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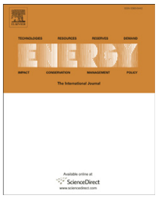

Mitigating crystallization of saturated fames in biodiesel: 1. Lowering crystallization temperatures via addition of metathesized soybean oil

Athira Mohanan, Laziz Bouzidi, Shaojun Li, Suresh S. Narine*

Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

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A B S T R A C T

The addition of self-MSBO (metathesized soybean oil) to biodiesel significantly depresses the onset temperature of crystallization (T_{on}). MSBO and self-MTO (metathesized triolein), used as model systems, were separated into their constituent "molecular families" using column chromatography and crystallization fractionation and tested as crystallization modifiers of biodiesel. The results indicate that *cis*-unsaturation combined with a straight chain moiety is a critical structural architecture for disrupting biodiesel crystallization. The data obtained with TAGs (triacylglycerols) propose that the most effective stereospecificity is when the two fatty acids in the *cis*-configuration are in the *sn*-1 and *sn*-3 positions and a *trans*-/saturated fatty acid is at the *sn*-2 position. The conversion of *cis*-double bonds to *trans*-double bonds by self-metathesis explains the lowering of T_{on} of biodiesel. The fractionation of MSBO, leading to a liquid fraction enriched with molecules having *cis*-unsaturated fatty acids out-performed MSBO in lowering T_{on} of biodiesel. This knowledge can be used for the design of economical and more functional materials from MSBO and other metathesized vegetable oils using selective and practical fractionation methods. The findings of the study suggest that the use of biodiesel with significant saturated methyl ester content can be extended in colder months of the year.

1. Introduction

Biodiesel is the subject of considerable research and development efforts due to environmental concerns, the decline of known petroleum reserves and price increase of fossil energy [1,2]. Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats and is produced using a variety of technological methods [3,4]. The quality of biodiesel is regulated by standards, the two most utilized being ASTM D6751 in the United States and EN 14214 in the European Union.

Biodiesel is a renewable feedstock compatible with existing fuel distribution infrastructure that have less of an environmental impact compared to petroleum based diesel (petrodiesel). It is miscible with petrodiesel in any proportion and offers facile use in current diesel engines [5]. Biodiesel offers several important advantages over conventional diesel fuel. It has a high CN (cetane number), inherent lubricity (even in blends of 1–2%), low toxicity, superior flash point, high biodegradability, and negligible sulfur content. Furthermore, its use results in significant reduction of most regulated exhaust emissions. Disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low temperature operability compared to petrodiesel, and in some cases, higher NO*x* exhaust emissions [6,7]. Many of these deficiencies can be mitigated through blending with petrodiesel [8] and/or reducing storage time [9]. However, blending with petrodiesel is only effective at relatively low biodiesel proportions (up to 30 vol.%) [10,11]. Standards have been introduced for inclusion of up to 20 vol. % biodiesel in petrodiesel (ASTM D975, ASTM-D7467 and EN 590).

One of the major limitations to wide-spread utilization of current biodiesel is its poor low-temperature performance [7]. Low-temperature operability of biodiesel is normally determined by three common parameters: CP (cloud point; ASTM D2500 or D5773), PP (pour point; ASTM D97 or D5949), and CFPP (cold filter plugging point; ASTM D6371). The thermal characteristics determined with DSC (Differential scanning calorimetry) can be reliably used to assess the cold flow properties of biodiesel that are ordinarily obtainable by standard tests [12]. DSC provides some advantages over standard methods. Evaluating CP from DSC curves,

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* Corresponding author. Tel.: +1 705 748 1011; fax: +1 705 748 1652.
E-mail address: sureshnarine@trentu.ca (S.S. Narine).

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Nomenclature

A	Area
CFI	Cold Flow Improver
D	Dimer
DSC	Differential Scanning Calorimetry
EEE	Trielaidin
EOE	1,3-dielaidioyl-2-oleoyl-sn-glycerol
EEO	1,2-dielaidioyl-3-oleoyl-sn-glycerol
F	Fraction
FAME	Fatty Acid Methyl Ester
LF	Liquid Fraction
LLP	1,2-dilinoleyol-3-palmitoyl-sn-glycerol
LLS	1,2-dilinoleyol-3-stearoyl-sn-glycerol
LPL	1,3-dilinoleyol-2-palmitoyl-sn-glycerol
LSL	1,3-dilinoleyol-2-stearoyl-sn-glycerol
LnPLn	1,3-dilinoleinoyl-2-palmitoyl-sn-glycerol
LnLnP	1,2-dilinoleinoyl-3-palmitoyl-sn-glycerol
LnLnS	1,2-dilinoleinoyl-3-staroyl-sn-glycerol
LnSLn	1,3-dilinoleinoyl-2-staroyl-sn-glycerol
MeLn	Methyl Linoleate
MeO	Methyl Oleate
MeS	Methyl Stearate
Mw	Molecular weight
MSBO	Self-Metathesized Soybean Oil
MTO	Self-Metathesized Triolein
OOO	Triolein
OOE	1,2-dioleoyl-3-elaidioyl-sn-glycerol
OPO	1,3-dioleoyl-2-palmitoyl-sn-glycerol
OOP	1,2-dioleoyl-3-palmitoyl-sn-glycerol
OSO	1,3-dioleoyl-2-stearoyl-sn-glycerol
Q	Quatrimers
SSS	Tristerin
SSO	1,2-distearoyl-3-oleoyl-sn-glycerol
SOS	1,3-distearoyl-2-oleoyl-sn-glycerol
SF	Solid fraction
T	Temperature
t	Time
TAG	Triacylglycerol

