Phase Equilibrium of Binary System Carbon Dioxide - Methanol at High Pressure Using Artificial Neural Network

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Summary: Interest in supercritical fluids extraction (SFE) is increasing throughout many scientific and industrial fields. The common solvent for use in SFE is carbon dioxide. However, pure carbon dioxide frequently fails to efficiently extract the essential oil from a sample matrix, and modifier fluids such as methanol should be used to enhance extraction yield. A more efficient use of SFE requires quantitative prediction of phase equilibrium of this binary system, carbon dioxide – methanol. The purpose of the current research is modeling carbon dioxide – methanol system using artificial neural network (ANN). Results of ANN modeling has been compared with experimental data as well as thermodynamic equations of state. The comparison shows that the ANN modeling has a higher accuracy than thermodynamic models.

Key words: Artificial neural network, Thermodynamic, carbon dioxide, methanol, high pressure.

Introduction

Supercritical fluid extraction (SFE) is one of the extraction methods which widely used in industrial settings. SFE is a new method for producing medicinal plant extracts [1]. Advantages of this method over classical methods of extraction are: 1- It has a higher quality product. 2- By changing the temperature and pressure, the product can achieve the desired quality. 3- Separation of solvent and solute is simply done by reducing the pressure. 4- Due to low operating temperature process, supercritical extraction is one of the common methods for extraction of temperature-sensitive materials, such as pharmaceutical industry. 5- The solvent is un-toxic. Carbon dioxide has been the solvent of choice for most SFE studies primarily because it has a relatively low critical temperature and pressure, low toxicity, relatively high purity and low cost [2, 3]. However, pure CO_2 frequently fails to efficiently extract several organics from a sample matrix, and modifier fluids (co-solvents) should be used to increase extraction efficiency [4]. Methanol is one of the most common co-solvent in SFE. Studying of this binary systems, carbon dioxide–methanol, behavior can leads to higher extraction efficiency. The experimental vapor-liquid equilibrium data (VLE) for this binary system is available only for some specified isotherms. However thermodynamic equation of state could predict the VLE data for each isotherm but they have poor prediction especially in high pressure region (the region of interest by SFE process). Artificial neural network which is used in many of engineering fields seems to be a good method for modeling of binary VLE system. About ANN modeling of SFE processes, Izadifar and Abdolahi [5] developed a feed-forward multi-layer neural network with Levenberg–Marquardt training algorithm to predict yield for supercritical carbon dioxide extraction of black pepper essential oil. Statistical analyses showed that the neural network predictions had an excellent agreement with experimental data. Also, Kamali and Mousavi [6] studied the extraction of α-pinene using supercritical carbon dioxide. They compared three modeling approaches including the dense gas model with Peng–Robinson equation of state as an analytical model, a three layers feed forward neural network and a hybrid analytical–neural network structure.

The purpose of a neural network is to calculate output values from input values by some internal calculations. Neural network have several layers. The first layer is named the input layer, and each of its neurons receives information corresponding to one of the independent variables used as inputs. The last layer is named output layer. The other layers called hidden layers. A neural network consists of numbers of simple processing elements called neurons. Each neuron of neural network is connected to others by means of direct communication link, each with an associated weight, which represents information being used by the net to solve the problem [7, 8]. The weights of the connections between neurons should be adjusted in order to decrease the error between estimated and expected values for the entire database. In this technique, the experimental data set was divided into three groups: 60 % for training, 20 % for validation, and 20 % for testing. The first group is totally used for learning and training the ANN and is termed the training set. The selection of the database to train a neural

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network is of great importance and it must be trained on large and comprehensive set of reliable experimental data. By using the data in this set, the weights of the parameters in the ANN model are determined. The second group is termed testing set used to calculate the ANN estimation power. The third group of data is termed validation set used to prevent overtraining probability. An over trained network has typically learned seen training set completely but cannot give accurate estimation for unseen data.

Neural network training can be made more efficient if perform certain preprocessing steps on the network inputs and targets. Network-input processing functions transform inputs into a better form for the network use. Processing functions associated with a network output transform targets into a better form for network training, and reverse transformed outputs back to the characteristics of the original target data. A common approach that used in the current study for scaling network inputs and targets is to normalize the mean and standard deviation of the training set.

