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Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition

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ABSTRACT

Biodiesel is a renewable bio-fuel derived from natural fats or vegetable oils, and it is considered as a promising alternative to substitute diesel fuels. Cetane number, viscosity, density, and higher heating value are important properties to affect the utilization of biodiesel fuels, because they are involved in the definition of fuel quality and are required as input data for predictive engine combustion models. This work presents the characterization of two biodiesel samples made from beef tallow and soybean oil through their fatty acid methyl esters (FAMEs) profile. Empirical equations were developed to estimate four physical properties of methyl esters; and an average absolute deviation (AAD) of 5.95%, 2.57%, 0.11% and 0.21% for the cetane number, kinematic viscosity, density, and higher heating value were founded. Cetane number, viscosity, and higher heating value increases because of the increase of molecular weight and these physical properties decrease as the number of double bonds increases. Unlike that of above properties, density decreases as molecular weight increases and density increases as the degree of unsaturation increases. Two general mixing rules and five biodiesel samples were used to study the influence of FAMEs over the physical properties of biodiesel. The prediction of the cetane number, kinematic viscosity, density and higher heating value of biodiesel is very close to the experimental values.

1. Introduction

Decline of available oil reserves and more stringent environmental regulations have motivated the global interest in renewable energy sources. Biodiesel is considered as an attractive alternative to replace diesel fuels. Biodiesel consists of a mixture of fatty acid alkyl esters that can be obtained from animal fats or vegetable oils, mainly by trans-esterification reactions. Biodiesel has several advantages because it is renewable, biodegradable, non-toxic, and friendly with environment. Currently, the main disadvantage could be the high costs of some types of raw materials. However, as the petroleum oil reserves become scarce, this behavior could be changed. The main differences between biodiesel and diesel are that the former usually has higher density, viscosity, cloud point and cetane number; and lower volatility, gross calorific value and sulfur content. Cetane number (ϕ), viscosity (η), density (ρ) and higher heating value (δ) are four important properties of fuels. Cetane number is widely used to evaluate the ignition quality of fuels. Viscosity and density have a direct effect on the atomization process during combustion. Higher heating value also known as the gross calorific value or gross energy is the amount of heat released during the combustion of one gram of fuel to produce CO_2 and H_2O at its initial temperature, this property is usually used to define the energy content of fuels and thereby their efficiency.

Efforts have been made to find useful methods to estimate physical properties of fatty acid methyl esters (FAMEs) from parameters related to its chemical structure. For instance, in the middle 1960s Gouw and Vlugter [1] used the Smittenberg relation to estimate the density of saturated methyl esters at 20 °C and 40 °C. Allen et al. [2] proposed empirical correlations to estimate the viscosity of saturate and unsaturated FAMEs as a quadratic function of their molecular weight. A difference comes from Krisnangkura et al. [3] who calculated the viscosity of saturated FAMEs as a function of temperature and the number of carbons that fatty acids contain. Another option for viscosity was proposed by Ceriani et al. [4] who used a group contribution methodology to estimate the viscosity of FAMEs. The Sugden's parachor method was used by Allen et al. [5] and Ejim et al. [6] to predict the surface tension of saturated and unsaturated FAMEs. Liquid heat capacity and absolute entropy at 25 °C of FAMEs was calculated by van Bommel et al. [7]. Klopfenstein, for his part, was proposed a nonlinear relationship between carbon chain length and cetane number of methyl esters [8].

On the other hand, the prediction of biodiesel properties using mixing rules has widely been studied. Allen et al. [2], Benjumea et al. [9], Goncalves et al. [10] and Krisnangkura et al. [3] were used

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Nomenclature

AD	absolute deviation
AAD	average absolute deviation
FAME	fatty acid methyl ester
M_i	molecular weight of the *i*th FAME
n	number of FAMEs
N	number of double bounds
BT	biodiesel made from beef tallow
CO	biodiesel made from corn oil
CT	biodiesel made from cottonseed oil
SB	biodiesel made from soybean oil
SF	biodiesel made from sunflower oil

Greek symbols

ϕ	cetane number
η	kinematic viscosity
ρ	density
δ	higher heating value

the Grunberg–Nissan equation to estimate the viscosity of biodiesel from their individual viscosity of FAMEs. Surface tension of biodiesel was calculated by means of the Dalton-type mass average equation by Allen et al. [5] and Shu et al. [11]. The effect which specific gravity of FAMEs has on the specific gravity of biodiesel was considered by Ejim et al. [6]. Ramos et al. [12] proved that the cetane number of biodiesel can be calculated using their fatty acid methyl composition and cetane number of FAMEs. Yuan et al. [13] suggested that biodiesel can be regarded as near-ideal solution and once the vapor pressure of each individual FAME is known, the vapor pressure of biodiesel could be calculated by a simple mixing rule.

