Full Length Article

Modeling viscosity of butanol and ethanol blends with diesel and biodiesel fuels

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HIGHLIGHTS

- Alcohols in diesel or biodiesel cause a strong non-linear decrease of viscosity.
- Viscosity of all butanol-diesel blends remains within a permissible range.
- Grunberg-Nissan equation fits well ethanol-biodiesel and butanol blends viscosity.
- Interaction parameters are proposed and related to polarity of the species involved.
- A 3-parameter model is needed to fit viscosity of gel-like ethanol-diesel blends.

ARTICLE INFO

ABSTRACT

Kinematic viscosities were measured for ethanol and n-butanol blends with diesel and biodiesel fuels, showing that increasing alcohol contents contributed to a non-linear decrease in the viscosity. Only ethanol blends with alcohol content lower than 36% (volume basis) fulfill diesel fuel quality standard, whereas the whole range of n-butanol blends fulfills this standard. Generalized correlations were tested for the estimation of the viscosity of ethanol and butanol blends with diesel and biodiesel fuels in the whole range of alcohol contents. Interaction coefficients were required for an adequate estimation due to strong molecular interactions. Two-parameter equations did not improve, and three-parameter equations improved only slightly, the estimations with respect to the Grunberg-Nissan equation, with only one interaction coefficient. This interaction coefficient decreases when the number of carbon atoms in the n-alcohol molecule increases for both diesel blends and biodiesel blends because the non-polar part of the molecule becomes dominant against the polar hydroxyl group. Original correlations were proposed for the modeling of the interaction coefficient in alcohol-diesel and alcohol biodiesel fuels as a function of the carbon number of the alcohol. Other n-alcohols (methanol, propanol and n-pentanol) were also tested to extend the validity of the correlation proposed. These correlations are useful for the design of transport equipment or pipelines in a scenario where alcohols may constitute a fuel component in diesel blends. Also the decision on feasible blends that fulfill the narrow viscosity ranges set by fuel standards (to avoid loss of vehicle operability) will benefit from the proposed correlations.

1. Introduction

Oxygenated fuels such as alcohols are recognized as an effective way to reduce soot emissions and to improve the combustion process [1,2]. Among the alcohols, ethanol has been suggested as one of the most promising blending components for diesel fuel. However, the higher viscosity of butanol with respect to ethanol, together with its higher heating value, better miscibility and lower hydrophilic nature, suggest that n-butanol is a better renewable component than ethanol in diesel blends.

Alcohols have been widely used in chemical and petroleum industries. Therefore, accurate and reliable knowledge of their viscosity is required for the design of transport equipment or pipelines [3]. In a diesel engine, the liquid fuel is sprayed into compressed air and atomized into small droplets near the nozzle exit. The viscosity affects the atomization of a fuel when it is injected into the combustion chamber, the size of the fuel droplets, the formation of engine emissions and deposits [4,5] and the lubricity of the fuel [6].

Fuels with high viscosity tend to form larger droplets in the injection which leads to a poor fuel atomization that increases the spray tip penetration and decreases the spray angle, deriving into a poor combustion. This finally increases the exhaust emissions and smoke opacity, and tends to form engine deposits [7]. Moreover, long-term durability problems may be related to the use of high viscosity fuels, and carbon deposits may dilute in the engine lubricant leading to engine damage. Also, high-viscosity fuels require more energy in the fuel pump and increase wear in the injection system [8]. At low temperature, filter plugging problems may occur because the viscosity increases with decreasing temperature [9]. On the contrary, fuels with excessively low viscosity may not provide sufficient lubrication for the injection system leading to greater pump and injector leakage, reducing maximum fuel delivery, and thus decreasing power output [7]. The addition of alcohol (ethanol or butanol) to diesel reduces fuel viscosity. However, it can be compensated by adding biodiesel, which is likely to yield the viscosity close to that of diesel fuel [10].