The main objective of this study is to model carbon dioxide – methanol system using ANN. For developing the ANN model, vapor-liquid experimental data of carbon dioxide – methanol have been used [9, 10].

Results and discussion

The ANN results were compared with the experimental data of Joung *et. al* [9] and Secuianu *et. al* [10] for the isotherms of 313.15, 320, 330, 335.65, 342.8, 293.15, 298.15, 310.15 and 323.15 K. In order to show the smooth trend of ANN predictions, the comparison results at several isotherms were shown in Fig. 1 and 2. In these Figures, the solid lines are the model prediction and the points are the experimental data. Based on these two Figures, the ANN results experiences a smooth and accurate trend and pass through the experimental data. In particular, the ANN model is capable to predict the VLE data at high pressure which is the interesting region for SFE process.

As mentioned, Joung *et. al* [9] and Secuianu *et. al* [10] were modeled the CO_2-methanol data using cubic equations of state. From Fig. 1 and 2 as well as the data available in the two mentioned references, it may be hard to understand which model, ANN or cubic equations of state, is more precisely. This vagueness can be clarified using the graphs of pressure and vapor mole fraction based on both models. When compared the performance of the ANN model with cubic equations of state model (Fig. 3), the ANN model is able to predict the equilibrium pressure much more efficiently. This is mainly due to the fact that the ANN model well learned with the training data. But, the error for vapor mole fraction prediction is almost the same for both models (Fig. 4). This may be attributed to the fact that the experimental vapor mole fraction data were laid in a narrow range cause achieving prediction with high accuracy to be difficult. It should be noted that the terms AADP% and AADy% in these Figures are calculated from the following equations:

$$AADP\ \% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_i^{\exp} - P_i^{ANN}}{P_i^{\exp}}\right| \times 100 \quad (1)$$

$$AADy\ \% = \frac{1}{N}\sum_{i=1}^{N}\left|y_i^{\exp} - y_i^{ANN}\right| \times 100 \quad (2)$$

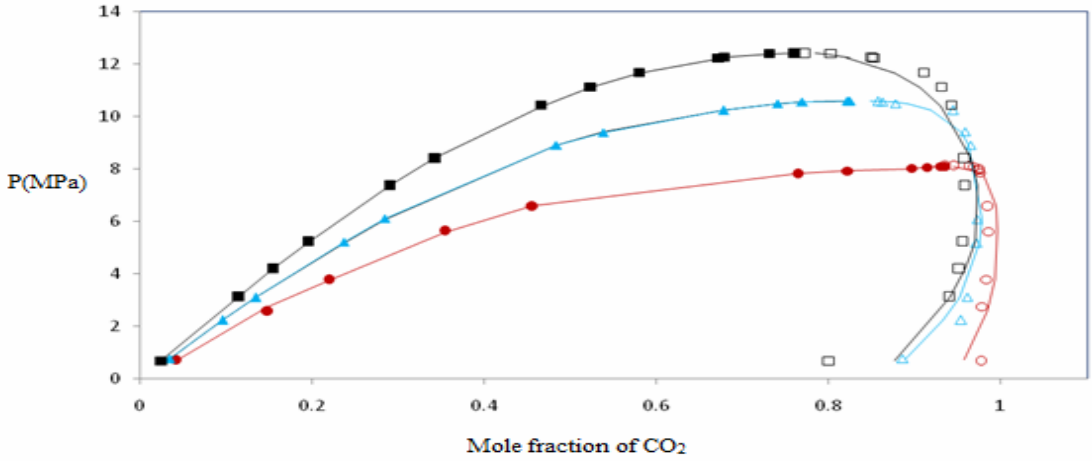

Fig. 1: Vapor liquid equilibria of carbon dioxide-methanol system, comparison between ANN results with experimental data at 313 K (●), 330 K (▲) and 342 K (■).

