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Mitigating crystallization of saturated FAMES in biodiesel: 5. The unusual phase behavior of a structured triacylglycerol dimer and methyl palmitate binary system

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ABSTRACT

A model binary system made of methyl palmitate (MeP) and (E)-1-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) 18-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) octadec-9-enedioate (dimer, D), a structured triacylglycerol dimer, one of a series of fatty molecules that have been found to significantly reduce the crystallization temperature of biodiesel, was investigated with DSC (differential scanning calorimetry), XRD and PLM (polarized light microscopy). A complex and unusual phase behavior was uncovered for this system. The exclusive orthorhombic crystal packing that was detected by XRD was shown to be guided by the bulky D molecules. The findings are explained by the formation of dimer/methyl palmitate composite units in which the dimer associates with the MeP molecules at its fatty acid branches as well as bridges. This association was initiated in the liquid state where the mobility of MeP and free rotation of the fatty branches of D are favorable. The disruptive effect of D on the packing of the saturated FAME was effective only at low concentrations (<0.10) with the system presenting a eutectic at 5% of D, followed by three stepped transformation lines indicating three concentration regions of defined phases of increasing stability. The findings indicate that the dimer may be an effective cold flow improver of biodiesel but only at concentrations lower than 5%.

1. Introduction

The increasing demand for energy is fueled by population growth, modernization and rapid development in many countries. The search for sustainable alternatives to fossil fuels is due to the finite nature of petroleum and environmental concerns over petroleum usage and related escalating climate change [1]. Biodiesel is currently considered as a sustainable alternative fuel and is increasingly used worldwide [2]. Biodiesel is generally produced by the transesterification of vegetable oil or animal fats with an alcohol in the presence of an acid or alkali catalyst [3]. It is mainly composed of saturated and unsaturated mono-alkyl fatty acid esters, mainly MeO (methyl oleate), MeL (methyl linoleate), MeS (methyl stearate) and MeP (methyl palmitate).

Biodiesel has low toxicity and is readily biodegradable and non-flammable, making it safe to store and handle. Compared to conventional fuels, biodiesel has lower smoke opacity, polycyclic aromatic hydrocarbon and other regulated emissions [4–7]. The most challenging problems associated with biodiesel are its poor long-term storage stability characteristics and poor performance in cold conditions [8]. Its high CP (cloud point) and PP (pour point) can lead to fuel starvation and result in engine failure during cold conditions. For example, the cloud point and pour point of soybean-based methyl esters, the most common biodiesel in the United States of America, are ~0 °C and ~ −5 °C, respectively [9]. As overnight temperatures during three seasons of the year can fall into this range, the saturated FAMEs (fatty acid methyl esters) present in the biodiesel nucleate and form crystals in the fuel [10].

Several approaches have been tested to modify commercial biodiesel so as to improve its cold flow properties, including additives, feedstock and biodiesel modification such as winterization and blending with conventional diesel fuel or with FAMEs which have low crystallization temperature [11–13]. Branched chain esters and bulky substituents in the chains have also been suggested to improve the cold flow properties of biodiesel [14,15].

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Nomenclature

CLM	chain length mismatch
D	dimer
DCL	double chain length
ΔH	enthalpy
DSC	differential scanning calorimetry
FAME	fatty acid methyl ester
GC	gas chromatography
MeL	methyl linoleate
MeP	methyl palmitate
MeO	methyl oleate
MeS	methyl stearate
PLM	polarized light microscope
SAXD	small angle X-ray diffraction
T	temperature
TAG	triacylglycerol
TCL	triple chain length
WAXD	wide angle X-ray diffraction
X	molar fraction
XRD	X-ray diffraction

Subscripts

c	crystallization
D	dimer
M	melting
p	peak
on	onset
off	offset

The crystallization of biodiesel at low temperatures is primarily due to the high melting point of its saturated FAMEs [16]. The removal of these compounds from biodiesel may be a way to reduce the crystallization temperature. However, the process is non-trivial and expensive [4]. It also significantly decreases the oxidative stability and cetane number [17], and further worsens the combustion performance and exhaust emissions of the biodiesel [10,18]. The current most popular approach is the use of additives to suppress the crystallization and lower the rate of nucleation and/or crystal growth [13]. The additive is usually designed to disrupt the arrangement of the linear saturated FAMEs [19]. The changes in the crystallization behavior of biodiesel due to the additives can be appreciated at different length scales through the modification introduced to the crystal structure, polymorphism, and microstructure.

