

THERMODYNAMIC MODELING AND SIMULATION AT HIGH PRESSURES OF BINARY SYSTEMS CONTAINING BIODIESEL COMPONENTS: DIFFERENT TYPES OF THE PENG-ROBINSON EQUATION OF STATE VS ARTIFICIAL NEURAL NETWORKS

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ABSTRACT

Biodiesel is a fuel made of renewable sources of animal, vegetal or algae lipids and a promissory substitute of petroleum diesel due to be environmentally friendly. Synthesized by the transesterification reaction between a triglyceride and an alcohol, this biofuel is focus in many studies to modeling its thermodynamic behavior with your compounds to improve the efficiency of its production. In this work, the phase behavior of the vapor-liquid equilibrium of binary systems containing biodiesel components and alcohol solvents was analyzed by the Peng-Robinson, Volume-Translated Peng-Robinson and Group Contribution Volume-Translated Peng-Robinson equations of state. By another hand, it was realized the thermodynamic simulating by using Artificial Neural Networks with Molecular Descriptors and comparing the calculated values obtained between these thermodynamic models with the experimental ones. It was demonstrated that, although the Peng-Robinson equation of state provide good results, the Volume-Translated and, mainly, the Group Contribution Volume-Translated models provide results more accurate and can be used for complex substances. Results obtained via Artificial Neural Networks with molecular Descriptors are slightly better than those obtained by Group Contribution Volume-Translated Peng-Robinson equation of state.

Keywords: Biodiesel, Peng-Robinson, Volume-Translated, Group Contribution, Artificial Neural Networks, Molecular Descriptors.

1. INTRODUCTION

1.1. BIODIESEL

With the increasing of the energy consuming in the world, the search for new sources of energy is focus of many studies. The biodiesel is a promissory alternative, a group of fatty acid esters synthesized by the transesterification reaction between a triacylglycerol and an alcohol with an alkaline catalysis or with supercritical solvent. The triacylglycerols may come from sources of vegetable, animal or algae origin [1].

To improve the efficiency of the production and separation processes, it is necessary know the thermodynamic behavior of biodiesel components in different conditions of pressure and temperature. To study this, it is modeling vapor-liquid equilibrium between the components of biodiesel, creating phase diagrams of them.

1.2. EQUATIONS OF STATE

To simulate the thermodynamic behavior of a pure substance or a mixture, it is used an equation of state to create phase diagrams of these systems. There are many types of equations of state. However, the cubic equations of state are the most used, due to their easy resolution. The Peng-Robinson equation of state is the one of the most used and provides good results to non-polar components. With some improves, as volume translation, this equation can model a larger number and types of substances [2].

This work aims model thermodynamically binary systems with biodiesel components with three equations of state (EoS): Peng-Robinson equation of state (PR), Volume Translation Peng-Robinson equation of state (VT-PR) and Group Contribution Volume Translation Peng-Robinson equation of state (GC-VT-PR).

1.3. ARTIFICIAL NEURAL NETWORK

Artificial neural networks (ANNs) are connectionist systems which are computing systems vaguely inspired by the biological neural networks that constitute animal brains[3]. These systems "learn" (i.e. progressively improve performance on) tasks by considering examples, generally without task-specific programming. To learn, neural networks need information, in our case of thermodynamic properties of the substances involved. If this information is not enough, we use the molecular descriptors.

1.4. MOLECULAR DESCRIPTORS

Molecular descriptors are very important in chemistry, pharmaceutical sciences, environmental protection policy, health researches, etc. the concept is based on the way molecules, thought of as real bodies, which are transformed into numbers, allowing some mathematical treatment of the chemical information contained in the molecule. In according with Todeschini and Consonni: "The molecular descriptor is the final result of a logic and mathematical procedure which transforms chemical information encoded within a symbolic representation of a molecule into a useful number or the result of some standardized experiment." [4]

2. METHODOLOGY

2.1. PENG-ROBINSON EQUATION OF STATE [5]

The Peng-Robinson equation of state was applied in the thermodynamic modeling in this work, using the van der Waals II mixing rule to determinate the constants 'a' and 'b' for a mixture of components.

$$a_{i,j} = (1 - k_{ij})\sqrt{a_i a_j}; \quad a = \sum_i^c \sum_j^c x_i x_j a_{i,j} \quad (1)$$

$$b_{i,j} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}); \quad b = \sum_i^c \sum_j^c x_i x_j b_{i,j} \quad (2)$$

In which k_{ij} and l_{ij} are binary interaction parameters of the mixture.

