acid ester (surfactant)

ABSTRACT

Winterization is one means of improving the low temperature flow properties of biodiesel fuel, by the separation of saturated FAMES. Additives are also employed to improve separation in the winterization process by modifying the crystallization behavior. This process is referred to as additive winterization. In a previous study, we investigated a novel additive winterization method in which FAMES are separated without agitation during cooling, allowing improved separation of saturated FAME and unsaturated FAME mixtures. This method is both facile and energy-efficient because vacuum filtration is not required. In this study, we examined the effects of additives (sorbitan mono fatty acids) and agitation on the separation of saturated FAMES from saturated and unsaturated FAME mixtures via winterization. The additive winterization process resulted in significant improvements in the cloud points of the FAME mixtures following a single separation run, with the cloud point being decreased by 8 K under optimum conditions. In contrast, winterization based on agitation required at least two cycles of sequential cooling, agitation and filtration to obtain similar results. This study therefore highlights the potential of additive winterization using sorbitan mono fatty acid esters to enhance the low-temperature flow properties of biodiesel fuels based on a simple process with reduced energy expenditures.

1. Introduction

Biodiesel fuels have received considerable attention as practical alternatives to petroleum-based diesel fuels. Biodiesel is renewable, environmentally innocuous due to its low toxicity and clean exhaust characteristics, and has a high flash point, making it relatively safe to store and handle. Fatty acid methyl esters (FAMES), which are the main components of biodiesel, can be derived from numerous edible and nonedible oils, including soybean, palm, jatropha, animal fats and waste cooking oils, via the esterification of these materials with methanol [1–4]. Biodiesel must also conform to the fuel properties stated in various regulations, including the American Society of Testing and Materials standards D6751 and D7467 and the European Committee for Standardization standards EN14214 and EN590. Unfortunately, a major disadvantage of biodiesel is that it exhibits poor flow characteristics at low temperatures because of the high melting points of saturated FAMES. As an example, soybean and palm biodiesels exhibit operability issues as the ambient temperature approaches 274 and 290 K, respectively [5,6]. The crystallization temperatures of biodiesels derived from other raw oils also fall within this same approximate temperature range [4,7,8]. At these temperatures, saturated FAMES tend to nucleate and form solid crystals that can lead to problems in fuel systems, including

fuel starvation, clogging of fuel filters and incomplete combustion. Therefore, at present, biodiesel fuel is primarily used in the form of blends with petroleum diesel at volume ratios of 5–20%.

Many researchers have investigated ways of improving the low temperature flow properties (LTFPs) of biodiesel. Crystallization modifier additives such as copolymers or surfactants are also used to modify the crystallization behavior of FAMES in biodiesel. These additives primarily improve the pour point of the fuel by preventing crystal growth and the agglomeration of crystals. However, these additives only minimally affect the cloud point (CP) of biodiesel. Crystallization modifiers have molecular structures with long carbon chains that interact with FAME molecules and generate steric hindrance that inhibits the molecular packing of the FAMES [9–12].

The removal of saturated FAMES from biodiesel is yet another means of improving LTFPs. One such strategy for enhancing the LTFPs of biodiesel involves the removal of saturated FAMES through winterization [7–9,13–19]. During this process, slow, prolonged cooling of a FAME mixture leads to the formation of a saturated FAME-rich solid phase. Ideally, the unsaturated FAME-rich liquid phase can then be separated from the saturated FAME-rich solid phase, with the unsaturated material then exhibiting higher fluidity at low temperatures. The saturated FAME-rich solid phase also typically has a higher cetane

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number and greater oxidative stability. Note that, the cetane number and oxidation stability of resultant liquid phase will decrease by saturated FAME separation. For example, the cetane number and oxidation stability of canola BDF having low saturated FAME concentration (approximately 8 wt%) were 54.1 and 2.6 h, respectively [20]. The cetane number met the EN ISO 5165 (lower limit of 51) but the oxidation stability did not meet the EN 14112 (lower limit of 6.0 h). Therefore, BDF having the low saturated FAME concentration such as canola BDF may need some antioxidant for practical use. As well, because the winterization process is performed under low temperature conditions there is almost no possibility of heat deterioration of the FAME components. In practice, the recovery of the liquid phase is typically very low because unsaturated FAMES can become trapped in the solid saturated FAMES [13]. This problem is particularly prevalent during the crystallization of mixtures consisting of FAMES with similar molecular structures.

Mechanical agitation is typically applied during winterization to prevent the inclusion of unsaturated FAMES in the solid saturated FAMES [7–9,14–18]. In this paper, winterization including agitation is termed agitation winterization. Because the biodiesel resulting from agitation winterization is in the form of a slurry, it is necessary to separate the solid crystals by vacuum filtration. Solvent winterization and detergent fractionation have also been suggested to improve the phase separation performance of biodiesel [15,16].

