Fuel 195 (2017) 59–68

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Dependence of cold filter plugging point on saturated fatty acid profile of biodiesel blends derived from different feedstocks

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HIGHLIGHTS

- 303 biodiesel blends from 15 common feedstocks were used.
- Roles of FAME components on the CFPP prediction were determined.
- Mathematical relationships between CFPP and FAMEs were established.
- CFPP Pattern of biodiesel blends from various feedstocks was determined.

ARTICLE INFO

Article history:
Received 21 August 2016
Received in revised form 10 January 2017
Accepted 13 January 2017
Available online 19 January 2017

Keywords:
Biodiesel
Blend
Fatty acid methyl ester
Cold filter plugging point
Biodiesel specifications

ABSTRACT

One of the major technical obstacles to the practical use of biodiesel fuel is its cold flow properties. Although attempts have been made to determine the correlation between the cold filter plugging point (CFPP) and the fatty acid methyl ester (FAME) profiles, the proposed models are valid only for certain combinations of feedstock oils. In this study, the contributing coefficients of individual saturated FAMEs used in predicting the CFPP were quantified statistically for the first time. Quantification was based on 303 most widely used biodiesel blends (125 from this work and 178 collected from previous studies) of 15 edible, non-edible, or low-molecular-weight oils and animal fats. Results based on a stepwise multiple regression method (Model 1) indicate that the amounts of myristic (C14:0), palmitic (C16:0), stearic (C18:0), and arachidic (C20:0) acid methyl esters significantly influence the CFPP. Considering unconverted monoglycerides as another independent variable for the stepwise analysis, the results (Model 2) indicate that the statistically significant variables are the same as those in Model 1. In order to improve the predictive power of and to reduce the number of parameters in the Models 1 and 2, several modified correlations (Models 3–5) were also established by stepwise analysis, especially for blends containing babaçu/coconut methyl esters or a large amount of rapeseed methyl esters. Through these correlations, the optimum FAME profile and blends of common biodiesel feedstocks that result in a satisfactory CFPP can be determined from their C16:0, C18:0, and C20:0 content.

1. Introduction

Biodiesel, which consists of monoalkyl esters of fatty acids obtained from the transesterification of vegetable oils or animal fats with lower alcohols, has received considerable attention because it can be used as a substitute or as an additive for petroleum-based diesel [1,2]. Methanol is the alcohol most commonly used in biodiesel production because of its wide availability and low cost; thus, another name for biodiesel is fatty acid methyl esters (FAMEs) [3]. Blending biodiesel with petroleum diesel leads to significantly reduced emissions of harmful air pollutants such as hydrocarbons, carbon monoxide, and particulate matter, albeit alongside a slight increase in nitrogen oxide emissions [4–6]. Moreover, the carbon dioxide emitted into the atmosphere by biodiesel combustion can be recycled through photosynthesis. The energy yield of biodiesel production may be around three times larger than that of fossil fuel production when considering the entire life cycles of these fuels [7]. >60 countries have thus already enacted targets or mandates for blending biodiesel with diesel fuel in order to reduce dependence on dwindling petroleum reserves, as well as emission of greenhouse gases and other pollutants [8].

Despite its positive effects on the environment, biodiesel fuel must meet strict quality specifications to ensure trouble-free per-

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http://dx.doi.org/10.1016/j.fuel.2017.01.054
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Nomenclature

ASTM	American Society for Testing and Materials
Cm:n	lipid numbers, fatty acid with carbon number “m” and double bond “n”.
C12:0	lauric acid or lauric acid methyl ester
C14:0	myristic acid or myristic acid methyl ester
C16:0	palmitic acid or palmitic acid methyl ester
C18:0	stearic acid or stearic acid methyl ester
C18:1	oleic acid or oleic acid methyl ester
C18:2	linoleic acid or linoleic acid methyl ester
C18:3	linolenic acid or linolenic acid methyl ester in the common feedstock oils; α-eleostearic acid orα-eleostearic acid methyl ester in tung oil
C20:0	arachidic acid or arachidic acid methyl ester
CFPP	cold filter plugging point
CNS	Chinese National Standards in Taiwan
EN	European Standards
FAME	fatty acid methyl ester
FID	flame ionization detector
HO	high oleic
LTFT	low-temperature flow test
MP	melting point
PP	pour point
R^2	the coefficient of multiple determination
SD	standard deviation
VIFs	variance inflation factors

formance. These specifications include the American Society for Testing and Materials (ASTM) D6751 in the United States, European Standard EN 14214, and Chinese National Standards (CNS) 15072 in Taiwan [9–12]. One of the major technical obstacles to the practical use of biodiesel fuel is its cold flow properties, which can be critical depending on the climate and seasonal conditions of the region in which the fuel will be used [3,13]. Crystal formation and agglomeration in cold weather can lead to large crystals that restrict or block flow through fuel lines and filters, leading to fuel starvation and subsequent engine failure [14–16].

