Energy 86 (2015) 500–513

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Mitigating crystallization of saturated FAMES (fatty acid methyl esters) in biodiesel. 3. The binary phase behavior of 1,3-dioleoyl-2-palmitoyl glycerol – Methyl palmitate – A multi-length scale structural elucidation of mechanism responsible for inhibiting FAME crystallization

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ARTICLE INFO

Article history:
Received 14 September 2014
Received in revised form
23 February 2015
Accepted 13 April 2015
Available online 21 May 2015

Keywords:
Biodiesel
Fatty acid methyl ester (FAME)
Triacylglycerol (TAG)
Binary phase behavior
Polymorphism
Microstructure

ABSTRACT

The thermal behavior, microstructure and crystal structure of 1,3-dioleoyl-2-palmitoyl glycerol (OPO); an additive demonstrated to improve the cold flow behavior of biodiesel, and methyl palmitate (MeP); a saturated FAME (Fatty acid methyl ester) implicated in the high melting temperature of common biodiesel, were investigated by DSC (Differential Scanning Calorimetry), PLM (polarized light microscopy) and XRD, respectively. Very complex and rich concentration dependent phase behavior was revealed attributed to specific intermolecular interactions between OPO and MeP. OPO delayed crystallization effectively and disrupted nucleation and growth altering crystal structure and microstructure profoundly. A steep drop in melting temperature accompanied a dramatic decrease of crystal size upon addition of OPO. A complete pseudo-equilibrium phase diagram of OPO/MeP including the thermal transitions below the liquidus line, polymorphism and microstructure development has been achieved. The study provides a comprehensive fundamental understanding that can help optimize the formulation of bio-sourced structured additives that would suppress crystallization and reduce crystal size of biodiesel effectively.

1. Introduction

Various factors including fossil fuel depletion and environmental concerns have resulted in an increasing demand for renewable and environmentally responsible fuels. Biodiesel is sought as a viable alternative to petroleum based fuel as it is renewable and less harmful to the environment. The most common biodiesel is a fuel derived from the transesterification of vegetable oil/animal fat and is constituted of FAMEs (fatty acid methyl esters) of these lipids [1]. It is particularly attractive as it has many of the conventional diesel characteristics and can be used neat or in blends with petroleum diesel in unmodified existing diesel engines. Definition and detailed specifications of biodiesel are outlined in standards such as ASTM D 6751 in the United States and EN 14214 of the European Committee for Standardization, in Europe.

The poor low temperature performance of biodiesel, indicated by relatively high cloud points (CP, ASTM D2500) and pour points (PP, ASTM D97), is a serious limitation to its wider use, particularly in cold climates [2]. Several approaches to mitigate the low-temperature problems of biodiesel have been investigated over the past decade and are reported in the literature. They include blending with conventional diesel fuel, winterization, and use of synthetic additives [3–5]. The current most popular approach is the use of crystallization depressant additives which generally suppress the crystallization and retards the rate of nucleation and/or crystal growth [6]. 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 is part of a series of investigations triggered by promising cold flow results obtained with self-MSBO (metathesized soybean oil) additives to commercial biodiesel [7]. It has been found that particular components of MSBO such as TAGs and

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http://dx.doi.org/10.1016/j.energy.2015.04.011
0360-5442/

Nomenclature

CLM	Chain Length Mismatch
DCL	Double Chain Length
ΔH	Enthalpy
DSC	Differential Scanning Calorimetry
E1	Eutectic-1
E2	Eutectic-2
FAME	Fatty Acid Methyl Ester
MeP	Methyl Palmitate
MSBO	Metathesized Soybean Oil
OPO	1,3 dioleoyl-2 palmitoyl-*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
E	Eutectic
M	Melting
p	Peak
on	Onset
off	Offset
s	start

oligomers of TAGs with two fatty acids in the *cis*-configuration and a saturated fatty acid or a fatty acid in the *trans*-configuration are 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 [8]. The paper reports on the phase behavior of the model binary system made of MeP (methyl palmitate), a high melting point component of biodiesel, and 2-palmitoyl diolein OPO (1,3 dioleoyl-2 palmitoyl-*sn*-glycerol). DSC (Differential Scanning Calorimetry) thermograms were used to construct detailed kinetic phase diagrams, encompassing the liquidus line as well as the various transformations below the onset of crystallization. The liquidus line in the phase diagram obtained upon heating was modeled using the so-called Bragg-William approximation, a thermodynamic model based on the Hildebrand equation and taking into account non-ideality of mixing. The work also investigates the polymorphism and microstructure of the OPO/MeP mixtures using XRD and PLM (polarized light microscopy).