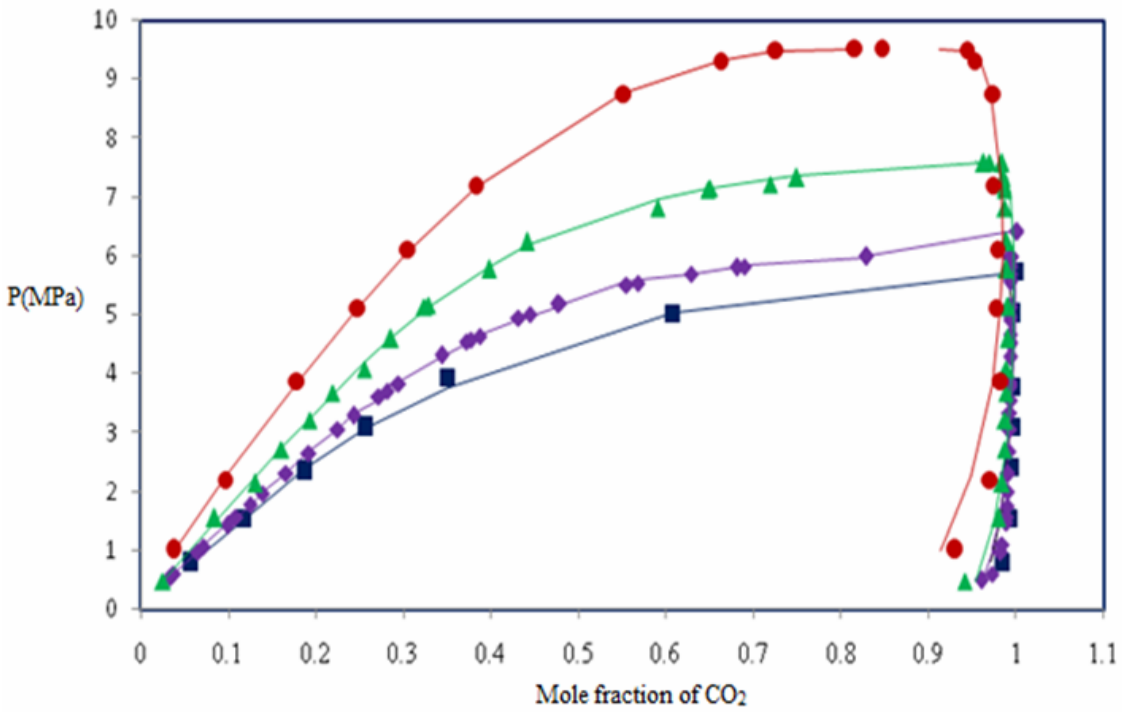

Fig. 2: Vapor liquid equilibria of carbon dioxide-methanol system, comparison between ANN results with experimental data at 293.15 K (■), 298.15 K (◆), 310.15 K (▲), and 323.15 K (●).

