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Predicting the temperature dependent density of biodiesel–diesel–bioethanol blends

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HIGHLIGHTS

- Using two types of biodiesel, 30 blends of biodiesel–diesel–bioethanol were prepared.
- Their density values were measured in 15 steps, in the temperature range of 273.15–343.15 K.
- The density of the blends was predicted with linear mixing rules, resulting an average relative deviation of under 0.125%.
- To improve accuracy, four new models were elaborated and tested, obtaining an average relative deviation of under 0.053%.

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ABSTRACT

Density is a very important fuel property because it influences production, transportation, and distribution processes as well as all processes that take place in the internal combustion engine. Elaborating models to describe the density of biodiesel–diesel–bioethanol blends with a high content of biofuel facilitates the production of blends that comply with the standard quality requirements for density and the modeling and simulation of injection and combustion processes. For predicting density of rapeseed oil biodiesel–diesel–bioethanol and used cooking oil biodiesel–diesel–bioethanol blends, 2×15 ternary mixtures were prepared, having a maximum amount of biofuel of 30% v/v. The concentration of biodiesel and bioethanol varies between 5% and 25%, in increments of 5%. Their density values were determined in 15 steps in the temperature range of 273.15–343.15 K. Based on experimental density values of components and blends, common linear mixing rules were evaluated, obtaining an average relative deviation under 0.125% and a regression coefficient above 0.996. In order to improve accuracy, four new mixing rules with different complexities were elaborated. The temperature dependent density of components was modeled based on experimental density values and constituents composition by linear and polynomial regression, by free version of Rackett equation and by group contribution methods. The elaborated mixing rules were tested for various combinations of component densities, yielding a very good accuracy, with an average deviation of under 0.053%. Taking into account the complexity and accuracy of the elaborated models, recommendations were made regarding their uses according to their concrete applications.

1. Introduction

Biodiesel–diesel–bioethanol (B–D–E) blends have become lately the subject of intense research which targets mainly the evaluation of performance and pollution of compression ignition engines (CIEs) fueled by such blends [1–16]. Data regarding the physical and chemical properties of B–D–E blends have been published, often only compared to those of diesel fuel. Density values

Abbreviations: CIE, compression ignition engine; EN, European Standard; EU, European Union; ARD, average relative deviation; SD, standard deviation; CFD, computational fluid dynamics; FAME, fatty acid methyl ester; RME, rapeseed oil methyl ester; UCME, used cooking oil methyl ester; B–D–E, biodiesel–diesel–bioethanol; RME–D–E, rapeseed oil methyl ester–diesel–bioethanol; UCME–D–E, used cooking oil–diesel–bioethanol; LR, linear regression; PR, polynomial regressions; MLR, multiple linear regression; RaSD, Rackett equation modified by Spencer and Danner; RaSD2Exptl, Rackett equation modified by Spencer and Danner particularized with two experimental data; DIPPR105, Rackett equation modified by Daubert; GCM, group contribution method; GCVOL, group contribution method for molar volume calculation; KMR, Kay's mixing rule; KMRVol, Kay's mixing rule using volume fractions; MRMass, mixing rule using mass fractions; KMRTCVol, Kay's mixing rule with temperature compensated volume fractions.

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have been given only for temperatures of 288.15 K [1,4–5,7,13–15] or 293.15 K [6,8,9], which are recommended temperatures in quality standards for establishing the density of automotive fuels.

Density is a very important fuel property because it influences production, transportation, and distribution processes as well as all processes that take place in the internal combustion engine. Knowing the density of fuels is necessary for: designing production and manufacturing facilities for fuels – reactors, tanks, distillation units; finding the mass and volume flows through such facilities; establishing the appropriate size of transfer pumps, transfer and safety valves, etc. [17,18]. Density, together with vapor pressure, vapor diffusivity, surface tension, and liquid dynamic viscosity, influence fuel spray structure, combustion and emission characteristics, engine deposits formation, and engine behavior in cold weather conditions [19–22]. Developing reliable models for injection and combustion processes implies the accurate description of the thermo-physical characteristics of fuels, including their density [23].

The injection system of CIE introduces discrete volumes of fuel in the combustion chamber, calculated by the electronic control unit, based, among others, on the functioning conditions of the engine [24] and the temperature of the fuel [25]. For this reason, knowing the precise density of fuel allows for accurate dosage and for a correct energy consumption, because density influences the mass of the injected fuel [26] and the heating value of the fuel is often given as energy content per unit mass [24]. Density influences the air/fuel mass ratio [27], i.e. the quality of the air–fuel mixture.