2.2. VOLUME TRANSLATION PENG-ROBINSON EQUATION OF STATE [6]

The PR equation can be improved with the addition of a correction constant 't'.

$$P = \frac{RT}{V+t-b} - \frac{a}{(V+t)(V+t+b)+b(V+t-b)} \quad (3)$$

This equation of state has a new function $\alpha(T)$:

$$\alpha_i(T) = [1 + m_i(1 - T_{r,i}) + N_i(1 - T_{r,i})(0,7 - T_{r,i})]^2 \quad (4)$$

In which N is a pure compound parameter determinate with vapor pressure and saturated liquid specific volume data of component i.

The constant 't' can be calculated by the following equation:

$$t_i = -0,252 \frac{RT_{c,i}}{P_{c,i}} \left[k_{1i} + k_{2i} \left(1 - T_{r,i}^{\frac{2}{3}} \right) + k_{3i} \left(1 - T_{r,i}^{\frac{2}{3}} \right)^2 \right] \quad (5)$$

In which k_3 is a pure compound parameter determinate with the vapor pressure and saturated liquid specific volume data of the component i . The parameters k_1 and k_2 are calculated with k_3 and acentric factor for each substance.

With all the main constants and parameters, the fugacity coefficients of the liquid and vapor phases can be calculated and using $\ln\phi$ - ϕ approach, according the equation:

$$x_i \hat{\phi}_i^L = y_i \hat{\phi}_i^V \quad (6)$$

This approach, in this work, was used in the PR and VT-PR equations.

2.3. VOLUME TRANSLATION PENG-ROBINSON EQUATION WITH GROUP CONTRIBUTION [7]

The group contribution method considers the influence of each functional group of the molecules present in the mixture to calculate the Gibbs free energy and doing the thermodynamic modeling of the system. The main equation of this method, present in the study of Schmid and Gmehling (2012), uses UNIFAC equations to determinate the influences between the groups with the parameters a_{nm} , b_{nm} and c_{nm} , besides de parameter Q_k and R_k , and is present in this study. The equations are in figure 1.

$$\begin{aligned} \Psi_{nm} &= \exp\left(-\frac{a_{nm} + b_{nm} \cdot T + c_{nm} \cdot T^2}{T}\right) \\ \ln \Gamma_k &= Q_k \left[1 - \ln\left(\sum_m \Theta_m \cdot \Psi_{mk}\right) - \sum_n \frac{\Theta_m \cdot \Psi_{kn}}{\sum_n \Theta_n \cdot \Psi_{nm}} \right] \\ \ln \gamma_i^R &= \sum_k v_k^{(i)} \cdot (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \\ g^{ER} &= R \cdot T \cdot \sum_i x_i \cdot \ln \gamma_i^R \\ a(T) &= b \cdot \sum_i x_i \cdot \frac{a_{ii}(T)}{b_{ii}} + \frac{g^{ER}}{-0.53087} \end{aligned}$$

$$\Theta_m = \frac{Q_m \cdot X_m}{\sum_n Q_n \cdot X_n} \quad X_m = \frac{\sum_j v_m^{(j)} \cdot x_j}{\sum_n \sum_j v_n^{(j)} \cdot x_j}$$

Figure 1 - Calculation method to 'a' constant in GC method [7]

In this method, is also determinate the values of active coefficient (γ), used in gamma-phi (γ - ϕ) approach, used in thermodynamic modeling in medium pressures [8].

$$x_i P_i^{SAT} \gamma_i = y_i P \hat{\phi}_i^V \quad (7)$$

This method, with VT-PR equation, calculates, in a fixed temperature and liquid phase molar fraction (x_i), the predicted values of pressure and vapor phase molar fraction (y_i), besides the value of the fugacity coefficient (ϕ) in the vapor phase.