The present work was motivated by promising cold flow results obtained with self-MSBO (metathesized soybean oil) additives to commercial biodiesel [20]. It was observed that MSBO stripped of olefins depresses the onset of crystallization of methyl soyate (biodiesel) at loadings as low as 1%. The compounds in MSBO responsible for this behavior were unclear, as was the mechanism. A number of approaches were therefore utilized to determine the compounds in MSBO responsible for this behavior and to provide an understanding of the underlying mechanism. GPC, HPLC (High Performance Liquid Chromatography) and MS methods were developed for analyzing MSBO compositions. Families of compounds present in MSBO and a large number of pure molecules of MSBO were tested on biodiesel and the most effective compounds were determined. The constituent "molecular families" of MSBO as well as and a series of model compounds representing the constituents prevalent in metathesized soybean oil were tested in order to determine the structures most effective in depressing crystallization onset [21]. TAGs with two unsaturated and a saturated/*trans*-fatty acids and their oligomers were found to be highly effective in depressing onset of crystallization with the most effective stereospecificity being when the *trans-/saturated* fatty acid is at the *sn*-2 position. It was hypothesized that these compounds, because of their particular structure and conformation, disrupts the regular packing of the linear saturated FAMEs, thereby delaying nucleation and mitigating crystal growth.

Phase behavior studies of model binary systems made of the pure molecules that most depressed the crystallization of commercial biodiesel and the two major saturated FAMEs of common biodiesel (MeS and MeP) were therefore conducted to uncover the fundamental mechanisms of disruption of the packing of the saturated FAMEs and to examine the extent to which it can delay nucleation and affect crystal growth and crystal size, and consequently the transformation behavior of biodiesel. (E)-1-(1-(oleoyloxy)-3-(stearoyloxy)propan-2-yl)18-(1-(oleoyloxy)-3-(stearoyloxy) propan-2-yl) octadec-9-enedioate (D), the dimer of the present work is an oligomer of unsaturated TAG (triacylglycerol), found to be particularly effective in lowering the crystallization temperature of commercial biodiesel [21]. Its effect was also puzzling as the addition of 1% by wt. of D into biodiesel depressed the crystallization onset temperature by 2.8 °C whereas 4% by wt. depressed it by 1.7 °C only. The hypothesis was that the chemical structure of D (shown in Scheme 1) would explain this behavior. As can be seen in Scheme 1, the structure of D has two saturated moieties similar to MeP and *cis*-double bonds in two of its carbon chains that can provide a structural element that would promote an initiation of packing with the straight FAME, and another that would prevent further crystallization due to the steric hindrance presented by the two kinked chains, which would explain its general effectiveness, but is also large enough to behave somehow like a small polymer additive, a feature that would explain its higher effectiveness at small loading compared to high concentration [22,23].

The TAG dimer, is interesting as it is a component of the metathesis of vegetable oil, a reaction that is increasingly used to produce fine chemicals and modified TAG. The self-metathesis of TAGs, such as soybean oil, results in a complex mixture comprising linear oligomers (from dimer to pentamer), macrocyclic structures, cross-linked polymers, as well as trans-/cis isomers [24]. The actual composition of a metathesis product is highly dependent on the reaction conditions, such as such as starting materials, temperature, type of catalyst, etc., giving the possibility to control the product composition [25–28]. The catalysts used for the self-metathesis of soybean oil were Grubbs' catalysts. Grubbs' Catalysts are a series of transition metal carbene complexes. MSBO was composed of 6% olefins, and oligomers of the TAG structures of the natural oil, soybean oil (8% monomers, 30% dimers, 50% trimers and quatrimers and 2% of other higher level oligomers) [21]. The compounds have saturated fatty acids (~14% in total) as well as unsaturated fatty acids in the cis- and trans-configuration with a trans-/cis ratio from 4.4 to 8.

To the best of our knowledge, no such feedstock nor any oligomer of TAG has been studied or applied as a cold flow modifier to biodiesel. Ozonized soybean oil, a transformed vegetable oil, was tried as a cold flow additive, but failed to improve the cold flow properties of biodiesel [29], outlining the limits of a serendipitous approach to searching for effective additives of biodiesel.

The thermal transformation properties of thirteen (13) D/MeP mixtures were investigated using DSC (differential scanning