Since 2002, in order to reduce pollution, the electronic control units of CIE can include a closed loop control for the quality of air–fuel mixtures, using pressure, temperature, wideband oxygen sensors, etc. [28]. In the case of these engines, knowing the exact density of the fuel becomes less important, since the quantity of fuel is calculated – together with the usual parameters – by taking into account the oxygen content of exhaust gases.

Difficulties in predicting characteristics of B–D–E are due to the diverse nature of components: diesel fuel is made of over 200 types of hydrocarbons, biodiesel of up to 25 fatty acid methyl and ethyl esters, while ethanol is a pure substance. Biodiesel density depends on the raw material of which it is made. Biodiesel density is regulated in the EU by the EN 14214 standard which states that its value must fall between 0.860 and 0.900 g mL^{-1} at 288.15 K. The same range is stated for quality standards in Australia, India, Japan, and South Africa. Biodiesel density is not regulated in the USA and Brazil. Diesel fuel density must range between 0.820 and 0.845 g mL^{-1}, in the EU; there is no standard in the USA. The EN 590 standard allows for variations during the cold season, lowering the inferior limit to 0.800 g mL^{-1}. In this case the fuel must meet all requirements imposed to diesel fuel designated for use in arctic climates and severe winters.

Ethanol characteristics, when used as a blending component for petrol, must comply with quality standard EN 15376. The same standard applies to bioethanol. Although this standard does not impose a certain value on ethanol density, regulating its purity determines a value of ethanol density close to that of the pure substance, which is 0.7938 g mL^{-1}.

For practical reasons, it is useful to predict B–D–E density by the density of its components, using the appropriate models [19]. Currently, there are several models for describing diesel–biodiesel blends density [21,23,29,30], but, to the best of our knowledge, there are no models for predicting B–D–E blends density. The aim of this work is to evaluate the models used to predict the density of fuel blends and to propose means to improve their accuracy by introducing correction terms.

2. Models for predicting the density of fuels

2.1. Models for predicting density of blends

Because the studied blends contain three components, which, in turn, are pure substances (ethanol), blends of closely related substances (biodiesel) or blends of substances having different nature (diesel fuel), identification of rules to determine the density of complex blends is important.

The most widely used method to evaluate properties of blends by the properties of their components is Kay's mixing rule, which describes the properties of blends by the concentration-weighted sum of the components properties. For density, Kay's mixing rule (KMR) is:

$$\rho_{est} = \sum_i f_i \rho_i, \tag{1}$$

where ρ_{est} is the predicted density of the blend, ρ_i is the density of component i, and f_i expressed in mass, volume or molar fraction. Eq. (1) was written to evaluate blends of components with closely related physical and chemical properties, but it was successfully used to predict density of biodiesel made of diverse raw materials based on the density of esters from its composition and the concentration of components expressed in mass [29], volume [18] or molar [31] fractions. Kay's mixing rule has also been successfully used to predict density of diesel–biodiesel blends [29]. Taking into account the quantities in Eq. (1), the correct way of expressing concentration is the volume fraction [18].

When the composition of constituents is expressed in mass fractions, the expression for predicting density of blends (MRMass) is:

$$\rho_{est} = \left(\sum_i \frac{f_i}{\rho_i} \right)^{-1}, \tag{2}$$

where f_i is the mass fraction of component i.

2.2. Models for describing density of components

For the purpose of describing the temperature dependent density of components, a significant number of mathematical models have been published, based on various entry data and valid for wider or narrower temperature ranges. Table 1 presents a summary of the most relevant methods and their applications for the constituents used in the present work.

A simple method for predicting the temperature dependent density is:

$$\rho = a_0 + a_1 \cdot T + a_2 \cdot T^2 + \cdots, \tag{3}$$

where ρ (g mL^{-1}) is the density, T (K) is the temperature, a_0 (g mL^{-1}), a_1 (g mL^{-1} T^{-1}), a_2 (g mL^{-1} T^{-2}) ... are parameters of linear (LR) or polynomial regressions (PR).

Rackett equation modified by Spencer and Danner (RaSD) represents a method to describe temperature dependent density of pure substances, based on critical properties (temperature, T_c, pressure, P_c, volume, V_c), normal boiling point, T_{nb} and acentric factor, ω. Using the appropriate mixing rules, the method can be also used for calculating entry data necessary to predict the density of pure substances blends, such as biodiesel. Data entries for these models can be predicted based on the molecular structure of the components, using numerous group contribution methods (GCM) with different degrees of accuracy, a reason for which they have been criticized. Recently, García et al. [32] have evaluated a number of GCMs in order to predict the density of 29 types of biodiesel and have recommended a combination of Marrero–Pardillo (T_{nb}, T_c

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