Subscripts

F	Fractionation
R	Retention
on	Onset
w	Weight

for example, greatly minimizes experimental error associated with ASTM method D2500 visual detection. This technique offers additional benefits by providing important information on the transformation mechanisms involved in the crystallization process of the materials. In fact the DSC is being used increasingly to investigate the flow properties of biodiesel due to additives or other means of modification in lieu of and in correlation with the CP, PP and CFPP [13–18]. It was shown for example that the onset temperature of crystallization as well as the first crystallization peak characteristics are closely associated with CP and PP of biodiesel [14]. The temperature at which the first crystals are observed is very closely related to the onset temperature of crystallization and is therefore a direct indication of CP [19]. A depression in PP due to additives, although less obvious as it relates to a later stage of crystallization, can be clearly indicated by the change in heat flow of the crystallization/melting peak because of its direct relationships to the amount of the solid phase [13]. For example, PP and CP, and CFPP have been obtained in a single DSC slow cooling experiment (0.5 °C/min) with better reproducibility than standard ASTM tests [18].

Several approaches to mitigate the poor low-temperature performance of biodiesel have been reported in the literature over the past decade [20], including the diversification of the fuel composition through genetic, chemical or/and physical modification of the feedstock [21,22]. The common and most popular approach used to improve the cold flow properties of biodiesel is, however, treatment of the fuel with CFI (cold flow improver) additives. Many examples and reviews of such additives and their function are reported in the scientific and patent literature (see for example works cited in Refs. [23–27]).

The existing CFI additives can be classified into two large categories: (a) Additives which affect one or more phases of the crystallization process, i.e., nucleation, growth, or agglomeration. These are commonly referred to as WCM (wax crystalline modifiers), and are intended to promote the formation of smaller crystals. These improve CP and affect beneficially CFPP as well as LTFT (low temperature flow test) favorably [28]. The Biodiesel Handbook [29] provides a good review of the different WCMs. (b) Additives that inhibit crystalline growth without affecting nucleation. These are primarily PPDs (pour point depressants) designed to aid pumpability. They function as crystal growth limiters and marginally affect the CP and filterability of biodiesel [30–33]. They are typically composed of low-molecular-weight copolymers and are similar in structure and melting point to *n*-alkane paraffins [29].

Unfortunately, no one approach has yet been able to simultaneously address both PP and CP effectively. Furthermore, current additives are generally not cost effective [10,34]. Most commercial CFI additives are designed with a high degree of structural selectivity to treat petroleum derivatives, and generally fail to effectively reduce CP in neat and blended biodiesel. In order to develop more efficient CFI additives specific to biodiesel, research efforts are currently directed to designing compounds with increased selectivity specific to biodiesel. The goal is to modify nucleation and disrupt crystalline growth of the high-melting-point alkyl ester compounds of biodiesel. Several approaches have been tried in this regard, including crystallization modifiers additives based on vegetable oils [35,36], synthesis of fatty compounds similar in structure to saturated esters and containing bulky moieties [37], branching of the unsaturated FAMEs [34,38–40], addition of branched diesters [41] and glycerol derivatives [42,43]. Several small chain compounds have been tried also as diluents in biodiesel [44–46].

The present study arose from the observation that self-MSBO (metathesized soybean oil) stripped of its olefins depresses the onset of crystallization of methyl soyate (biodiesel) at loadings as low as 1% [47]. The compounds in MSBO responsible for this behaviour were unclear, as was the mechanism.

Olefin metathesis is an important organic synthesis technique that is increasingly used in oleochemistry to produce fine chemicals [48–51]. It is a powerful tool that can increase the molecular diversify and reactivity of natural oils and fats dramatically. It produces novel compounds which can serve as petrochemical replacements. Olefin metathesis (Scheme 1) is a reversible reaction involving the exchange of alkylidene groups between the reactant