Generalized correlations for the prediction of the viscosity of liquid mixtures are needed for the design of combustion equipment. If the viscosity of hydrocarbon blends is to be predicted, the interaction between components can usually be considered as negligible. In these cases, it can be assumed that the viscosity is additive and it can be modeled through ideal additivity. In the case of biodiesel fuels, small interaction coefficients have been used to account for the interactions between methyl esters [11] and the same occurs for diesel-biodiesel blends [4,12,13]. However, for alcohol blends with diesel and biodiesel fuels, species interact strongly between them and interaction parameters obtained from experimental data are needed to correct the ideal model [14]. For this reason, in this study, the viscosity of butanol and ethanol blends with diesel and biodiesel fuels have been measured and modeled using the correlations proposed by Arrhenius [15], Kendall-Monroe [16], Bingham [17], Grunberg-Nissan [18] and McAllister [19]. Other n-alcohols were also tested to propose a correlation for the interaction coefficient of the Grunberg-Nissan equation.

2. Experimental procedure and fuels

2.1. Fuel properties and blends

The main characteristics of pure alcohols and reference fuels (diesel and biodiesel) are shown in Table 1.

Diesel fuel used for this study was supplied by Repsol (Madrid, Spain) and it follows the European standard EN 590 [27]. It has no oxygen content and its main properties fall in the range of most of the diesel fuels supplied by petrol stations in Europe in winter. The biodiesel fuel was donated by Bio Oils (Huelva, Spain). It was produced from soybean oil (around 80%) and palm oil (around 20%) and it fulfills the European standard EN 14214 [28]. The methyl ester profile of the biodiesel fuel tested is shown in Table 2. Its saturated-ester content amounts 20.64%, which is not far from an average saturation content of biodiesel fuels used in Europe and

the iodine number amounts 119 which is slightly below the upper limit established in standard EN 14214 [28]. In this table the number of carbon atoms of the acid chain (n) and the number of double bonds (db) is indicated. Although both diesel and biodiesel fuels, as any other commercial fuel, are batch-dependent, they were selected to represent the typical winter diesel and biodiesel fuels used in Europe to be further blended in order to comply with the renewable energy targets in European transport. Butanol was supplied by Green Biologics Ltd., as a member of the Consortium of ButaNexT Project (see aknowledgements) and methanol, ethanol, propanol and pentanol were purchased from PanReac AppliChem. All the properties were measured in the authors' laboratory except purities (for alcohols) and mono-, di- and triglycerides, and glycerol contents (for the biodiesel fuel), which were measured by the supplying companies.

For this study, blends with diesel and biodiesel as reference fuels have been tested. Diesel blends with alcohol (ethanol or n-butanol) at 2.5%, 5%, 7.5%, 10%, 15%, 20%, 30%, 40%, 50%, 75% (volume basis), and biodiesel blends with alcohol (ethanol or n-butanol) at 2.5%, 5%, 10%, 20%, 40% and 75% (volume basis) were tested. Most of the blends were defined with low alcohol content because the low cetane number of high alcohol-content blends is unfeasible in diesel engines. No stabilizing additives were used in any of the blends. The use of additives would be expected to modify the viscosity trends observed hereinafter as far as they improve the miscibility of the blends.

Furthermore, to obtain an equation for modeling the viscosity of alcohol-biodiesel blends, additional biodiesel blends with other n-alcohols (methanol, propanol and n-pentanol) at 2.5%, 5%, 10%, 20%, 40%, 75%, 90% and 95% (volume basis) were tested.

2.2. Equipment

The kinematic viscosity of the blends was measured at 40 °C following the EN ISO 3104 standard. Every experiment was replicated twice, and the standard desviation was ±0.008 cSt. Cannon-Fenske viscosimeters were used in order to measure the kinematic viscosity of blends. The temperature was maintained at 40 °C, according to standard EN ISO 3104, for all samples using a thermostatted bath Tamson TV 2000 purchased from Fisher Scientific.

2.3. Equations for viscosity modeling

The equations used for modeling the viscosity of the liquid mixtures tested are summarized in Table 3, where x_i, z_i, ρ_i and υ_i are the mole fraction, volume fraction, density and kinematic viscosity, respectively, of component i (i = 1 or 2) in the binary blends.

Linear, Arrhenius, Kendall-Monroe and Bingham equations predict the viscosity of binary mixtures without using any adjustable parameter. Linear equation is the application of the Kay's mixing rule (i.e., mole fraction average) to the dynamic viscosity. Arrhenius equation is a logarithmic-scale average of the dynamic viscosities. Kendall-Monroe equation estimates the viscosity as a