VAPOR PRESSURE MEASUREMENTS FOR ETHYL MYRISTATE

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Temperature dependence of vapor pressure for the ethyl myristate (ethyl tetradecanoate) has been measured, on the temperature domain 150 to 220 °C. The experimental results are in good agreement with available literature data and satisfactorily approximated by Ceriani-Meirelles group contribution method. The experimental data were used to estimate the parameters of an Antoine type equation, predicting more accurately the vapor pressure on the investigated temperature domain.

Keywords: vapor pressure, ethyl myristate, Antoine equation, Ceriani-Meirelles method

1. Introduction

Biodiesel fuels derived from different type of animal or vegetable oils are considered as a promising alternative to petroleum derived diesel fuels. Their advantages stem in renewable raw materials, combustion with low level of particulate matter emissions and negligible net production of carbon dioxide during its overall natural cycle.

Physical and chemical properties of biodiesel components are influencing the spray, combustion and emission characteristics of air- mixture in the engine. Vapor pressure is an important property of biodiesels components, as it is defining the volatility, safety and stability of the fuel. Good predictions of vapor pressure and other temperature-dependent properties are required also for accurate modeling of biodiesel dispersion in air and its combustion process. In the same

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time, the vapor pressure is an essential element in the design and development of separation processes. Therefore, continuous research efforts are made to measure experimentally and to develop predicting equations for the vapor pressure of fatty acid esters [1-4].

Ethyl myristate (ethyl tetradecanoate) is one of the fatty acid esters present in the biodiesel, when triglycerides transesterification is performed with ethanol. Coconut and palm kernel oils contain high amounts of medium chain saturated fatty acids as myristic and lauric ones.

Goodrum [5] measured the boiling temperature of methyl and ethyl esters derived from rapeseed oil, canola oil, soybean oil and tallow, by thermogravimetric analysis (TGA/laser orifice capsule method). Benziane et al. [6] measured, by using a static apparatus, the vapor pressures of five saturated fatty acid ethyl esters (FAEE): ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate and ethyl tetradecanoate. The experimental data were correlated by the Antoine equation and compared with the available literature values. The authors are reporting also estimated values for vaporization enthalpies for the investigated compounds. Yuan, Hansen and Zhang [7] investigated the temperature dependence of vapor pressure for fourteen pure fatty methyl esters, compoents of biodiesel (C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C22:0, C22:1, C24:0), as well as for three typical biodiesel mixtures (derived from soybean oil, rapeseed oil and tallow). The authors developed predicting methods for vapor pressure, based on the Antoine equation and a group contribution procedure, using published experimental data. The prediction abilities of several models usable for the estimation of FAEEs vapor pressures, were tested by Saxena, Patel and Joshipura [8] for several fatty esters (C8:0, C12:0, C14:0, C16:0, C18:0, C18:1 and C18:2). The percentage average relative deviations, comparative with published experimental data, are between 2 % and 19 % in the case of the best result.

Freitas et al. [3] reported measured vapor pressures for three pure methyl esters (C12:0, C14:0 and C16:0) and ten biodiesel fuels (soybean, sunflower, rapeseed and palm, alone or in their binary or ternary mixtures). The vapor pressure and boiling point data for the investigated compounds were used to evaluate the predictive ability of three theoretical methods: Yuan's model, Ceriani's model and cubic-plus-association equation of state (CPAEoS). The results evidenced that Yuan's model and CPAEoS models provide a better

Vapor pressure measurements for ethyl myristate prediction as compared with Ceriani's model, for the compounds and domains investigated.

For the ethyl myristate, the published information regarding the vapor pressure is rather limited. The aim of this work is to bring a contribution to this subject, by adding new data and confirming the validity of the previous published

values. In the same time, there are given the parameters of the simpler Antoine equation, to estimate the vapor pressure on the investigated domain.

2. Experimental

2.1 Chemicals

Ethyl myristate of 98 % purity was purchased from Sigma–Aldrich. In Table 1 are reported the most important characteristics of ethyl myristate.

