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Mitigating crystallization of saturated FAMEs (fatty acid methyl esters) in biodiesel: 2. The phase behavior of 2-stearoyl diolein–methyl stearate binary system

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ABSTRACT

The phase behavior of a model binary system made of OSO (2-stearoyl diolein) and MeS (methyl stearate) was investigated with differential scanning calorimetry and X-ray diffraction. The study is part of a series of investigations of unconventional additives such as TAGs (triacylglycerols) and dimers of TAGs with a demonstrated potential to significantly alter the crystallization of biodiesel. The TAG (triacylglycerol) was found to be effective in depressing the crystallization onset of the FAME (fatty acid methyl ester) significantly even at low concentration. OSO was shown to affect the crystallization of the mixtures strongly, and to dramatically alter their polymorphism. The system's phase diagram involved marked transformation lines including eutectics and solid–solid transitions. The molecular interactions were evaluated using a simple thermodynamic model. A mechanism for disruption of crystallization was proposed to be dependent on the peculiar geometry of OSO: the “straight” stearic acid participates easily in the lamellar packing of the equally “straight” FAME, whilst its kinked oleic acids effectively halt additional saturated FAMEs from participating due to steric hindrances. The findings of the study indicate that judicious loadings of TAGs which would target biodiesel's saturated FAMEs will have a substantial beneficial effect on the low temperature performance of the fuel.

1. Introduction

Biodiesel is a domestic and attractive renewable alternative which is increasingly replacing some of the conventional petroleum diesel fuels [1]. Its advantages and disadvantages are very well documented [2]. A critical inherent problem currently limiting the use of biodiesel in cold climates is its relatively poor low-temperature flow properties, indicated by high CP (cloud points) and PP (pour points) [3–5]. The gelling of the fluid and subsequent operability problems, such as plugging of filters which occurs below the CP, is essentially dependent upon the amount and size of the crystals. The actual temperatures at which the operability of biodiesel is compromised are defined by standards (e.g., the CFPP (cold-filter plugging point); (ASTM D-6371, EN 116, IP-309)).

A number of approaches have been investigated to mitigate the cold flow issues of biodiesel. The strategies employed are not only aimed at lowering the freezing point (CP and onset of crystallization) of biodiesel constituents but also at controlling the crystallizing solids (size and amount). They include winterization, dilution, additives and blending with petrodiesel and/or other fuels such as kerosene [5]. Alcohols other than methanol are used to make biodiesel with chemical compositions with inherent improved cold temperature performance and similar advantages to methyl ester fuel [2]. Nonetheless, these strategies are applied with varying degrees of success and come mostly at the detriment of other properties, or are not cost effective [2].

In fact, the behavior of biodiesel is dictated by its molecular composition, and its properties are largely linked especially to fatty acid structure [4]. Structural features such as chain length, degree of unsaturation, orientation of double bonds, symmetry, and type of ester head group strongly influence the MP (melting point) of individual chemical constituents of biodiesel. The wide diversity of biodiesel feedstock and the interdependencies of its properties make it very difficult to solve the problems simultaneously. However, the overall thermal behavior of the fuel is principally affected by the relative concentration of its saturated and unsaturated

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Nomenclature

CLM	chain length mismatch
DCL	double chain length
ΔH	enthalpy
DSC	differential scanning calorimetry
FAME	fatty acid methyl ester
MeS	methyl stearate
MSBO	metathesized soybean oil
OSO	2-stearoyl diolein
PPP	tripalmitin
PPS	1,2-Palmitoyl 3- Stearoyl sn-glycerol
PSP	1,3-Palmitoyl 2- Stearoyl sn-glycerol
PSS	1-Palmitoyl 2,3- Stearoyl sn-glycerol
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
p	peak
on	onset
off	offset
E1	eutectic-1
E2	eutectic-2

FAMEs (fatty acid methyl esters) components. As thermodynamic simulation have indicated, low-temperature operability of a biodiesel fuel is mainly determined by the saturated FAMEs content or other higher melting minor components, regardless of the chemical nature of the unsaturated esters [6]. The highest melting components of biodiesel, such as MeS (methyl stearate) and MeP (methyl palmitate), disproportionately affect its cold flow properties even at low concentration [7].