2.4. THERMODYNAMIC SIMULATION WITH ARTIFICIAL NEURAL NETWORKS.

In this work, there were used several architectures of 3-layer and four-layer type: IV-X-2 and IV-X-X-2. "IV" represents the number of independent variables (temperature, mole fraction in the liquid phase, critical properties, and molecular descriptors), "X" represents the hidden layers, and "2" represents the dependent variables. In this work, these dependent variables are the bubble pressure and the mole fraction in vapor phase.

Thermodynamic properties of biodiesel systems are analyzed to study the capabilities of artificial neural networks (ANNs) to learn, test and predict the fluid phase behavior

properties: bubble pressure and the vapor phase composition. Molecular descriptors were obtained from the computational chemistry (Dragon 7) and were also considered as independent variables. In this work, first, in accordance to the molecular structure of the biodiesel component, it was found the SMILES code of each one. Second, with the SMILE code known, there were obtained, using the Dragon 7, the numeric value for the selected molecular descriptors.

For learning, testing and predicting the fluid phase behavior properties of the biodiesel systems, a spreadsheet file (MS-Excel) with six worksheets, each one with special function, was used. The first, third and fifth worksheets for the learning, testing and predictions steps, respectively, contain the independent variables. The second, fourth and sixth worksheets for the learning, testing and prediction steps, respectively, contain the dependent variables. Data and number of data are different for the first, third and fifth worksheets. A computer program for three dependent variables, in MatLab, was developed by one of the authors to interact with each worksheet of the spreadsheet file. In this form, to obtain the best architecture, several network architectures were studied.

3. RESULTS AND DISCUSSION

3.1. THERMODYNAMIC PROPERTIES OF THE STUDIED BINARY SYSTEMS

In Table 1, it is shown some thermodynamic properties of the binary systems studied in this work for the modeling of the fluid phase behavior using the thermodynamic models (PR, VT-PR and GC-VT-PR EoS) and the mathematical models (ANN).

Table 1 - Binary systems involving biodiesel components

System	Temperature (K)	N° of points	Pressure (bar)	Molar fraction x1	Molar fraction y1	Reference
methanol + methyl laurate	493,15	8	19,6 - 84,9	0,41 - 0,89	0,9926 - 0,9998	[9]
methanol + methyl myristate	493,15	4	24,1 - 37,0	0,47 - 0,70	0,9997 - 0,9999	[9]
methanol + methyl palmitate	493,15	4	18,6 - 37,6	0,37 - 0,64	0,9977 - 0,9981	[10]
ethanol + ethyl laurate	493,15	4	22,4 - 30,1	0,44 - 0,83	0,9987 - 0,9995	[11]
ethanol + ethyl myristate	493,15	4	20,8 - 28,4	0,45 - 0,78	0,9990 - 0,9995	[11]
methanol + glycerol	493,15	6	22,4 - 87,8	0,32 - 0,89	0,9994 - 0,9999	[12]
ethanol + glycerol	493,15	6	30,3 - 95,5	0,43 - 0,96	0,9976 - 0,9999	[12]
methanol + triolein	473,15	4	29,0 - 48,6	0,07 - 0,97	0,9996 - 0,9999	[13]
CO ₂ + ethyl caproate	308,15	8	17,0 - 92,2	0,21 - 0,85	0,9963 - 0,9994	[14]
CO ₂ + ethyl caprylate	308,15	9	17,0 - 92,2	0,21 - 0,89	0,9985 - 0,9997	[14]
CO ₂ + ethyl caprate	308,15	9	17,0 - 92,2	0,21 - 0,84	0,9992 - 0,9998	[14]

3.2. CRITICAL PROPERTIES, PURE COMPONENT AND GROUP INTERACTION PARAMETERS OF THE BIODIESEL COMPONENTS AND SUPERCRITICAL FLUIDS.

For the thermodynamic modeling of these binary systems, it is necessary to know the critical properties of the substances to calculate the constants and parameters of cubic equation of state. These critical properties are present in Table 2. VT-PR and GC-VT-PR pure component parameters, N and k_3 , are determined through the vapor pressure and saturated liquid density pure of each substance.