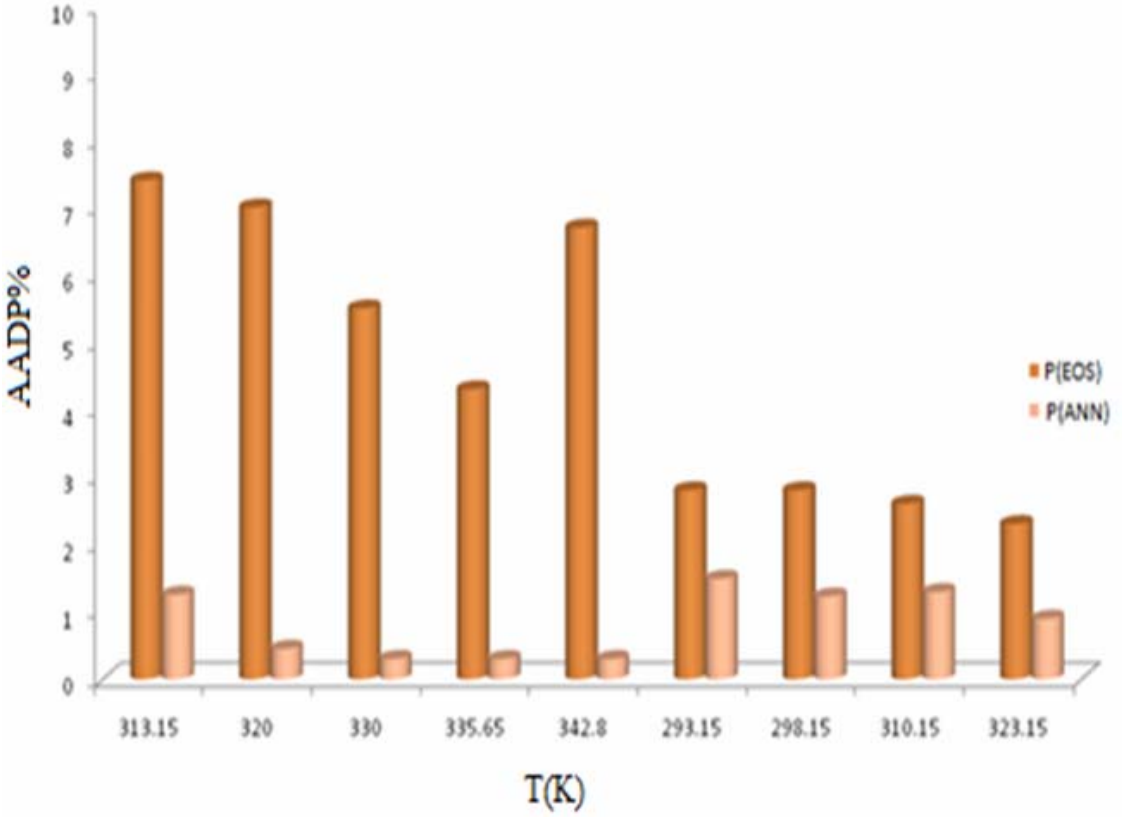

Fig. 3: Average relative errors in pressure, comparison between ANN results with EOS results.

