Fuel 171 (2016) 94–100

Contents lists available at ScienceDirect

Fuel

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

Thermodynamic selection of effective additives to improve the cloud point of biodiesel fuels

Masahiro Abe, Shiori Hirata, Hiroyuki Komatsu, Kazuaki Yamagiwa, Hideo Tajima *

Graduate School of Science and Technology, Niigata University, 2-8050 Ikarashi, Niigata 950-2181, Japan

HIGHLIGHTS

- A thermodynamic model was used to screen CP improvement additives for FAMEs.
- The molar mass of the additive had the most significant effect on the CP.
- The selected additives lowered the CP of model FAME mixtures.
- These additives also improved the CP of FAMEs derived from cooking oils.

ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form 18 November 2015
Accepted 24 December 2015
Available online 31 December 2015

Keywords:
Biodiesel fuel
Crystallization
Cloud point
Low temperature flow property
Thermodynamic method
Improver

ABSTRACT

We assessed a simple thermodynamic model, with the aim of identifying biodiesel fuel cloud point (CP) improving additives, by predicting the CP values of fatty acid methyl esters with additives. The results showed that the molar mass of the additive has a significant effect in terms of improving the CP; the melting point and fusion enthalpy of the additive, however, produce lesser effects. On the basis of these results, we selected the additives tert-butyl alcohol, 2-butanol, cineol, 2-decanol, 2-decanone and oleyl alcohol, and examined their effects on the CP of a model biodiesel fuel (a methyl oleate and methyl palmitate mixture). The same trials were carried out using fatty acid methyl ester mixtures derived from commercial cooking oils. As predicted, the selected test additives decreased the sample CP values, with the optimum reduction obtained when using 10 wt.% of the additive. The results demonstrate that additives capable of improving the CP can be readily screened using a simple thermodynamic model.

1. Introduction

For some time now, fatty acid methyl esters (FAMEs) have received significant attention as alternative light oils and biomass fuels (also known as biodiesel fuels). In fact, the production and use of FAMEs are both increasing yearly. Recently, various edible vegetable oils and a number of inedible vegetable oils, waste oils, animal fats and algae oils have been used as the raw materials for the synthesis of FAMEs [1–7].

Among the disadvantages of biodiesel fuel made from FAMEs are the poor flow properties that result primarily from the presence of saturated FAMEs at lower temperatures. The flow properties of FAME mixtures may be improved through several means, including the use of a light oil blend, reduced-pressure distillation, winterization, and treatment with additives. Additives are often found in petroleum diesel fuels, where they are known as cold flow improvers, and they are a convenient and economical way to improve flow properties. As an example, additives derived from vegetable oils can noticeably decrease the pour point (PP) of biodiesel fuel [8,9]. Polymeric improvers can also reduce the PP and the cold filter plugging point (CFPP) of biodiesel made from waste cooking oils [4,10]. The use of additives, however, does not significantly decrease the crystallization temperature of the biodiesel fuel, known as the cloud point (CP).

In neat biodiesel, both the PP and CFPP are typically lower than the CP, and it has been reported, based on empirical studies, that the PP and CFPP are both functions of the CP [11]. Therefore, a prediction of the CP will allow for an estimate of the PP and CFPP values. Many studies have found that the CP of FAME mixtures may be theoretically estimated on the basis of several assumptions [11–14]. According to these studies, the ideal solution of the Hildebrand equation readily provides an approximate prediction of the CP [14]. If the theoretical equation for the crystallization temperature of

* Corresponding author. Tel.: +81 25 262 7277.
E-mail address: h_tajima@eng.niigata-u.ac.jp (H. Tajima).

http://dx.doi.org/10.1016/j.fuel.2015.12.053
0016-2361/

FAME mixtures is also applicable to FAME-additive mixture systems, the selection of CP-improving additives may be possible, based on specific additive properties.

The aim of the present study was to identify additives that effectively improve the CP values of FAMEs by using a thermodynamic model based on solid–liquid equilibrium, and to test the selected additives in conjunction with FAMEs derived from commercial cooking oils.

2. Material and methods

2.1. Preparation of biodiesel fuel

Methyl oleate (>60.0%) and methyl palmitate (>95.0%) were purchased from Wako Pure Chemical Industry, Ltd. (Osaka, Japan) and used without further purification. We blended the methyl oleate and methyl palmitate to prepare the FAME mixture we used as a pseudo-biodiesel fuel. In this process, the methyl palmitate was melted using a mantle heater set at approximately 333 K, after which the molten methyl palmitate and methyl oleate were quickly blended. The resulting FAME mixture was further agitated on a hotplate stirrer and then allowed to sit at room temperature for 1 day. The FAME mixtures were formulated to contain specific weight percentages of saturated FAME: Samples 1 and 2 contained 12.9 and 44.5 wt.% methyl palmitate, respectively. The trial concentrations of methyl palmitate, 12.9 wt.% in low concentration case and 44.5 wt.% in high concentration case, were determined from the ratio of methyl palmitate to methyl oleate contents in rapeseed oil and olive oil, and palm oil in reference respectively [15]. The selected additives were combined with the FAMEs and the resulting FAME-additive mixture was agitated on a hotplate stirrer.

