



A new equation of state for modeling thermodynamic properties of some fatty acids alkyl esters, methyl ester-based biodiesels and their blends



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ABSTRACT

A perturbed hard trimer chain (PHTC) equation of state (EOS) is developed for several biomaterials. This model employs a trimer expression from the statistical associating fluid theory-Trimer (SAFT-T). The performance of this model has been checked by predicting 3039 volumetric data points related biomaterials for pressures and temperature up to 210 MPa and 393 K, respectively. The average absolute deviation (AAD) of the predicted densities from the experimental ones for 3039 data points of studied biomaterials and also 407 data points of biodiesel blends were found to be 0.13% and 0.14%, respectively. Besides, the isothermal compressibility (κ_T), liquid bulk modulus (B_T), isobaric expansivity coefficients (α_P), heat capacity at constant pressure (C_P) and speed of sound (u) have been estimated by the proposed model and compared with literature data.

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1. Introduction

The main problem of using fossil resources is that they are not renewable and their availability is reducing very rapidly. In this respect, the main goal of green chemistry is to use renewable raw materials and biomass rather than fossil resources to produce new chemicals. Therefore, biodiesels can be considered for future energy sources. Biodiesel fuels are produced by adding methanol to raw materials including: rapeseed (R), soybean (S), and palm (P) oils, which results in a product comprising of a mixture of fatty acid methyl esters (FAMEs) [1–4]. The methyl ester-based biodiesels are employed for the combustion process. These materials have the non-toxicity and biodegrade ability character [5,6]. As it is well known now biodiesel fuels are more environmentally friendly, nontoxic, and biodegradable compared to diesel fuel. However, thermophysical properties of this class of fluids are scarce [7,8]. To characterize the biodiesels several thermophysical properties such as viscosity, density, and thermal conductivity must be determined. By knowing this information researchers are able to use them in

new chemical processes, such as synthesis routes, analysis methods, or purification processes, and therefore they can substitute traditional materials by biomaterials. Among aforementioned thermophysical properties of biodiesels the viscosity and density are two of the main properties which depend on the raw materials used in the biodiesel fuel production. Volumetric properties are important properties in fuel injection systems which deliver the amount of fuel to provide proper combustion. Although some experimental data for thermophysical properties of FAMEs and methyl ester-based biodiesel fuels exist, however, a review of the literature reveals that both measured and calculated thermophysical properties of biomaterials are scarce [9,10] and therefore, prediction of these properties is an important task. Under this circumstance, the development of equation of state (EOS) methods is very useful. Unlike correlations, an equation of state can be employed to predict vast relevant properties such as first and second derivatives thermophysical properties of pure materials and their mixtures.

During past years, several models have been proposed to predict thermophysical properties of biodiesels. There are several publications in the literature presenting density and viscosity data for biodiesels in wide ranges of temperatures and pressures. Najafabadi et al. [11] employed Wilson, NRTL, and the Wilson-NRF local

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composition-based models to correlate density, viscosity, and surface tension of biodiesels. Pratas et al. [12] measured densities of biodiesels and employed several group contribution approaches along with some mixing rules to predict biodiesel densities. Pratas et al. [7] applied a cubic-plus-association equation of state (CPA EOS) to model high-pressure experimental data reported with a maximum deviation of 2.5%. Perdomo and Gil-Villegas [13] used the SAFT-VR approach [14,15] to model the vapor–liquid equilibria of three fatty acid methyl esters (FAME) and thermophysical properties of biodiesel fuel blends. Besides, Schedemann et al. [16] used the volume translated Peng–Robinson (VTPR) group contribution EOS to model the densities of methyl linoleate at high pressures. Their method produced the density with relative deviations up to $\pm 7\%$. In 2009, Huber et al. [17] developed a Helmholtz-type EOS to predict thermodynamic properties of five FAMES. The model was able to predict density and speed of sound to within 0.6% and 0.4%, respectively, for temperatures up to 700 K and pressures up to 50 MPa. Finally, a group contribution method was proposed to predict speed of sound and compressibility of pure fatty acid methyl and ethyl esters with an uncertainty of 0.1% [18].