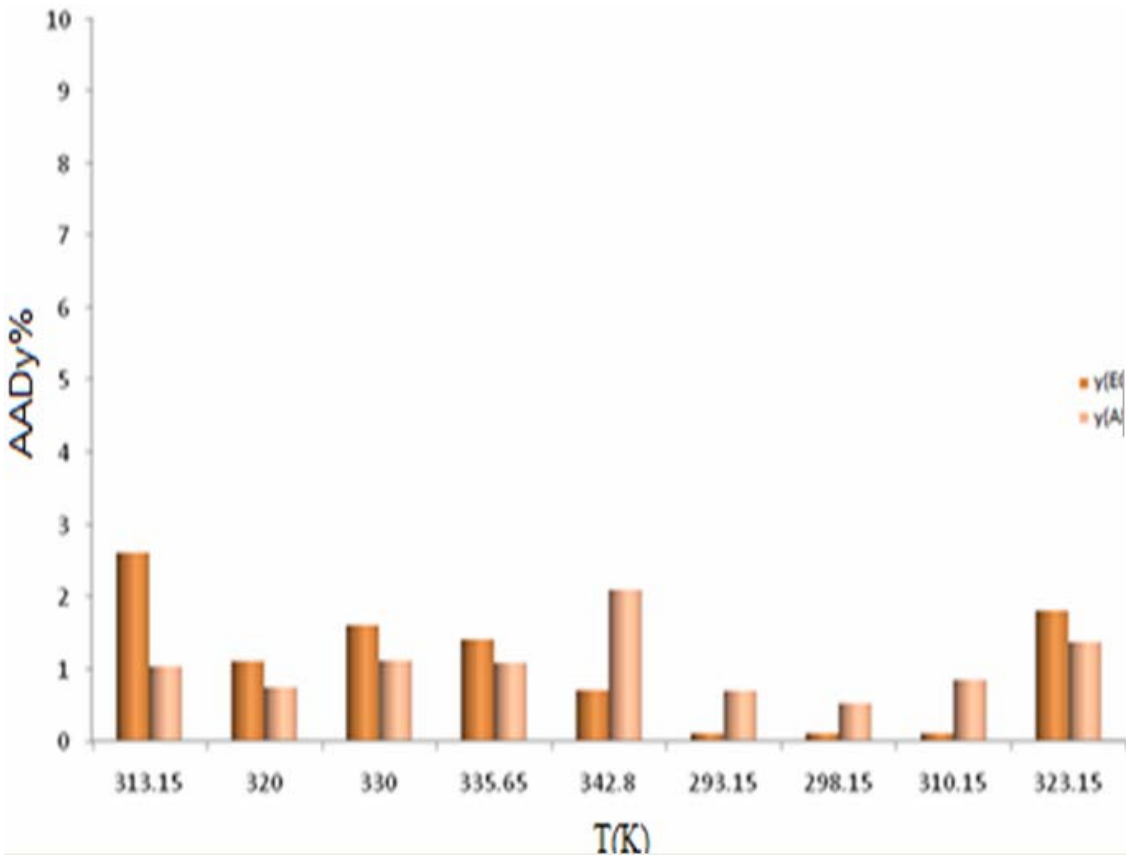

Fig. 4: Average relative error of carbon dioxide mole fraction in vapor, comparison between ANN with EOS results.

Where P_i^{exp} and y_i^{exp} are the experiment pressure and carbon dioxide mole fraction in vapor phase, respectively. Also, P_i^{ANN} and y_i^{ANN} are the pressure and carbon dioxide mole fraction in vapor phase predicting by the ANN model, respectively. In addition, N is the number of employed data.

The absolute errors of pressure and vapor mole fraction, for the whole data set, were depicted in Fig. 5. Based on this Figure, the ANN prediction for vapor mole fraction is much more accurate than pressure. Also, the maximum error for pressure and vapor mole fraction don't exceed from 0.16 and 0.08, respectively.

Generally, ANN does not exhibit the extrapolation capability. But, a well-trained neural network is not only capable of calculating the expected outputs of any input set of training data, but should also be able to forecast with an satisfactory degree of accuracy the outcome of any unfamiliar set of input located within the range of training data. Many other VLE data for the carbon dioxide-methanol systems have been published in literature [11-17]. In order to show the ANN model capability for prediction of VLE data at other temperature, the model was further validated with some unseen experimental data from the mentioned literature. This comparison for the temperature range from 290 to 310K was shown in Fig. 6, and for temperature ranges from 310K to 350K was shown in Fig. 7. The red plus sign in these Figures are the experimental data and the black plus sign are the ANN results. The results indicate that ANN model not only predict reasonably the train, test and validation data, but also well model the unseen experimental data in the literature. Taking a closer look to these Figures it is concluded that unlike cubic equation of state that cannot predict the critical region of VLE data, the ANN has well results in this region. As obtaining the VLE data close to critical point is very difficult than low pressure region, ANN can be taken into account for obtaining the required data at the high pressure without need to any additional experiments.