Table 1

Characteristics of ethyl myristate

chemical name	synonym	CAS no.	chemical formula	molecular weight	purity/ mol%
ethyl tetradecanoate	ethyl myristate	124-06-1	$CH_3(CH_2)_{12}COOC_2H_5$	256.42	98

2.2 Equipment

The boiling temperatures of ethyl myristate (ethyl tetradecanoate) were measured at pressures ranging from 600 to 9400 Pa, at a fixed global composition. In this aim it was used the vapor-liquid equilibrium equipment VLE 50 bar produced by *i-Fischer Engineering GmbH,* Germany (Fig. 1).
In the apparatus, a part of the liquid is evaporated by an electrical heater, insuring an intensive contact of the liquid and vapor phases, which favors the phase equilibrium approach. The fine liquid drops carried out by the vapor phase are retained in a separation chamber [10].

The status of equilibrium is approached by constant recycling of liquid phase and condensed vapor phase, mixing the recirculated flows in a chamber. The compositions of the two phases are measured at steady state conditions.

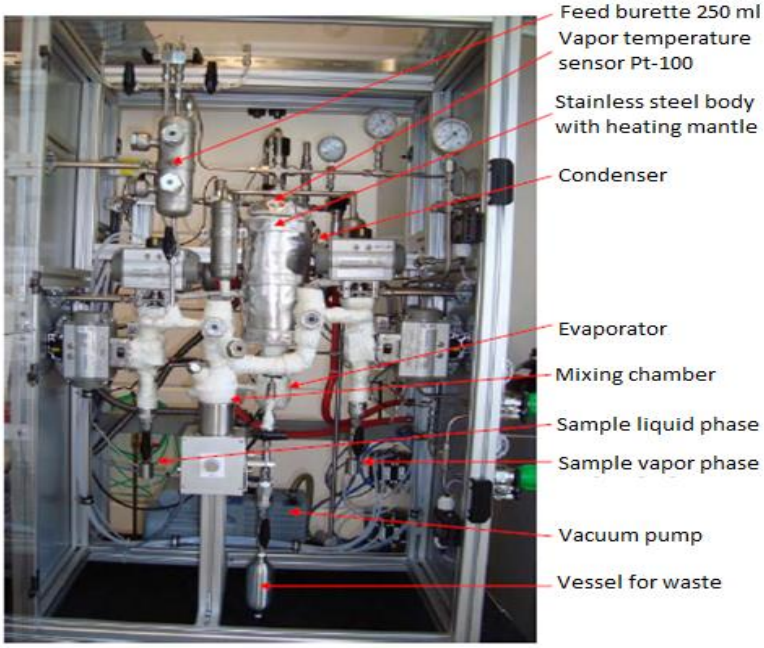

Fig. 1 The vapor-liquid equilibrium equipment VLE 50 bar

3. Results and discussion

3.1 Comparison of experimental vapor pressures with literature data

In order to minimize the errors, the experimental measurements were repeated three times in each point. The measured vapor pressures of ethyl myristate at different temperatures are shown in Fig. 2 and their numerical values (three replicates and their average) are reported in Table 2.

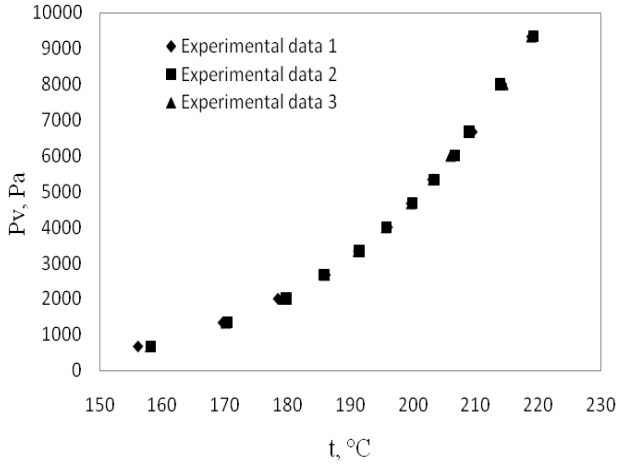

Fig. 2 The experimental vapor pressures of ethyl myristate

Based on these experimental data, standard deviation (STD) was calculated using equation (1):

$$STD = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x}_i)}{N-1}} \quad (1)$$

where:

x_i - measures value in the experiment i; $\overline{x}_i$ - average value of x_i; N - number of data points.

