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Cold flow properties for blends of biofuels with diesel and jet fuels

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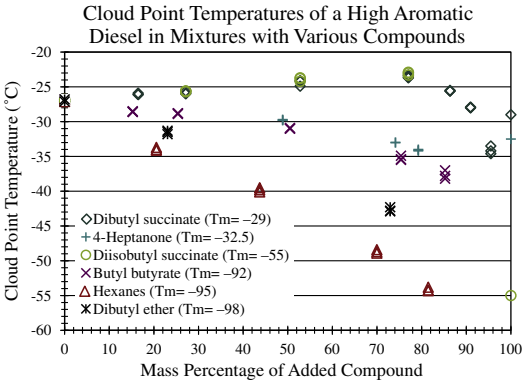
HIGHLIGHTS

- We report cloud point temperatures of diesel, jet fuel, and biofuel mixtures.
- Compound classes included alkanes, ethers, ketones, esters, and diesters.
- Cloud point depression depends on functional groups present.
- Trends are apparent based on the oxygen content of the added compound.
- Diesters display liquid–liquid phase behavior above the solidification temperatures.

GRAPHICAL ABSTRACT



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ABSTRACT

Twelve potential biofuel compounds were tested in mixtures with three diesel fuels and one jet fuel to determine the effects of different functional groups on low temperature properties. Functional groups evaluated include diesters, esters, ketones, and ethers; alkanes were used for comparison. The length of the hydrocarbon chains on either side of the oxygen-containing functional groups and branching were varied. Some test compounds are not anticipated to be commercial biofuels, but were compared to understand the effect of functional groups on cold flow behavior.

Trends were observed relating to the compound class or oxygen-containing functional group present in the compound. Generally, alkanes, ethers, esters, and ketones with a low melting point temperature decreased the cloud point temperature of a fuel. Adding diesters resulted in low temperature liquid–liquid immiscibility. Multiple methods were used to confirm the presence of two liquid phases with diesters, including cold filter plugging point measurements. These general behaviors are independent of chain length and branching, as long as the melting point temperature of the compound is not significantly higher than the cloud point temperature of the fuel.

1. Introduction

By the year 2022, it is projected that 60 billion gallons of biofuel will be required worldwide to meet government mandates [1]. There are many logistical issues for consideration of fuel blends ranging from fuel standards to acceptability in distribution systems. Various fuel properties must be evaluated for biofuels to be considered compatible, including energy content, octane/cetane number, materials compatibility, volatility and cold flow properties. In this work, we take an expanded view of possible biofuels, considering those that contain oxygen in different functional groups.

First-generation biofuels are made primarily from starches, sugars, or vegetable oils. This includes ethanol from corn and fatty acid methyl esters (FAME) produced from vegetable oil or animal

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fats. While FAME from soybean oil is the most commonly used form of biodiesel in the United States [2], the use of this fuel is limited in cold climates due to its high cloud point temperature, even when mixed with petroleum diesel [2–4]. FAME biodiesel is more problematic as a bio-jet fuel, due to the low temperatures encountered at high flight altitudes [5]. Without additional processing, such as distillation [6] or the use of urea to precipitate the saturated esters [7], FAME is not able to achieve the required low cloud point temperatures. There are many papers in the literature which describe the effects of biodiesel on low temperature and various fuel properties of diesel fuels [8–10].

Second-generation biofuels are often defined as biofuels made from non-food feedstocks, including ethanol from corn stover and other lignocellulosic sources, Fischer–Tropsch oils from wood, and butanol or mixed alcohols from renewable sources [11]. In addition, these fuels can be reacted together or upgraded to produce fuels with more desirable qualities [12–14]. Chemical reactions create compounds with a wide variety of functional groups and oxygen content, and can usually be tailored to produce a specific molecule type. Dibutyl succinate has previously been considered as a diesel-range oxygenate [15], as well as other ethers [16]. Evaluations of the functional group's effects on cloud points and other cold flow properties are needed to streamline the development of these fuels, and to identify which types of molecules would be desirable as fuels.

We examine twelve compounds representing different chemical classes (alkanes, ethers, esters, ketones, and diesters) in fuel blends, to develop an understanding of the impact of molecular functionality on cold flow properties. ASTM D7683 and D2500 were used to determine cloud point temperatures, and ASTM D6371 was used for cold filter plugging point temperatures. Multiple types of both diesel and jet fuels were used to determine the effects of the molecule types across fuel specifications. The compounds evaluated have the potential to be produced through bio-derived pathways. Most are usually not produced directly by fermentation, but are envisioned as products of the upgrading of fermentation products.