The cold flow properties of biodiesel and all diesel fuels can be described by the cold filter plugging point (CFPP), cloud point, pour point (PP), and the low-temperature flow test (LTFT) [3,15,16]. Among these parameters, the LTFT (applied in North America) and the CFPP (applied in countries outside North America) are direct and reliable indicators for low-temperature engine operability. Nevertheless, the CFPP is more commonly used than the LTFT as an estimate of the lowest temperature at which a fuel gives trouble-free flow in certain fuel systems [17]. The CFPP has also been adopted by the prescribed biodiesel limits in the European Union and in Taiwan as the only criteria for the evaluation of cold flow properties and low-temperature engine operability.

Previous studies have shown that the fatty acid profile of the feedstock influences the CFPP of biodiesel samples because of the different melting points (MP) of individual FAMEs. Saturated FAMEs have MPs higher than those of unsaturated FAMEs, and the MPs tend to increase with chain length [9,10,18–20]. Consequently, biodiesels with higher levels of saturated FAMEs having longer carbon chains tend to show inferior CFPPs [9–13]. Blending these fuels with biodiesel samples exhibiting better cold flow properties (e.g., rapeseed, soybean, and jatropha methyl esters) has shown promising results in efforts for improving the CFPP of biodiesel from highly saturated feedstock (e.g., palm) [17,21,22]. Other methods include blending with another type of fuel (e.g., kerosene, diesel fuel, or ethanol), utilization of additives (PP depressant or cold-flow improvers), winterization, and other treatments [13–15,23–25]. Changing the formulation of the biodiesel feedstock is the most effective method for modifying the cold flow properties and other fuel properties related to FAMEs. In particular, using cheaper or non-edible FAMEs (e.g., jatropha or waste cooking oils) in the blend can also reduce feedstock cost, which accounts for 60–90% of the operating costs for biodiesel production [26–28].

In order to determine the optimum fatty acid profile for a satisfactory CFPP, several prediction models based on biodiesel blends of multiple feedstocks have been proposed [17,21,22,29–32]. Moser [21] used the total saturated FAME content to predict the CFPP of blended samples of palm, soybean, canola, and sunflower methyl esters. Echim et al. [17] extended Moser’s correlation to the CFPP of binary mixtures of vegetable and animal-fat methyl esters, including those from palm, rapeseed, soybean, jatropha, chicken fat, and tallow. Park et al. [29] showed that the total unsaturated FAME content can be used to predict the resulting CFPP from mixtures of palm, rapeseed, and soybean methyl esters. Sarin et al. [22] found evidence of the dependence of the CFPP on the total unsaturated FAME content and palmitic acid methyl ester (C16:0) content of sample blends of palm, jatropha, and pongamia methyl esters. Ramos et al. [30] identified two factors affecting long-chain saturated components of neat vegetable oil methyl esters derived from palm, olive, peanut, rapeseed, grape, sunflower, almond, and corn oils used in the prediction of the CFPP. These factors, which take into account individual saturated FAME components from C16:0 to C24:0, indicate a large influence of chain length. These regression models have been shown to accurately predict the CFPP of neat biodiesels [30] and of palm–soybean and sunflower–rapeseed methyl ester mixtures [31].

Although the above studies attempted to determine the relationship between CFPPs and FAME profiles, some of the models they propose are valid only for certain combinations of feedstock oils. For example, Sharafutdinov et al. [31] demonstrated that Moser’s correlation, which predicts a value of −4 °C, [21], does not successfully predict the CFPP of a biodiesel mixture of 50% sunflower and 50% rapeseed (the actual CFPP of which is −8 °C). Additionally, Park’s correlation [29] underestimated the CFPP of 100% rapeseed methyl ester (which has a CFPP of −8 °C), giving a value of −15.3 °C. Correlation models that consider only the total amounts of saturated or unsaturated FAMEs may incur significant errors with vegetable oils having a high content of short-chain saturated fatty acids (C12:0 and C14:0), such as coconut and babaçu oils, because the MPs of C12:0 and C14:0 are significantly lower than those of long-chain saturated FAME compounds. Consequently, Serrano et al. [32] examined the influence of the chain length and the degree of saturation on the CFPP of vegetable oil mixtures (palm, soybean, rapeseed, and high oleic (HO) sunflower) and low-molecular-weight oil (coconut and babaçu) methyl esters. They used the total content of saturated FAME consisting of short-chain and long-chain groups and the total unsaturated FAME content as factors.

As the cold flow property in terms of the CFPP is mainly dependent on the fatty acid profile of the feedstock, the present study aimed to determine the overall effect of biodiesel feedstock blending on the CFPP. This work examined the relationship between the CFPP and the fatty acid profile for 303 methyl ester blends obtained from 125 biodiesel blends derived from transesterified edible oils (palm, soybean, canola, and sunflower) and non-edible oils (jatropha, oleic acid, soapnut, and tung), as well as 178 biodiesel blends from previous studies on CFPP correlation