Values for the parameters of group contribution method are shown in Table 3. Values of a , b and c for the group interactions: CH₃OH-CH₂COO and OH-CH₂COO, were determined with VLE data for the binary systems composed by alcohol and biodiesel esters. The interaction between C=C and CH₂COO, for the thermodynamic modeling, was not relevant in the results, not changing the relative errors.

Table 2 - Critical properties of substances present in binary systems

Substance	Tc (K)	Pc (bar)	w	N	k ₃	Reference
methanol	512,58	80,96	0,566	0,03221	-0,0443	[6] [15]
ethanol	513,9	63,0	0,649	0,20761	0,0269	[6] [15]
carbon dioxide	304,2	73,78	0,2275	0,11333	0,28996	[6] [15]
glycerol	850,0	75,0	0,5127	0,60923	0,1826	[15] [16] [17]
methyl laurate	712,0	17,4	0,6924	0,29683	-0,0764	[16] [17] [18]
methyl myristate	740,0	14,29	0,7365	0,28474	-0,2608	[16] [17] [18]
methyl palmitate	765,0	12,77	0,8037	0,34676	-0,3391	[16] [17] [18]
ethyl caproate	615,2	26,57	0,540	0,16041	0,25307	[15] [16]
ethyl caprylate	656,4	21,6	0,628	0,07189	0,02829	[15] [16]
ethyl caprate	690,2	18,46	0,709	0,09051	-0,13055	[15] [16]
ethyl laurate	719,13	15,97	0,787	-0,0689	-0,2525	[16] [17] [19]
ethyl myristate	744,27	14,02	0,862	0,04307	-0,1892	[16] [17] [19]
triolein	954,1	3,6	1,6862	6,8171	-3,0034	[16] [17] [18]

Table 3 - Values for the group interaction parameters (GC-VT-PR EoS)

Group n	Group m	a _{nm}	b _{nm}	c _{nm}	a _{mn}	b _{mn}	c _{mn}	Reference
CH ₂	C=C	171,47	-0,0432	0	-87,609	-0,0544	0	[7]
CH ₂	OH	1809,50	-0,4856	-0,00031	725,66	-0,905	0,001636	[7]
CH ₂	CH ₃ OH	1733,40	1,8057	-0,0061885	50,672	-0,6378	0,0001775	[7]
CH ₂	CH ₂ COO	138,56	1,5746	-0,00219	779,9	-4,5744	0,005804	[7]
CH ₂	CO ₂	403,11	-0,1999	-0,000067	204,83	-1,3096	0,00197	[7]
C=C	CH ₃ OH	3394,30	0,1123	0	-113,11	0,1866	0	[7]
CH ₃ OH	CH ₂ COO	-228,94	0,1278	0	2277,48	-5,0882	0	-
OH	CH ₂ COO	-1446,84	4,3202	0	4015,24	-9,721	0	-
CO ₂	CH ₂ COO	-146,54	0	0	95,601	0	0	[7]

3.3. MOLECULAR DESCRIPTORS

In Table 4, it is shown the molecular descriptors used in this research work. Numerical values for these molecular descriptors were obtained from Dragon (v. 7.0)

Table 4- Molecular descriptors used in this work

Molecular descriptor	Name	Sub-block	Block
AMW	Average molecular weight	Basic descriptors	Constitutional indexes
nH	Number of Hydrogen atoms		
nC	Number of Carbon atoms		
Pol	Polarity number	Distance-based indexes	Topological indexes
XMOD	Modified Randic index	Randic-like connectivity indexes	Connectivity Indexes
RDCHI	Reciprocal distance sum Randic-like index		
nRCOOR	Number of esters (aliphatics)	Basic descriptors	Functional group counts
SA _{tot}	Surface area (total)	Basic descriptors	Molecular
V _{vdwMG}	Van der Waals volume for McGowan volume		
PDI	Packing density index		

SMILES codes for some biodiesel components are shown in Table 5, while in Table 6, numerical values of the molecular descriptors for some biodiesel components studied in this work, are shown.

3.4. RESULTS FOR THE THERMODYNAMIC MODELS (GC-VT-PR, VT-PR AND PREOS) AND FOR THE THERMODYNAMIC SIMULATION (ANN)

Results for the fluid phase behavior (bubble point) of the binary systems (Table 1) are shown in Table 7.