The cold flow issue is primarily a multifaceted problem of crystallization (of saturated FAMEs) in solution (unsaturated FAMEs) which can be approached from several angles. Fundamentally, the objective, if not to prevent, would be to adequately disrupt the crystallization process at both the nucleation and growth stages in order to lower the onset temperature of crystallization and decrease the number and size of the crystals. This is not an easy task as the wide diversity of biodiesel systems involves complex molecular interactions, intersolubility issues, and promote special phase transformations. In this regard, a better understanding of the phase behavior of the biodiesel components and any potential additive that would serve as an "improver" of cold flow, or any other property for this matter, is of critical importance. The development of specific thermodynamic models for predicting crystallization/melting behavior of biodiesel and biodiesel/additive would be a valuable tool in the hands of the industry. Unfortunately, studies of the phase behavior of the individual FAMEs constituting the biodiesel and their mixtures as a means to better understand the thermodynamics and kinetics of phase change in biodiesel [4] are limited. Note that phase behavior and modelling of phase diagrams have been published for few binary FAME systems, providing valuable information that can be used to understand biodiesel performance [6,8,9].

The present work was triggered by promising cold flow results obtained with MSBO (metathesized soybean oil) additives to a commercial biodiesel [10]. The most effective fractions constituents of MSBO were determined in our laboratories [11]. Oligomers of TAGs (triacylglycerols) and TAGs with two unsaturated fatty acids in the *cis*-configuration and a fatty acid in the *trans*-configuration or a *saturated* fatty acid were found to be highly functional in depressing the onset of crystallization of biodiesel. The most effective stereospecificity is when the *trans/saturated* fatty acid is at the *sn*-2 position. This suggested that the particular molecular conformation of these TAGs has a profound effect on the cold flow properties of biodiesel. We have hypothesized that the peculiar geometry of the TAG (triacylglycerol) molecules which present two kinked and one "straight" fatty acid chains may disrupt the packing of the FAMEs at the nucleation stage and therefore delay crystallization significantly.

In order to shed light on the mechanisms at the origin of the crystallization delay observed in biodiesel induced by the addition of specifically structured TAGs, we have performed a series of binary phase behavior studies of the most prevalent saturated FAMEs contained in biodiesel and TAGs containing two *cis*-unsaturated fatty acids and one saturated fatty acid corresponding to the FAME. The present paper reports on the binary system made of MeS and OSO (2-stearoyl diolein). To our best knowledge, there is no other published work on FAME/TAG systems.

2. Experimental methods

2.1. Materials

MeS (Methyl stearate) purchased from Sigma–Aldrich (Oakville, Ontario) at a claimed purity of 96% was further purified in our laboratory to better than 99%. OSO was synthesized in our laboratory according to known procedures [12,13] with a purity exceeding 99%. The purity of MeS was determined by GC-FID. The sample was run as is in chloroform, using a Zebron Capillary GC (ZB-5HT Inferno) Column (Terrance, CA, USA). OSO purity was determined by a Waters Alliance (Milford, MA) e2695 HPLC system fitted with a Waters ELSD 2424 evaporative light scattering detector. The purified OSO and MeS were mixed in the desired molar fractions (OSO molar fraction being $X_{OSO} = 0$, 0.05, 0.25, 0.40, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.85, 0.95 and 1.00), then heated at 80 °C and stirred for 5 min to ensure complete homogeneity. Special care was taken for the overall handling and storage (4 °C) of the samples.

2.2. Thermal processing

The samples were subjected to the same thermal protocol to allow for comparison between the different techniques used. The sample was first equilibrated at 80 °C for 5 min, a temperature and a time over which crystal memory was erased, and then cooled at 5 K/min down to −40 °C. For DSC measurements, the sample was subsequently held at −40 °C for 5 min then reheated to 80 °C at 2.0 K/min to obtain the melting profiles. All measurement temperatures are reported to a certainty of better than ±0.5 °C.

2.3. Analytical methods

2.3.1. X–ray diffraction

A Panalytical Empyrean X-ray diffractometer (PANalytical B.V., Lelyweg, The Netherlands) equipped with a filtered Cu-K_α radiation source ($\lambda = 0.1542$ nm) and a PIXcel^{3D} detector was used in line-scanning mode (255 lines over 3.347° wide detector). The XRD