The values reported in Table 2 are compared with several data published by Benziane et al. [6].

Table 2

Experimental and reported vapor pressure of ethyl myristate

	Pressure, Pa											
Ethyl myristate	667	1333	2000	2666	3333	4000	4666	5332	6000	6666	8000	9333
	Temperature, °C											
Experimental 1	156.2	169.7	178.5	186.1	191.3	196	199.7	203.1	206.6	209.5	214.2	218.9
Experimental 2	158.2	170.4	179.8	185.8	191.4	195.8	199.9	203.4	206.7	209	213.9	219.2
Experimental 3	158	170.1	179.3	185.9	191.2	195.7	199.7	203.2	206	209	214.4	218.9
Average	157.5	170.1	179.2	185.9	191.3	195.8	199.8	203.2	206.4	209.2	214.2	219
Silva et.al., 2011		172.9		186.9		197.1		203.6		208.2	213.9	219.3
Benziani et.al., 2011	153.4	169.2	179.1	189.2						202.8		
STD, grd	1.10	0.35	0.66	0.15	0.10	0.15	0.12	0.15	0.38	0.29	0.25	0.17

As seen from this Table, it was obtained a good reproducibility of measurements and a fairly good concordance with the measurements previously published by the two researching groups.

3.2 Prediction of the vapor pressure for ethyl myristate

The experimental vapor pressure results were fitted using the Ceriani-Meirelles method based on group contributions [9]. In accord with this method, the vapor pressure is estimated by the equation:

$$\ln P = \sum_k N_k \left(A_{1k} + \frac{B_{1k}}{T^{1.5}} - C_{1k} \ln T - D_{1k} T\right) + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T^{1.5}} - C_{2k} \ln T - D_{2k} T\right) \right] + Q \quad (2)$$

where:

P - vapor pressure (Pa); T - temperature (K); N_k - the number of groups k in the molecule; M_i - component molecular weight that multiplies the "perturbation term"; A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, and D_{2k} are parameters obtained from the regression of the experimental data; k represents the groups of component i; and Q a correction term, calculated using equation (3):

$$Q = \xi_1 q + \xi_2 \tag{3}$$

where:

$$\xi_1 = f_0 + N_c \cdot f_1 \tag{4}$$

$$q = \alpha + \frac{\beta}{T^{1.5}} - \gamma \ln(T) - \delta T \tag{5}$$

$$\xi_2 = s_0 + N_{cs} \cdot s_1 \tag{6}$$

In the above expressions, these parameters are used:

N_c - number of carbon atoms in the molecule;
N_{cs} - number of carbon atoms of the alcoholic part;
f_0, f_1, α, β, γ, δ, s_0, s_1 - optimized parameters obtained by regression of the experimental data, given in Table 3 [9].

All the fatty compounds found in the separation processes discussed here were divided into three functional groups: $-CH_3$, $-CH_2$ and -COOH. Table 3 shows the values of the group parameters, specific for the Ceriani-Meirelles method.