Saturated FAME removal using these conventional winterization procedures requires several stages, including agitation, filtration and solvent removal. Given that these processes lead to increases in equipment and energy costs, as well as considerable material losses, the development of a much simpler and cost-effective winterization process is highly desirable.

Winterization yields can also be improved by the use of chemical additives that act as cold flow improvers by preventing crystal growth and modifying the crystallization behavior of fuels [9–12]. Winterization of soybean biodiesel using commercial petroleum diesel additives (Winterflow and DFI-200), also known as additive winterization [17], has been used to inhibit the crystallization of saturated FAMES and could therefore be used as a strategy to improve low temperature flow. The use of Winterflow or DFI-200 has been found to improve liquid recovery and CP compared with agitation winterization. Our previous work [21] determined that the additive winterization process with sorbitan mono fatty acid esters (that is, nonionic surfactants) was applicable to the separation of saturated FAMES from FAME mixtures. This process does not require agitation during cooling or vacuum filtration for phase separation and thus may represent a simple, energy-efficient means of improving the low temperature flow properties of biodiesel.

The aim of the present study was to investigate the effects of employing additives and agitation on the phase separation of FAME mixtures, as well as to evaluate the removal of saturated FAMES from the mixtures. We compared the separation performances of several winterization techniques, including additive only, agitation only, and additive and agitation. Finally, we evaluated the liquid recovery and CP of each liquid phase. Span40 (sorbitan monopalmitate) and Span60 (sorbitan monostearate) were selected as the additives because these compounds have fatty acid ester chains similar to those of the saturated FAMES evaluated in this study. Additionally, these additives are used in various applications, including as food additives and lubricants, and so are mass-produced and can be obtained easily and inexpensively. These additives were also found to improve the separation of saturated FAMES from FAME mixtures in a previous study [21].

2. Material and methods

2.1. Sample preparation

Methyl oleate (nominally > 60.0% but certified by the supplier as

Table 1
Initial FAME concentrations of samples.

	FAME concentration [wt%]	
	Palmitate-oleate mixture	Stearate-oleate mixture
Palmitate	31.7 ± 1.2	3.5 ± 0.7
Stearate	1.0 ± 0.02	29.2 ± 1.7
Oleate	61.9 ± 2.0	62.4 ± 2.0
Linoleate	5.8 ± 0.8	4.4 ± 0.4
Σsaturated	32.7 ± 1.5	33.0 ± 2.1
Σunsaturated	67.7 ± 1.5	66.8 ± 2.5

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. Raw materials of FAME mixture were prepared by blending methyl oleate with methyl palmitate or methyl stearate, with a saturated to unsaturated FAME ratio of 1:3 (w/w). The associated preparation process has been reported in detail previously [21]. Briefly, the saturated FAME was heated to approximately 333 K, 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, as summarized in Table 1. Different concentrations (0.25–2.0% by weight) of Span40 and Span60 (> 95.0%, Wako Pure Chemical Industries, Ltd.) were added to the FAME mixtures with magnetic stirring at approximately 333 K.

2.2. Winterization process

Prior to 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. The cooling temperature for each winterization was selected based on the cloud point of raw materials such that the saturated FAME removal ratio and liquid recovery were as high as possible. A cooling time sufficient to ensure that the phase transition was in the steady state was applied in each case.

2.2.1. Additive winterization process

In each trial, a 40 g saturated/unsaturated FAME mixture was placed into a glass vial and cooled to a temperature equal to or below the CP of the mixture, without agitation. This temperature was selected so as to enhance the saturated FAME removal ratio, given that saturated FAME crystals do not grow at a suitable rate at the CP temperature, meaning that a low saturated FAME removal ratio would be obtained [21]. This cooling step was carried out over 48 h in a low temperature incubator (LTI-1200W, TOKYO RIKAKIKAI Co., Ltd., Japan) in conjunction with a thermistor thermometer. After cooling, the liquid and solid phases were separated by carefully decanting the supernatant out of the vial.

2.2.2. Agitation winterization process

In each trial, a 300 g sample was transferred into a 500 ml separation flask. Each sample was cooled in a thermostatic bath while being stirred (using a six-blade turbine impeller) at 50, 100 or 200 rpm. Cooling operation was started at approximately the sample CP + 3–4 K. The temperature was reduced by 0.5 K every 20 min until crystallization occurred. At the onset of crystallization, as determined by visual inspection, the FAME mixture was held at that temperature for 48 h. That temperature was determined to be cooling temperature to prevent excessive crystal growth of the saturated FAME. When agitation winterization was carried out at the same initial temperature as additive winterization, the solid FAME was found to trap a greater amount of liquid FAME and so the liquid recovery ratio decreased. Therefore,

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