In this study, we also prepared FAME mixtures derived from cooking oils through a transesterification reaction using canola (Ajinomoto Co. Inc., Tokyo, Japan), olive (Garcia de la Cruz, Toledo, Spain) or soybean oils (Ajinomoto Co. Inc.), methanol (>99.8%, Wako Pure Chemical Industry, Ltd.) and KOH (>85.0%, Wako Pure Chemical Industry, Ltd.) as the alkaline catalyst. The raw oil was heated to 333 K in a water bath, after which a portion of KOH in methanol was added (KOH:methanol:oil mass ratio = 1:15:34) and the mixture was agitated for 1 h. The resulting mixture was then washed with water several times, filtered, and dried under vacuum. Molecular sieves (3 Å) (Wako Pure Chemical Industry, Ltd.) were subsequently added to the FAME mixture to ensure that it remained dry. The sample was stored at room temperature prior to use.

2.2. Analysis of samples

The cloud point (CP) values of the samples were determined by visually observing the extent of sample crystallization during cooling at $1-K$ intervals. The CP test apparatus consisted of a low temperature circulating bath and a platinum resistance temperature measurement device. This apparatus closely matched that required by the Japanese Industrial Standard (JIS) K2269 [16]. The bath temperature was set at 273, 255 or 243 K depending on the predicted sample CP. The accuracy of the test apparatus was confirmed by measuring the CP of a light oil standard (CP = 269 K, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) and of dodecane (m.p. = 263.6 K, >99.0%, Wako Pure Chemical Industry, Ltd.) before measuring the FAME samples.

The FAME contents of the samples were assessed using a gas chromatograph (GC-17A, Shimadzu) equipped with an Rtx-Wax column (30 m × 0.25 mm I.D., 0.25 μm film) and an FID detector. The FAME concentrations were calculated based on the internal standard method in a manner similar to that provided in the EN Standard (EN 14013) and in JIS K2390 [17], using hexadecane (>99.0%, Wako Pure Chemical Industry, Ltd.) as the internal standard. The validity of the internal standard was confirmed by comparing the hexadecane peak area with that of other internal standard materials (methyl heptadecanoate (>99.0%, Sigma–Aldrich Co. Llc., St Louis, MO, USA) and methyl nonadecanoate (>98.0%, Sigma–Aldrich Co. Llc.)), thus determining a correction factor for hexadecane. The accuracy of the correction factor was confirmed by analyzing a standard FAME mixture (RM-6, Sigma–Aldrich Co. Llc.).

2.3. Thermodynamic prediction of cloud point

As noted, the CP of FAME mixtures, defined as the temperature at which crystals begin to form in a liquid sample, has been explained based on the solid–liquid equilibrium [11,12,14]. Generally, the activity coefficient (γ_i^L) of the liquid phase is an important factor in the crystallization behavior of a non-ideal liquid. Imahara et al. [12] proposed a simple model in which the activity coefficient is unity $(\gamma_i^L = 1)$. The CP values predicted by this model correspond well with the experimentally determined CP values of FAMEs, since the non-ideality of the liquid phase $(\gamma_i^L \neq 1)$ is negligible at atmospheric pressure in the case of FAMEs [13]. Because the CP may be approximately predicted by assuming that a FAME mixture is an ideal solution, crystallization behavior in FAME mixtures may be estimated based on the FAME composition (x_i), fusion enthalpy $\Delta H_{m,i}$ and melting point ($T_{m,i}$) [14]. In this study, therefore, the simple crystallization model was applied to the prediction of CP values for the FAME-additive systems. In this model, each component i in the FAME-additive system will begin to crystallize at a temperature, T, predicted by the equation

$$T = T_{m,i} \Big/ \left(1 - \frac{RT_{m,i}}{\Delta H_{m,i}} \ln x_i\right). \quad (1)$$

The value of T was calculated for each component in this manner. The highest T was taken as the crystallization temperature of the system. According to the definition of CP, this temperature can be converted into CP. Because the FAME composition (x_i) is a function of molar mass (M_i), the CP of the FAME-additive system was simulated using three parameters: molar mass (M_i), melting point ($T_{m,i}$) and fusion enthalpy ($\Delta H_{m,i}$). The following test additives were selected according to the simulation results: tert-butyl alcohol (>98%, Wako Pure Chemical Industry, Ltd.), 2-butanol (>99%, Wako Pure Chemical Industry, Ltd.), cineole (>90%, Kanto Chemical Co., Inc., Tokyo, Japan), 2-decanol (>98%, Tokyo Chemical Industry Co., Ltd.), 2-decanone (>99%, Tokyo Chemical Industry Co., Ltd.) and oleyl alcohol (>70%, Kanto Chemical Co., Inc.). The details of this selection method are discussed below. These test additives were used without further purification and the CP values of the resulting FAME-test additive mixtures were measured.

The additives as a cold-flow improver are used in a wide range of concentration. A low additive concentration (0.1–2 wt.%) is used in a case of polymeric material because of prediction of viscosity increase [4,18,19]. On the other hand, fat derivatives, FAME derivatives and agent consist of C, H, O elements only were used as additives at higher concentration (1–20 wt.%) [8,9,20]. Dunn et al. used 0.5, 1, 2, 5, 10, 25 and 50 wt.% of the branched-chain FAME as improver [21]. In this study, the additives consist of C, H, O elements only, and thus the agents meet the letter criterion. According to the previous research, the concentration of additives was chosen at 5 wt.% and 10 wt.%.