This work was developed by the need for simple and reliably calculation methods to estimate some physical properties of bio-fuels, which could avoid experimental work, which we know it is difficult, costly, and time consuming. Thus, this paper deals with the prediction of four properties of biodiesel from their fatty acid methyl esters and the use of mixing rules. For this purpose, two biodiesel samples from beef tallow and soybean oil are characterized by gas chromatography–mass spectrometry (GC–MS) in order to obtain its FAME profile; subsequently, these FAME distributions are used to study the influence of FAMEs over the properties of biodiesel samples. In addition and taking on that a better understanding of connections between molecular structure and physical properties of FAMEs is important to establish the quality of biodiesel, our work aims to develop four new empirical correlations to estimate the cetane number, viscosity, density and higher heating value of FAMEs as a function of their molecular weight and degree of unsaturation.

2. Experimental methods

2.1. Materials

The biodiesel samples used in this study were made from beef tallow (BT) supplied by "Total Energy Services"; and from soybean oil (SB) certified and purchased by "Chevron Phillips". Because the samples were in compliance with the ASTM 6751-08a specification (only there were minor deviations in both the flash point of BS as in the total sulfur of BT), no attempt was made to purify them further. The properties of biodiesel samples are given in Table 1.

2.2. Biodiesel FAMEs characterization

Biodiesel samples studied in this work were analyzed by gas chromatography, using a 6890 Agilent Technologies device coupled to a mass detector (GC–MS) and an Agilent capillary column (HP-88; 100 m × 0.25 mm i.d. × 0.20 μm film). The FAME analysis was carried out by electron ionization mass in the full scan mode and transfer line at 250 °C, the injection temperature was 225 °C, whereas the sample volume injected was 1 μL. GC-grade helium was used as carrier gas with a flow rate of 1.2 mL/min. The oven program was given as follows: initial temperature, hold time No. 1, heating rate, final temperature and hold time No. 2 was 100 °C, 4 min, 3 °C/min, 240 °C and 15 min, respectively. In order to determine the retention times of the fatty acid methyl esters, a standard mixture of 37 FAMEs solved in methylene chloride (with a standard concentration of 30 mg/mL) was run (see Table 2 and Fig. 1). The standard sample that was used in this work has a certificate of RESTEK Co. (ISO 9001 registered quality system). Fig. 1 shows the chromatogram obtained by GC–MS of the standard with 37 FAMEs.

2.3. Cetane number measurements

The cetane number was determined by comparing its combustion characteristics in a test engine with those for blends of reference fuels of known cetane number under standard operating conditions. This is accomplished using the bracketing handwheel procedure which varies the compression ratio (handwheel reading) for the sample and each of two bracketing reference fuels to obtain a specific ignition delay permitting interpolation of cetane number in terms of handwheel reading (ASTM D 613-05 method). The measurements were carried out with a CFR F-5 equipment (cetane method diesel fuel rating unit) that was calibrated with two standard samples of low cetane number (45.5) and high cetane number (60.0) supply by Chevron Phillips. The repeatability (the difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material) and reproducibility (the difference between two single and independent results obtained by different operators working in different laboratories on similar material) were estimated approximately in ±0.9 and ±4.3, respectively. The experimental determination of this property is usually difficult and expensive, and it requires large volume of sample for testing (approximately 500 mL in the case of the ASTM 613-05 method).

2.4. Kinematic viscosity measurements

The ASTM D 445-04e was used to measure the kinematic viscosity of biodiesel. It was measured the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer at 40 °C. The repeatability and reproducibility were 0.11% and 0.65%, respectively.

2.5. Density measurements

A digital analyzer (APPAR) was used to measure the density of biodiesel at 20 °C, this equipment consisting of a U-shaped, oscillating sample tube, a system for electronic excitation, and frequency counting. The repeatability and reproducibility were ±0.0001 g/mL and ±0.0005 g/mL, respectively.