XRD is a powerful tool for studying crystallization at the molecular and nanoscale levels. It allows access to the details of the lamellar packing as well as the subcell structure of the fat crystals and provides information on the intermolecular interactions at play during the development of the crystal phases [9]. XRD also provides valuable information on the crystal arrangement, homogeneity and order state at the crystallized domains which are usually at the nanoscale. The technique provides access to the electronic density map which in turn provides an indication of the localization of atoms/group of atoms. This in fact can be used to understand the molecular mechanisms involved in the crystallization of TAG/FAME systems and help unravel the role of TAGs in the dramatic reduction of crystallization temperature of FAMEs.

PLM is an efficient technique to study the microstructure of lipid systems. The development of fat crystals from the start of crystallization to the complete fat network can be exposed by time/temperature resolved PLM, or thermo-microscopy. The technique also allows access to nucleation parameters when the rate of nucleation is low or the rate of crystal formation (number of crystals per time) is low, i.e., when individual crystals can be individually counted and considered as nuclei [10].

2. Experimental methods

2.1. Materials

OPO (1,3-dioleoyl-2-palmitoyl glycerol) was synthesized and purified in our laboratory according to known procedures [11,12] and MeP (methyl palmitate) was purchased (Aldrich Chemical Co. Inc.). Their purities were greater than 99% as determined by HPLC (high performance liquid chromatography). OPO and MeP were mixed in 0.05 molar fraction increments. The melted sample was homogenized using a mechanical stirrer.

2.2. Differential scanning calorimetry (DSC)

DSC measurements were carried out on a Q200 model (TA Instruments, New Castle, DE) under a nitrogen flow of 50 mL/min. Approximately 4.0–5.0 (±0.1) mg of melted sample was placed in an aluminum DSC pan then hermetically sealed. An empty aluminum pan was used as a reference. The sample was fully melted and held for 5 min at 80 °C in order to erase crystal memory. It was then cooled at a rate of 5 K/min down to −90 °C, a temperature at which crystallization was deemed complete. The sample was equilibrated at this temperature for 5 min and subsequently reheated to 80 °C at a rate of 2 K/min to record the melting cycle.

The "TA Universal Analysis" software was used to analyze the data and extract the main characteristics of the peaks (peak (T_p), onset (T_{On}) and offset (T_{Off}) temperatures, and enthalpy (ΔH). Non-resolved peaks were located using first and second derivatives of the heat flow versus temperature curve.

2.3. Polarized light microscopy

A PLM (polarized light microscope, Leica DM2500P, Leica Microsystems, Wetzlar, Germany) fitted with a Leica (DFC420C) digital camera was used for image capture. A Linkam LS 350 temperature − controlled stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) fitted to the PLM was used to process the samples. A small droplet of material was carefully pressed between a preheated glass microscope slide and cover-slip ensuring a uniform thin layer of sample. The sample was melted at 80 °C for 5 min to delete all crystal memory then cooled at 1 K/min down to −50 °C. Images were recorded at 50X, 100X and 500X magnification.

The sample was measured as it was cooling using the automatic multi-time image capture available in the PLM. The start temperature of crystallization (T_s) was recorded at the appearance of the first "white spot" in the PLM. The development of the size and shape of the crystals were determined as a function of temperature. The final crystal network was particularly scrutinized.

2.4. X-ray diffraction

A Panalytical Empyrean X-ray diffractometer (PANalytical B.V., Lelyweg, The Netherlands) equipped with a filtered Cu-K_α radiation source (λ = 0.1542 nm) and a PIXcel^{3D} detector was used in line-