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Harnessing the synergies between lipid-based crystallization modifiers and a polymer pour point depressant to improve pour point of biodiesel

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A B S T R A C T

A series of binary mixture additives made of a pour point depressant (PPD) and a vegetable oil based crystallization modifier (VOCM) have been used to substantially improve the cold flow performance of fatty acid methyl esters (FAME) of soybean oil (Soy1500). An apparatus improving on the ASTM methods was designed to measure the cloud point (CP) and pour point (PP). The mixtures dramatically altered Soy1500 crystallization from nucleation to aggregation, and delivered PP depressions reaching 30 °C. The effect was confirmed to be due to synergistic effects wherein the VOCM delays the nucleation by first combining with the saturated FAME of the biodiesel then growing structure specific crystal surfaces that effectively adsorb the PPD which provides barriers to agglomeration. The VOCM-PPD mixture constrains the biodiesel microstructure to very small crystals that are prevented from aggregating over an extended temperature range, leading to a significant depression in the PP. The most dramatic effects were achieved when the PPD is combined in optimal concentration with a VOCM having a structural element which initiates packing and another that prevents further crystallization. Importantly, the results and understanding gathered from the study can be used for the design of highly functional cold flow improver cocktail additives.

1. Introduction

The use of liquid fossil fuels in the transportation and industrial sectors is a major environmental concern as it increases even when their prices rise and despite government policies and incentives promoting the use of non-fossil energy sources [1]. Biodiesel, the mono-alkyl esters of vegetable oils or animal fats, typically fatty acid methyl esters (FAME), is a recognized renewable fuel that is sought as an alternative liquid energy source [2,3]. Its quality is regulated by standards, the two most utilized being ASTM D6751 in the United States and EN 14214 in the European Union.

Biodiesel is particularly attractive because it possesses many of the characteristics of conventional diesel and can be used neat or blended with petroleum diesel in unmodified existing diesel engines [4]. However, due to its poor cold flow performance, its wider use is prevented in cold climates.

The cold flow characteristics of biodiesel are described by standardized measurements of temperatures related to field operability such as the cloud point (CP, ASTM D2500), the cold filter plugging point (CFPP, ASTM D6371) and the pour point (PP, ASTM D97). The CP as defined in ASTM D2500, is "*the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions*". CFPP as defined in ASTM D6371 is the "*highest temperature, expressed in multiples of 1°C, at which a given volume of fuel fails to pass through a standardized filtration device in a specified time when cooled under the conditions prescribed in this test method*". ASTM D6371 specifies a standard filter of plain weave stainless steel wire mesh gauze with a nominal aperture size of 45 μm. The PP as defined in ASTM D97 is "*the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test*". The PP is reached when the fluid is viscous enough to be immobilized or when the crystals form a three dimensional solid network capable of trapping the liquid.

Among the several approaches taken to improve the cold flow performance of biodiesel, the application of cold flow improver

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Nomenclature

CP	Cloud Point
CPD	Cloud Point Depressant
CFI	Cold Flow Improver
D, Dimer	(E)-1-(1-(oleoyloxy)-3-(stearoyloxy)propan-2-yl) 18-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) octadec-9-enedioate
FAME	Fatty Acid Methyl Ester
MSBO	Metathesized Soybean Oil
MeP	Methyl Palmitate
MeS	Methyl Stearate
OSO	1,3 dioleoyl 2-stearoyl *sn*-glycerol
OPO	1,3 dioleoyl 2-palmitoyl *sn*-glycerol
PMTAG	Cross-Metathesized Palm Oil
PP	Pour Point
PPD	Pour Point Depressant
PLMA	Poly Lauryl Methacrylate
T	Temperature
TAG	Triacylglycerol
VOCM	Vegetable Oil based Crystallization Modifier

(CFI) additives is the most popular [5,6]. Generally CFI additives are designed to interrupt the crystallization process of the biodiesel at given stages and given length scales [5]. There is convincing evidence that the action of the additives is controlled by similar dominating mechanisms despite the variety and complexity of their chemical structures. The overriding trend that emerges from the studies on the subject [7–17] indicates that in order to be effective, the additive must possess a structural similarity that initiates association with the molecules of the host material rather than undergoing self-association, and a structural dissimilarity which then would obstruct and delay, if not prevent, further growth or organization and aggregation of the initial crystals. The effectiveness of a CFI additive can be traced to a structural selectivity which would be high enough to allow the disruption of the crystallization process from nucleation, growth to the aggregation stages.

