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Predicting the viscosity of diesel/biodiesel blends

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HIGHLIGHTS

- Test of 12 models for predicting viscosity of petroleum/biodiesel blends.
- The majority of existing models did not perform well on oxygenates.
- Six models were modified and 3 new were developed.
- All modified and developed models produced $R^2 \geq 99.6\%$.

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ABSTRACT

Viscosity is one of the most important properties of biodiesel and conventional diesel fuels derived from petroleum. A large number of empirical correlations exist in the literature, which predict the blended viscosity of binary oil mixtures but they have not been proved for oil/oxygenate blends. In this work, twelve mixing rules, which were developed for predicting the viscosity of petroleum based fuels, were tested for their predicting accuracy in oxygenated blends. In order to test these models in diesel/biodiesel blends with adequate experimental data, three different diesel fuels and seven biodiesels were blended in eleven different volume fractions, giving 231 samples, whose viscosities were experimentally measured. The majority of the mixing rules tested, produced similar results and predicted the viscosities with poor accuracy, with just one of them exhibiting satisfactory accuracy. In an attempt to improve the predictions of these equations, some of the mixing rules were modified by using alternative forms or new constants. The modified equations gave reasonable predictions for the viscosities of the oxygenated mixtures. Two new equations were developed to estimate the constant in Lederer's model, to avoid the necessity of further experimental data that the original model required for the prediction of the viscosity. The results were in closer agreement with the experimental data and the accuracy was of the same order of magnitude for all the modified equations, $R^2 \geq 99.6\%$. The most accurate estimations were given by the Modified Shu and Barrufet & Setiadarma's mixing rules, and one more rule which was developed in this study based on Grunberg and Nissan's model.

1. Introduction

The introduction of biodiesel into the automotive diesel fuel in almost all over the world, brought new challenges in almost every aspect of the fuel's specifications. Biodiesel, which is produced through the transesterification of vegetable oils, edible or non-edible, used frying oils and animal fats, is one of the environmentally friendly, almost free of sulphur, non-toxic alternative biofuels. It is completely miscible with diesel and can be used neat or blended with petroleum diesel fuels in diesel engines without modifications [1–7].

Biodiesel fuels are generally more viscous than diesel fuels. Kinematic viscosity is one of the most important parameters among the biodiesel properties because of the effect on engine performance and emission characteristics. The viscosity of the fuel affects the quality of the atomization process, the size of fuel droplets and the in-cylinder penetration of the fuel spray [1,8,9]. High viscosity causes the mixture to burn lean in the engine as fuel moves slowly through the fuel filter and fuel lines and causes poor fuel atomization and low volatility, leading to incomplete combustion, severe engine deposits, injector coking and piston ring sticking [10–15]. It also deteriorates the cold startability of diesel engine as the viscosity increases when the temperature decreases [2,10–17].

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Nomenclature

x_v	volume fraction
x_w	mass fraction
VBI	viscosity blending index
COME	corn oil methyl esters
JCME	Jatropha curcas methyl esters
POME	pomace oil methyl esters
SEME	sesame oil methyl esters
SOME	soy oil methyl esters
SUNME	sunflower oil methyl esters
WFOME	waste frying oil methyl esters

Greek symbols

v	kinematic viscosity
ρ	density
σ	standard deviation

Constants

a	l
b	m
c	n
e	q
g	s
k_i	

Subscripts

1	heavy component
2	light component
blend	blend
B	Bingham
C	Cragoe
KM	Kendall & Monroe
exp	experimental
pr	predicted

Numerous empirical correlations have been developed, which relate various performance parameters, such as ester profile, with the viscosity of biodiesel. The effect on viscosity of blending biodiesel and conventional diesel fuel was investigated by scientists, and equations were derived that allow the calculation of the viscosity of such blends [18,19]. These equations can predict the viscosity of the blend using biodiesel's molar and volume fraction and temperature [1,8–10,20–25]. Early observations made evident that for the prediction of the viscosity of petroleum mixtures the simple linear law was never exactly obeyed and the experimental/measured viscosities were uniformly lower than those obtained by the linear law. Generally, the greater the difference in the viscosities of the two components, the greater the error. The first proposed formula was developed by Arrhenius in 1887 [26,27]. Then Bingham discarded the prevailing assumption that viscosities are additive and proposed another formula [28]. Later, an exponent equation based on measurements of molar fractions was recommended by Kendal and Monroe [29]. Subsequently, more researchers proposed more complex rules correlating the viscosity of blends with the viscosity of pure components [26,27,30–32]. However, it is not known if all these rules apply to the prediction of the viscosity of diesel and biodiesel mixtures.

In this study, the most widely used expressions in the literature predicting the viscosity of oil mixtures were examined, in order to establish whether they can predict the blended viscosity of mixtures of oils/biodiesel. Twelve equations were examined and blends were prepared for three diesel fuels and seven different biodiesels for eleven biodiesel volume fractions, giving an overall number of 231 fuels tested. The results showed poor predictions in most cases when the oxygenates were used, and the equations were modified or new equations were proposed to improve the accuracy.

2. Experimental

2.1. Fuels

The main variables used for the majority of the equations examined in these series of experiments, were fuel density and viscosity. Three different commercially available diesel fuels were used, Table 1. Also, seven biodiesel fuels were used (SUNME, COME, POME, SOME, SEME, JCME and WFOME) whose properties were experimentally measured, Table 2.

All diesel fuels used were automotive diesel fuels and contained no biodiesel. All biodiesels, except one, were prepared in the laboratory. The method applied was the conversion of triglycerides to Fatty Acid Methyl Esters (FAME), with basic transesterification in the presence of methanol and sodium methoxide as catalyst. In the case of two feedstocks, jatropha curcas oil and the waste cooking oil, pretreatment was needed because the acid number of these oils was greater than 1 mg KOH/g. This step consisted of acidic esterification with sulfuric acid for the conversion of free fatty acids (FFAs) to FAME. The only commercial biodiesel was the one produced by sunflower oil (SUNME), which was obtained from a local biodiesel producer.

A series of blends was prepared by blending each diesel with all biodiesels. The percentage of biodiesel added in the diesel fuel, varied from 5, 7, 10, 20, 30, 40, 50, 60, 70, 80 and up to 90% by volume. In this manner 11 blends were prepared for each diesel fuel, giving overall 3×11 base blends for the three diesel fuels used and each biodiesel. Since 7 different biodiesels were used, a matrix of $11 \times 3 \times 7$ blends was prepared, giving an overall number of 231 fuels tested, Table 3. The notation BX represents a blend that contains X% v/v biodiesel. To facilitate the discussion which follows, twenty-one (21) series of diesel/biodiesel blends were defined, and each series consisted of 11 biodiesel fractions.

2.2. Measurement of viscosity

In this study, the Stabinger Viscometer (SVM 3000) was used to determine the viscosity of the samples, Table 3, according to ASTM D 7042 method [33]. It requires a minimum of 4 ml of sample for the analysis and provides the values of density (EN ISO 12185) and dynamic viscosity at any temperature. The device can also calculate the value of kinematic viscosity by dividing the dynamic viscosity by the density. The density was measured at 15 °C and the viscosity at 40 °C.

2.3. Accuracy of the experimental data

Numerous measurements took place in order to verify that the experimental values of density and viscosity were adequate. To demonstrate that the presented results ensure the required accuracy, a number of plots was prepared. Density and viscosity were plotted against the percentage of biodiesel in the blends. Fig. 1 shows the linear correlation of the density with the increased percentage of biodiesel in the blends ($R^2 > 99.9\%$) and Fig. 2