Relative errors between the experimental and calculated values of the bubble pressure and the molar fraction of vapor phase were calculated according the equations:

$$\Delta P = \frac{|P_{exp} - P_{calc}|}{P_{exp}} \times 100; \quad \Delta y_1 = \frac{|y_{1,exp} - y_{1,calc}|}{y_{1,exp}} \times 100 \quad (8)$$

Table 5 -SMILES code for some biodiesel components

Component	SMILES code
triolein	CCCCCCCC\C=C/CCCCCCCC(=O)OCC(COC(=O)CCCCCCCC\C=C/..... C/CCCCCCCC)OC(=O)CCCCCCCC\C=C/CCCCCCCC
ethylmyristate	CCCCCCCCCCCCCCCC(=O)OCC
ethyl laurate	CCCCCCCCCCCCCCCC(=O)OCC
methyl laurate	CCCCCCCCCCCCCCCC(=O)OC
methylmyristate	CCCCCCCCCCCCCCCC(=O)OC
glycerol	OCC(O)CO

Table 6- Numeric values for the molecular descriptors of the biodiesel components

Molecular descriptor	AMW	nH	nC	Pol	XMOD	RDCHI	nRCOOR	SAtot	VvdwMG	PDI
triolein	5,303	104	57	65	190,531	7,617	6	1553,171	108,434	563,947
ethylmyristate	5,130	32	16	16	54,334	3,298	2	472,669	36,145	169,313
ethyl laurate	5,191	28	14	14	48,334	3,034	2	420,515	36,145	150,128
methyl laurate	5,229	26	13	13	45,541	2,910	2	394,438	36,145	140,536
methylmyristate	5,159	30	15	15	51,541	3,178	2	446,592	36,145	159,721
glycerol	6,579	8	3	4	18,840	1,559	3	186,906	128,050	51,536

Table 7- Results for the PR, VT-PR and GC-VT-PR EoS and ANN model

System	EoS	k _{ij}	l _{ij}	ΔP	Δy ₁	System	EoS	k _{ij}	l _{ij}	ΔP	Δy ₁
methanol + methyl Laurate	PR	0,039	0,025	6,65	0,32	ethanol + glycerol	PR	-0,127	-0,157	1,69	0,50
	VT-PR	0,042	0,029	6,69	0,56		VT-PR	-0,145	-0,190	1,71	0,66
	GC-VT-PR	----	----	4,07	0,10		GC-VT-PR	----	----	10,76	0,35
	ANN	----	----	1,15	0,12		ANN	----	----	0,81	0,13
methanol + methyl myristate	PR	0,041	0,005	5,71	0,34	methanol + triolein	PR	-0,038	0,169	20,65	0,03
	VT-PR	0,035	0,001	5,75	0,50		VT-PR	-0,016	0,144	20,09	0,03
	GC-VT-PR	----	----	2,61	0,13		GC-VT-PR	----	----	9,17	0,03
	ANN	----	----	0,72	0,11		ANN	----	----	1,41	0,08
methanol + methyl palmitate	PR	-0,010	-0,042	9,02	0,10	CO ₂ + ethyl caproate	PR	-0,011	-0,005	4,98	0,07
	VT-PR	-0,014	-0,045	8,88	0,09		VT-PR	-0,010	-0,009	4,96	0,02
	GC-VT-PR	----	----	7,55	0,11		GC-VT-PR	----	----	3,55	0,50
	ANN	----	----	1,54	0,13		ANN	----	----	0,79	0,10
ethanol + ethyl laurate	PR	-0,077	-0,061	10,23	0,33	CO ₂ + ethyl caprylate	PR	0,013	0,001	3,70	0,03
	VT-PR	-0,094	-0,073	9,75	0,51		VT-PR	0,028	0,005	3,17	0,02
	GC-VT-PR	----	----	1,95	0,10		GC-VT-PR	----	----	1,04	0,60
	ANN	----	----	0,81	0,14		ANN	----	----	0,51	0,16
ethanol + ethyl myristate	PR	-0,038	-0,015	11,54	0,08	CO ₂ + ethyl caprate	PR	0,035	0,006	1,83	0,02
	VT-PR	-0,066	-0,049	11,24	0,21		VT-PR	0,051	0,009	1,69	0,02
	GC-VT-PR	----	----	1,56	0,02		GC-VT-PR	----	----	6,57	0,46
	ANN	----	----	0,65	0,08		ANN	----	----	1,31	0,14