2. Materials and methods

2.1. Materials

Three petroleum diesel fuels and one jet fuel with properties shown in Table 1 were used, covering a range of intended application temperatures. These fuels include a representative US standard #2 diesel (USD), a representative European standard diesel (ESD), and a diesel with comparatively high aromatic content, denoted high aromatic diesel (HAD). Three samples of HAD fuel were used, obtained from three fuel batches prepared to the same specifications, but with slightly different measured properties. HAD was the initial sample, HAD^{+} was obtained 2 months later, and HAD* was obtained 4 months after the first sample. The same batch of HAD used in these cloud point studies was previously characterized by Windom et al. [17]. The JP-8 jet fuel was donated by the US Air Force. JP-8 is the petroleum-based fuel used by the US military and it is very similar in specifications to the commercially available fuel Jet A1. However, JP-8 contains an additional additive package to improve low temperature performance and to inhibit corrosion.

Hexanes (99.8% purity), butyl butyrate (98% purity), dibutyl ether (99.3% purity), dihexyl ketone (97% purity), and dihexyl ether (97% purity) were obtained from Sigma Aldrich. All other chemical compounds were synthesized in our laboratories and purities were confirmed using gas chromatography. Water contents were analyzed using Karl-Fisher titration. All compounds had $\geqslant$97% purity and<0.1% water.

Chemical classes for the selected biofuel compounds include diesters, esters, ketones, ethers, and alkanes. Table 2 summarizes all compounds tested, their structures, and their melting temperatures. For FAME, we show the structure of methyl oleate as a representative component. All melting points are either from NIST Chemistry WebBook [18], or the DIPPR database [19] and for FAME we tabulate the cloud point. The compounds can be divided into two classes based on molecular weight. The lighter components contain 7 or 8 carbons, and the heavier components contain from 12 to 17 carbons.

Dibutyl succinate (DBS) is a possible biofuel component because it can be made from succinic acid and butanol, which are both potential products of fermentation. Dibutyl succinate and diisobutyl succinate were produced adapting the method of Kolah et al. [20], using n-butanol or isobutanol, respectively, instead of ethanol. Dibutyl ether, 4-heptanone, and butyl butyrate were selected because they can be made from butanol and butyric acid. Butyric acid is also a fermentation product [21]. Dibutyl ether can be made by acid-catalyzed dehydration of n-butanol, 4-heptanone by ketonization of butyric acid [22,23], and butyl butyrate can be produced by esterification of n-butanol with butyric acid [24].

The cetane numbers (CN) of certain compounds such as DBS (CN = 15–20 [25]) or butyl butyrate (CN = 17.5 [26]) are too low to be viable as a diesel fuel in their own, but could be envisioned as blending components to provide other beneficial properties (e.g., oxygen content, reduction in exhaust particulates, etc.). The DBS CN of 15 is based on extrapolation of ASTM D613 testing DBS/FAME blends by Paragon Laboratories, Livonia, MI. The experimental cetane numbers are listed here in the format of (v/v% DBS, CN): (0%, 59.3), (20%, 46.5); (40%, 40.1), (50%, 35.6). Larger compounds (CNs measured by Paragon Laboratories, ASTM D613) such as butyl nonanoate (CN = 51), isobutyl nonanoate (CN = 45), and ethylhexyl nonanoate (CN = 59) have higher cetane numbers that are more typical of diesel fuel and thus are more desirable for diesel blending.

Dihexyl ketone and dihexyl ether are included to evaluate whether the trends exhibited by esters, ethers, and ketones

Table 1
Base petroleum fuel characteristics. USD – US standard #2 diesel; ESD – European standard diesel; HAD – high aromatic diesel.

	USD	ESD	HAD	JP-8	Test method
Cloud point (°C)	−15	−23	−27	−52	ASTM D2500
Cold filter plugging point (°C)	n/a	−33	−36	n/a	ASTM D6371
Specific gravity at 15.6(°C)	0.847	0.834	0.859	0.798	ASTM D4052
Distillation T10 (°C)	207	209	214	177	ASTM D86
Distillation T50 (°C)	256	263	253	203	
Distillation T90 (°C)	313	332	312	241	
Aromatics (%vol)	29	22	34	15.7	ASTM D1319 ASTM D5291
Saturates (%vol)	68	74	63	n/a	
Olefins (%vol)	3	4	3	0.8	
Cetane Number	44	52	41	n/a	ASTM D613