In the case of viscosity, a thermodynamic model has been proposed for determining kinematic viscosities of saturated fatty acid methyl esters (FAMES) of various chain lengths at different temperatures [19]. It was found that the linearity of the natural logarithm of viscosity-carbon number plot is limited to a narrow carbon number range. The predicted viscosities of FAMES of $C_{12:0}$ – $C_{18:0}$ were in good agreement with the experimental values. The Grunberg–Nissan equation combined with a group contribution method was used as the mixing rule to calculate viscosities of mixtures of fatty acid esters [20].

In the present study, we aim to develop a new version of a perturbed-hard-chain EOS for predicting the volumetric properties of several FAMES, FAEE, methyl ester-based biodiesels and their blends. The predicted densities of the studied systems are compared with those reported in literature [7,9,12,16,21] as well as other models [7,22].

2. Theory

In perturbation theory the Helmholtz free energy, A of the system is expanded in the inverse temperature around that of a reference system whose thermodynamic structural properties are known. The first-order expansion of the Helmholtz free energy is of

$$\left(\frac{A}{Nk_B T}\right) = \left(\frac{A^{H3}}{Nk_B T}\right)_0 + \left(\frac{A^{disp.}}{Nk_B T}\right)_1 \quad (2)$$

where, subscripts 0 and 1 refer to the hard-trimer-chain reference system (A^{H3}) and the perturbation part arising from the dispersion forces ($A^{disp.}$), respectively.

The compressibility factor of PHTC EOS may be obtained by differentiating the corresponding Helmholtz free energy term with respect to the density or packing fraction, η :

$$Z^{PHTC} = \frac{\eta}{Nk_B T} \left(\frac{\partial A}{\partial \eta}\right) \quad (3)$$

where, Z^{PHTC} represents the hard-chain reference system perturbed by the long-range attraction ($Z^{Pert.}$) for the representation of the attractive forces.

2.1. Perturbed hard-trimer-chain equation of state

Based on the above-mentioned approach, the general frame of the proposed PHTC EOS can be derived in terms of the compressibility factors comprising the hard-trimer-chain (Z^{H3}) reference system and a perturbation part ($Z^{Pert.}$) as follows:

$$Z^{PHTC} = \left(\frac{P}{\rho k_B T}\right)^{PHTC} = Z^{H3} + Z^{Pert.} \quad (4)$$

Where P is the pressure, ρ is the number (molar) density, $k_B T$ is the thermal energy per molecule. The reference EOS for the hard-sphere long-chain molecules based on the trimer hard chain term is as follows [23]:

$$Z^{H3} = \left(\frac{P}{\rho k_B T}\right)^{H3} = 3 \left(1 + b \rho g_{MV}^{HS}(\sigma^+)\right) - 2 \left\{ 1 + \eta \frac{\partial \ln g_{MV}^{HS}(\sigma^+)}{\partial \eta} \right\} \quad (5)$$

Here, $g_{MV}^{HS}(\sigma^+)$ denotes the RDF of hard-spheres at contact which is developed by Malijevsky and Veverka (MV) [24]. The exact expression can be evaluated from the general relationship:

$$g_{MV}^{HS}(\sigma^+) = \frac{Z_{MV}^{HS} - 1}{4\eta} = \frac{(1 - 0.444\eta + 0.66108\eta^2 - 0.20373\eta^3 - 0.081225\eta^4 + 0.0769\eta^5)}{(1 + 0.0560\eta + 0.5979\eta^2 + 0.3076\eta^3)(1 - \eta)^3} \quad (6)$$

the form:

$$\left(\frac{A}{Nk_B T}\right) = \left(\frac{A_0}{Nk_B T}\right) + \left(\frac{A_1}{Nk_B T}\right) \quad (1)$$

where, A is the Helmholtz free energy, A_0 is the Helmholtz free energy of the hard-chain reference system and A_1 is the first-order perturbation term for the Helmholtz free energy. N is the number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature. A_0 is derived from knowledge of the equation of state and the radial distribution function (RDF) of the reference fluid.

The PHTC EOS in terms of the Helmholtz free energy is given by:

Where, η is the packing fraction of hard-core-chain defined as:

$$\eta = \frac{m\pi\rho\sigma^3}{6} \quad (7)$$

In Eq. (7), m is the chain-length. b , the van der Waals co-volume, is theoretically related to the hard-core diameter by the following equation:

$$b = \frac{2\pi\sigma^3}{3} \quad (8)$$

The second term in the right hand of Eq. (4) represents an attractive part of the van der Waals equation of state which is

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