	PR	0,001	-0,009	1,30	0,36
methanol	VT-PR	0,005	-0,005	1,26	0,42
+ glycerol	GC-VT-PR	----		2,84	0,25
	ANN	----		0,88	0,12

Observing some numerical (Table 4) and graphical results (Figures 2 and 3), can be concluded that the PR and VT-PR equations provides generally results very close, although the VT-PR equation has more accuracy in substances in which the values of N and k_3 were well defined. In another hand, the GC-VT-PR equation is more accurate than the PR and VT-PR to predict the behavior of the binary systems. Even the GC with gamma-phi approach works better at low and medium pressures, this method still provides good results near of the critical point of the solvents even with complex substances.

Besides, the accuracy of VT-PR and GC-VT-PR equations may be improved with a good determination of the parameters N and k_3 with vapor pressure, saturated liquid specific volume data and critical properties.

When comparing the results obtained by the GC-VT-PR EoS and those obtained with the optimal architecture (3-10-5-2) of the neural network model, we can notice a slight difference, and the results of the neural network are closer to the experimental data.

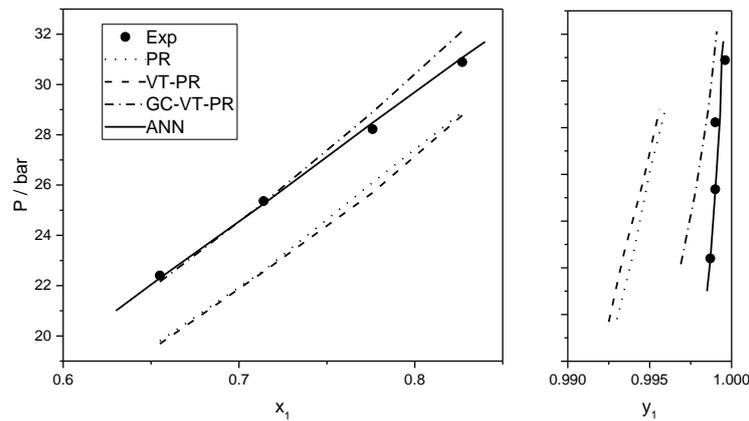


Figure 2 – Fluid phase behavior of the ethanol + ethyl laurate system at 493,15 K

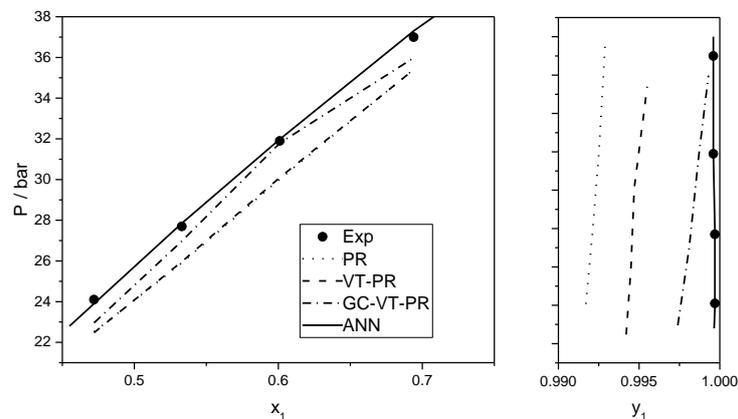


Figure 3 – Fluid phase behavior of the methanol + methyl myristate system at 493,15 K

4. CONCLUSIONS

It is possible to conclude, based in the results present in this work, that the PR and VT-PR equations, although do good thermodynamic modeling in high values of pressure and

temperature with simple substances, with VT-PR providing a better accuracy, the relative errors are still considerable. However, the group contribution method, even in systems with large molecules and high pressures, provides better results in the majority of cases. Thus, the thermodynamic modeling of biodiesel components can be done reliably with the group contribution method, providing good results in conditions near of solvent critical temperature. In all cases, the results obtained by the neural network model, with the optimal architecture (3-10-5-2), were more accurate than those obtained by the other cubic equations of state.

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