CFI additives are commonly classified as cloud point depressants (CPD) or pour point depressants (PPD). The PPDs work by disturbing the crystallization process at small length scales, principally at the nucleation and early stages of growth [18]. The growth and aggregation of the biodiesel crystals can follow quite rapidly, drastically limiting the effectiveness of the additive on the PP. For example, Silva et al. [6] reported that at 5% v/v. loading, a glycerol derivative, glycerol butanal acetal, depressed the CP of animal fat biodiesel by ~5 °C but achieved a PP that was just 1 °C below the CP.

The PPDs are designed to aid pumpability, and as a result affect the CP and the filterability of biodiesel marginally [19–21]. PPDs are typically composed of low-molecular-weight copolymers and function as crystal growth limiters [22,23]. They are essentially crystal morphology modifiers which may participate in the early steps of crystallization of the saturated components of biodiesel, even after nucleation, but are able to provide a barrier to further growth, therefore reducing crystal size and limiting crystal aggregation [24]. Ozonized vegetable oil is an example of an efficient PPD found to not interfere in the crystallization of the saturated FAMEs, but works by modifying the crystal morphology of the unsaturated FAMEs [25,26]. Poly lauryl methacrylate (PLMA) is a known PPD which has been reported to be very effective in decreasing the PP of biodiesel [27].

Unfortunately, no single approach has yet been able to simultaneously address both PP and CP effectively. For a single CFI additive to achieve simultaneously a significant depression in both CP and PP, and keep a large difference between them, the additive must delay nucleation, limit crystal growth and prevent aggregation. In short, such a CFI must develop specific interactions at each length scale involved. Although this might be possible, the actual fundamental knowledge about the mechanism(s) at play is not sufficient to design a universal single additive which would simultaneously incorporate the structural features of a CPD and a PPD.

The present work builds on previous studies on vegetable oil based CFI additives, specifically the products of the metathesis of vegetable oil such as self-metathesized soybean oil (MSBO) and 1-butene cross-metathesized palm oil (PMTAG) [8–12]. It explores the actions of the combination of a CPD and a PPD in mixture additives as an alternate means to improve the cold flow performance of biodiesel. The hypothesis was that with appropriate structural specificity, synergistic effects which would coordinate and amplify the actions of the CPD and the PPD can be reached.

The CPDs of the present work were selected from the most effective compounds reported in Refs. [8–12]. These are MSBO, PMTAG and a selection of their components. PLMA was used as the PPD. Although having some effect on the PP of biodiesel, MSBO, PMTAG and their components were found to be predominantly crystallization depressors, particularly effective in lowering the onset of crystallization and decreasing the crystal size [8–12]. They were revealed to be primarily vegetable oil crystallization modifiers (VOCMs). PLMA was expected to work in Soy1500 as in canola oil biodiesel because of structural similarities [26].

The selected VOCMs include MSBO, PMTAG, purified triacylglycerols (TAGs) such as 1,3 dioleoyl 2-stearoyl *sn*-glycerol (OSO), 1,3 dioleoyl 2-palmitoyl *sn*-glycerol (OPO), and (E)-1-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) 18-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) octadec-9-enedioate, a dimer of OPO (referred to as the dimer or simply Dimer). The IUPAC names and chemical structures of the VOCMs are provided in the Supplementary Information in Table S1.

Each VOCM was tested individually and in combination with PLMA. A method inspired by ASTM D97 and ASTM D2500 was especially designed to measure the CP and PP of the biodiesel mixtures much more precisely (see Section 2.2.1). In order to determine the role of concentration or particular structural features that favor synergistic effects and uncover the mechanism of action, the mixtures were investigated with polarized light microscopy (PLM).

2. Materials and methods

2.1. Materials

Soy 1500 is a mixture of FAME derived from soybean oil, donated by AG Environmental products, LLC, Omaha, NE. It is also referred to in the text as the biodiesel. Its composition which was previously determined by GC [10] is provided in Table 1. The physicochemical properties of Soy 1500 as provided by the supplier are presented along with its composition in Table 1. OSO, OPO, and the dimer were synthesized in our laboratory according to known methods [28,29]. OSO and OPO were synthesized by the Steglich esterification reaction in the presence of DCC or DMAP as the catalysts (Scheme 1). The synthesis of the dimer (Scheme 2) was detailed in a previously published paper [9]. The dimer was prepared from 1-oleyol-3-stearoyl-2-hydroxyl propane and 1,18-otadec-9-enedioic acid. 1-oleyol-3-stearoyl glycerol was synthesized from 2,3- dihydroxypropyl oleate and stearoyl chloride in the

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