Fluid Phase Equilibria 389 (2015) 55–63

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Equation of state modeling for the vapor pressure of biodiesel fuels

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 11 December 2014
Accepted 31 December 2014
Available online 5 January 2015

Keywords:
Biodiesel fuels
Fatty acid methyl ester
Vapor pressure
Heat capacity
Cubic equation of state modeling

ABSTRACT

The vapor pressure and liquid heat capacity of seven biodiesel fuels and its components (fatty acid methyl esters – FAMEs) were modeled using the advance Peng–Robinson equation of state. The dataset used for the modeling was obtained from the literature and included FAME properties and the composition, vapor pressure, and liquid heat capacity of the biodiesel fuels from different sources at temperatures from 50 to 130 °C and −30 to 75 °C, respectively. New values for the critical properties and acentric factor of FAMEs are introduced as well as new models for the ideal gas heat capacity for the FAMEs. The average AARD is 12% for vapor pressure and 3% for liquid heat capacity.

1. Introduction

Biodiesel fuels constitute one of the most promising alternatives to supplement or reduce petroleum diesel (petro-diesel) usage. They are renewable, non-mutagenic, non-carcinogenic, biodegradable fuels that can be domestically produced. Biodiesel fuels are refined mixtures of esters produced by the transesterification of fatty acids from vegetable oil and animal fat (fatty acid methyl esters or FAMEs for short). These fuels can be used directly or blended with petro-diesel to improve lubricity without adding any sulfur. These fuels may also improve engine firing due to their oxygen content [1–6].

The measurement and prediction of bio-diesel properties are required for their effective commercial use. One important property for the quality control of biodiesel fuels and their blends is volatility, which is directly related to the vapor pressure of their individual constituent compounds [2]. For instance, vapor pressure is used to calculate the latent heat in order to compare rates of vaporization and injection characteristics with other fuels. Heat capacity is another important thermo-physical property used to characterize biodiesel for fuel blending with petro-diesel and is directly related to the vapor pressure.

Yuan et al. [7] modeled the vapor pressure data of three different biodiesel fuels at temperatures above 215 °C [1,2]. They assumed that biodiesel fuels were ideal mixtures of their constituent FAMEs. They fitted the vapor pressure of the individual FAMEs with the Antoine equation and predicted the vapor pressures of the biodiesel fuels using Raoult's law. However, the prediction of vapor pressures at lower temperatures requires extrapolation using the fitted Antoine equations and the accuracy of the extrapolation is unknown.

Castellanos Diaz et al. [8] modeled the vapor pressure of several biodiesel fuels at temperatures from 50 to 130 °C using Raoult's law. They modeled the FAMEs vapor pressure using the Cox equation and constrained the equation parameters to also match the liquid heat capacities. They demonstrated that more accurate vapor pressure fits were obtained when calorimetric data are included in the optimization function used to determine the vapor pressure equation parameters. They also proposed new equations for calculating the vapor pressure and liquid heat capacities of FAMEs.

Experimental data for the liquid heat capacity of biodiesel fuels are also scarce and, in most cases, are available only for specific biodiesel fuel sources. Conceiçao et al. [3] presented liquid heat capacity data from thermo-gravimetric methods for castor oil-based biodiesel fuel at temperatures between 55 and 125 °C. The same methodology was applied by Narvaez et al. [9] for palm oil-based biodiesel fuel at temperatures ranging from 30 to 100 °C. Dzida and Prusakiewicz [10] measured the liquid heat capacity of rapeseed oil-based biodiesel fuel using differential scanning calorimetry at temperatures between 20 and 45 °C. No modeling was included in any of these cases.

The model developed by Castellanos Diaz et al. [8] based on vapor pressure fitting using relatively simple equations is sufficient for calculations where only vapor pressure, enthalpy of vaporization and liquid heat capacity values are required. However, a more comprehensive approach is to model vapor pressure of FAMEs and

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http://dx.doi.org/10.1016/j.fluid.2014.12.050
0378-3812/

Nomenclature

$a_{PV,i}$	Adjustable parameter for Eq. (5)
ΔC_P	Phase transition heat capacity kJ/kmol K
$C_{P,L}$	Liquid heat capacity kJ/kmol K
C_P^0	Ideal gas heat capacity kJ/kmol K
C_P^{Res}	Residual heat capacity kJ/kmol K
J	Optimization objective function
MW	Molecular mass Kg/kmol
N_{UC}	Number of unsaturated carbon
P, P^V	Pressure, vapor pressure kPa
T	Temperature °C
T_{Ref}	Reference temperature
x_i	Mole fraction
α	Similarity function, Eq. (13)
ν	Stoichiometric value of an element in a compound

biodiesel fuels using an equation of state (EoS), since an EoS can also be used for phase equilibrium calculations in processes with additional components and/or processing stages and also provides a consistent structure to introduce pressure effects on phase equilibrium calculations. An equation of state model is also more convenient for most commercial process simulation software.