Table 3

Values of the parameters in the Ceriani-Meirelles method

Group	**A_{1k}**	**B_{1k}**	**C_{1k}**	**D_{1k}**	**A_{2k}**	**B_{2k}**	**C_{2k}**	**D_{2k}**
CH3	−117.5	7232.3	−22.7939	0.0361	0.00338	−63.3963	−0.00106	0.000015
CH2	8.4816	−10987.8	1.4067	−0.00167	−0.00091	6.7157	0.000041	−0.00000126
COOH	8.0734	−20478.3	0.0359	−0.00207	0.00399	−63.9929	−0.00132	0.00001

Compound	**f0**	**f1**	**s0**	**s1**
Esters	0.2773	−0.00444	−0.4476	0.0751

q

α	**β**	**γ**	**δ**
3.4443	−499.3	0.6136	−0.00517

The calculated temperature dependence of ethyl myristate vapor pressure is presented in Fig. 3, comparatively with the measured one. As seen from this Fig., the predicted values are in a fairly good agreement with the experimental measurements. The predicted accuracy of vapor pressure is better on the first interval of temperatures and slightly worse on the last interval, where the vapor pressure is under-evaluated.

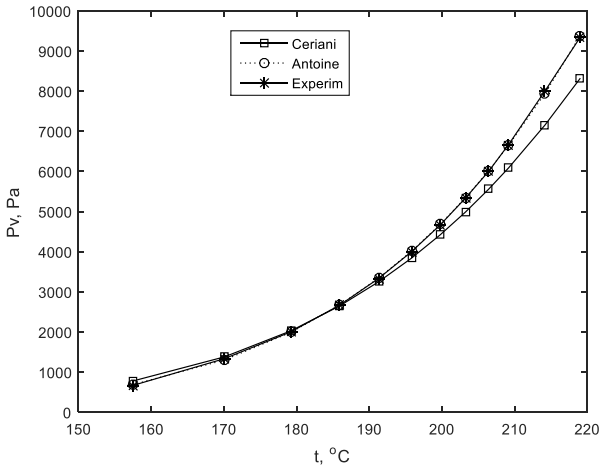

Fig. 3 Ethyl myristate vapor pressure *vs* temperature

In order to provide a simpler and more accurate relation for the prediction of ethyl myristate vapor pressure, the experimental data were correlated by the Antoine equation (with t in ^{o}C):

$$\log P = A - \frac{B}{C + t} \tag{7}$$

The parameters A, B, and C, involved in the equation (7) were estimated by the least square method. The numerical values so determined are: A=8.38, B=1322.7 ^{o}C and C=81.26 ^{o}C. The vapor pressure values estimated with Antoine equation are very close to those determined experimentally. Fig. 4 shows that the Antoine equation is suitable for representation of the vapor pressures of the ethyl myristate.

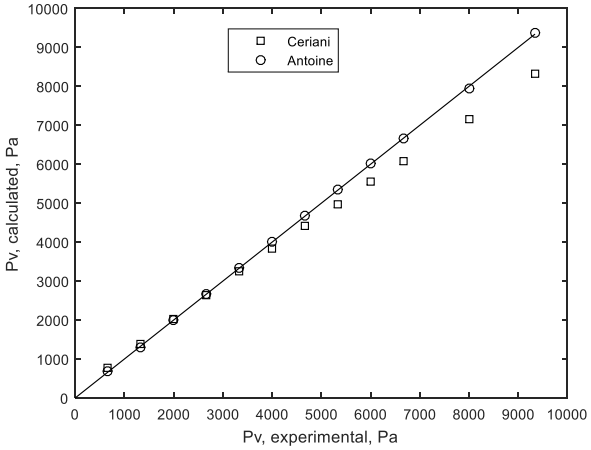

Fig. 4 Parity plot of experimental data *vs* calculated models

4. Conclusion

In this study, we determined vapor pressures of ethyl myristate on the temperature domain 150-220 ^{o}C, by using a special purpose vapor-liquid (V-L) equilibrium equipment. The results are in good agreement with available literature data. The measured vapor pressure - temperature data were compared with the values predicted by using Ceriani - Meirelles group contribution method. The predictions are better on the first half of investigated temperature interval and slightly worse on the second half. To provide a better predicting relation, there were estimated the parameters of the Antoine equation, using the experimental data. The obtained Antoine equation insures a good accuracy of vapor pressure predictions on the investigated temperature domain.

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