The purpose of this study is to develop an equation of state (EoS) model for the representation of vapor pressures and liquid heat capacities of fatty acid methyl esters and biodiesel fuels. The biodiesels were characterized as mixtures of FAMEs with a known composition. The first step was to characterize the FAMEs. Their critical properties were determined from literature data or correlations and then tuned to fit the equation of state model to measured FAME vapor pressures and enthalpies. Next, the ideal heat capacities of the FAMEs were calculated and the liquid heat capacity of FAMEs predicted. Finally, the vapor pressure and liquid heat capacity of biodiesels was determined. The vapor pressure and heat capacity datasets used to develop the model were taken from the literature and are summarized below. The equation of state model and optimization methodology are then presented followed by a discussion of the results.

Table 2
Temperature range of vapor pressure and heat capacity data for selected biodiesel fuels [8].

Biodiesel fuels source	Code	Vapor pressure	Liquid heat capacity
Canola (South Alberta)	CB-01	60–196 °C	13–55 °C
Canola (Saskatchewan)	I-25	–	12–55 °C
Soy (Sunrise, US)	SB100	–	14–55 °C
Soy (Mountain Gold, US)	MGB100	140 °C	10–55 °C
Rapeseed (Europe)	S102550	80–110 °C	13–55 °C
Palm (Europe)	S090824	70–100 °C	23–55 °C
Coconut (Europe)	S070717	95–125 °C	10–55 °C

2. Datasets

2.1. FAMEs dataset

Eighteen FAMEs ranging in carbon number from 6 to 22 were examined, as presented in Table 1. The vapor pressure dataset [11] ranges in temperature from 25 to 300 °C whereas liquid heat capacity data range from the FAME freezing point to 50 °C. Data that were not available from the database were predicted using the models developed by Castellanos Diaz et al. [8].

2.2. Biodiesel fuels dataset

The composition, liquid heat capacity, and vapor pressure data of seven biodiesel fuels were reported previously by Castellanos Diaz et al. [8]. Briefly, the compositions were determined using GC and mass spectrometry [12–15]. The accuracy of the compositions based on standards is approximately ±2 wt%. Liquid heat capacities were measured using a differential scanning calorimeter (DSC) TA Q2000 V24.9 calibrated against indium with an average accuracy of ±2% [16]. vapor pressures were measured using an in-house static flash test apparatus at pressures ranging from 0.1 to 200 Pa. The average 95% confidence interval for the measured vapor pressure data is ±13% [17]. Table 2 lists the seven biodiesels and the temperature range of their vapor pressure and heat capacity data.

Table 1
Data available for selected FAMEs and temperature range in °C [11].

FAME	Formula[a]	P_V			C_{PL}			ΔH_V		
		Points	T_{min}	T_{max}	Points	T_{min}	T_{max}	Points	T_{min}	T_{max}
Methyl hexanoate	C6:0	65	7.55	146.52	–	–	–	2	25.0	25.0
Methyl caprylate	C8:0	53	33.69	145.70	12	−33.15	76.85	3	25.0	25.0
Methyl caprate	C10:0	70	−12.74	188.20	10	−3.15	76.85	2	25.0	25.0
Methyl laurate	C12:0	112	−11.00	226.85	8	6.85	76.85	4	25.0	25.0
Methyl myristate	C14:0	90	0.00	237.8	7	25	76.85	4	25.0	25.0
Methyl pentadecanoate	C15:0	29	21.85	226.85	5	26.85	76.85	4	25.0	25.0
Methyl palmitate	C16:0	110	18.00	321.95	5	36.85	76.85	2	25.0	25.0
Methyl heptadecanoate	C17:0	27	21.85	226.85	5	36.85	76.85	2	25.0	25.0
Methyl stearate	C18:0	101	21.85	346.95	4	46.85	76.85	2	25.0	25.0
Methyl arachidate	C20:0	29	38.00	226.85	3	56.85	76.85	2	25.0	25.0
Methyl behenate	C22:0	12	21.85	258.95	–	–	–	2	25.0	25.0
Methyl lignocerate	C24:0	–	–	–	–	–	–	–	–	–
Methyl palmitoleate	C16:1	4	26.85	176.85	–	–	–	1	25.0	25.0
Methyl heptadecenoate	C17:1	–	–	–	–	–	–	–	–	–
Methyl oleate	C18:1(11)	33	26.85	218.50	–	–	–	2	25.0	25.0
Methyl vaccenate	C18:1(9)	–	–	–	–	–	–	–	–	–
Methyl *cis*-11-eicosenoate	C20:1(11)	–	–	–	–	–	–	1	25.0	25.0
Methyl erucate	C22:1	8	26.85	176.85	–	–	–	1	25.0	25.0
Methyl linoleate	C18:2	18	26.85	214.95	–	–	–	1	25.0	25.0
Methyl linolenate	C18:3	12	26.85	185.7	–	–	–	1	25.0	25.0

[a] In the CN:S nomenclature for biodiesels, N stands for the carbon number of the carboxylic acid from which the biodiesel was generated, and S stands for the number of unsaturated carbon bonds. For instance, C18:1(11), methyl oleate, is a biodiesel formed from oleic acid (with 18 carbon atoms) and one double bond between the eleventh carbon and twelfth carbon atoms.