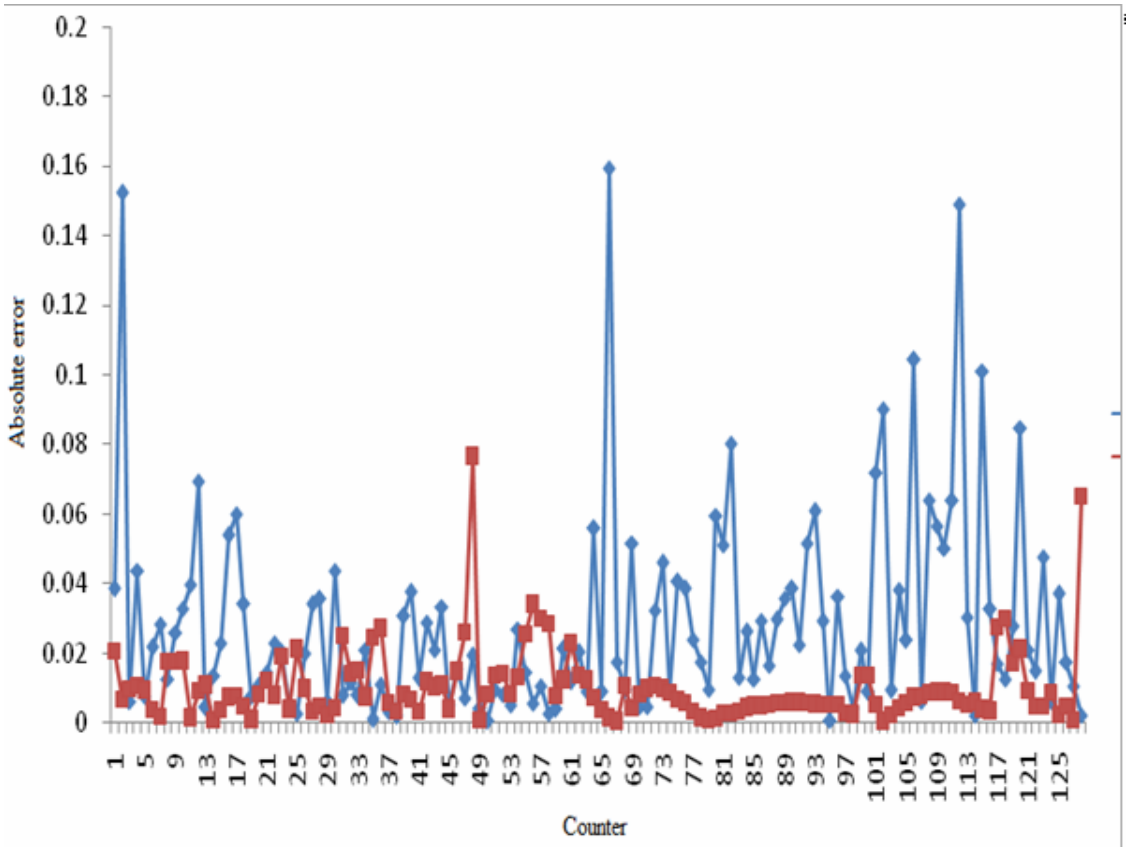

Fig. 5: Absolute error of ANN model in pressure and vapor mole fraction for the whole experimental data.

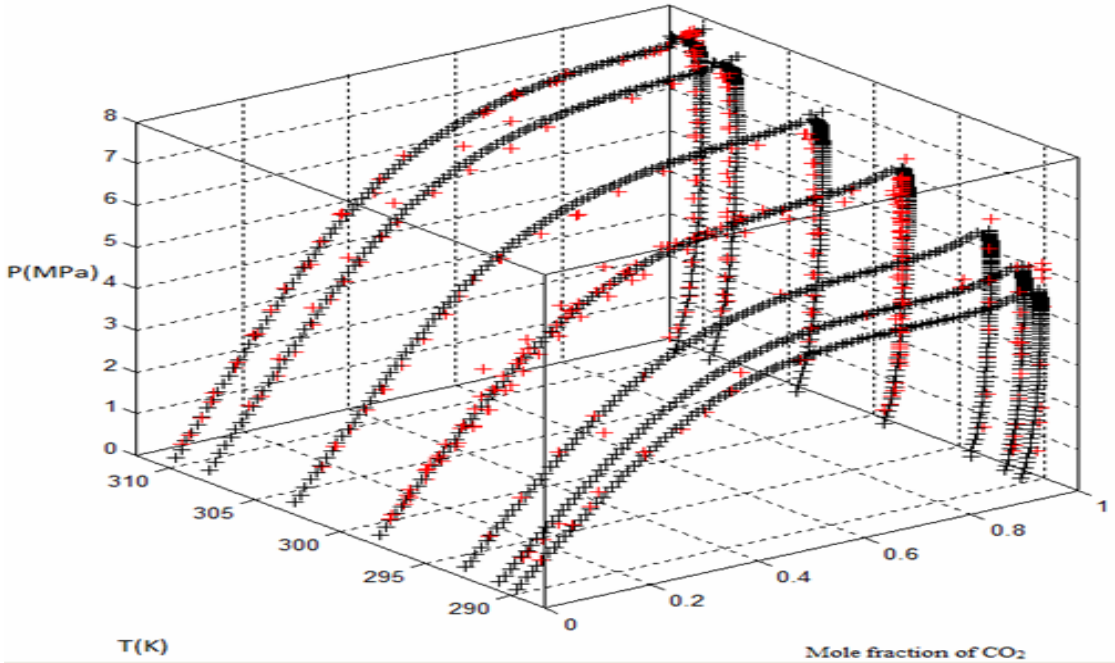

Fig. 6: Vapor liquid equilibria of carbon dioxide-methanol system, comparison between ANN results (black plus sign) with experimental data (red plus sign) at 290K to 310K.

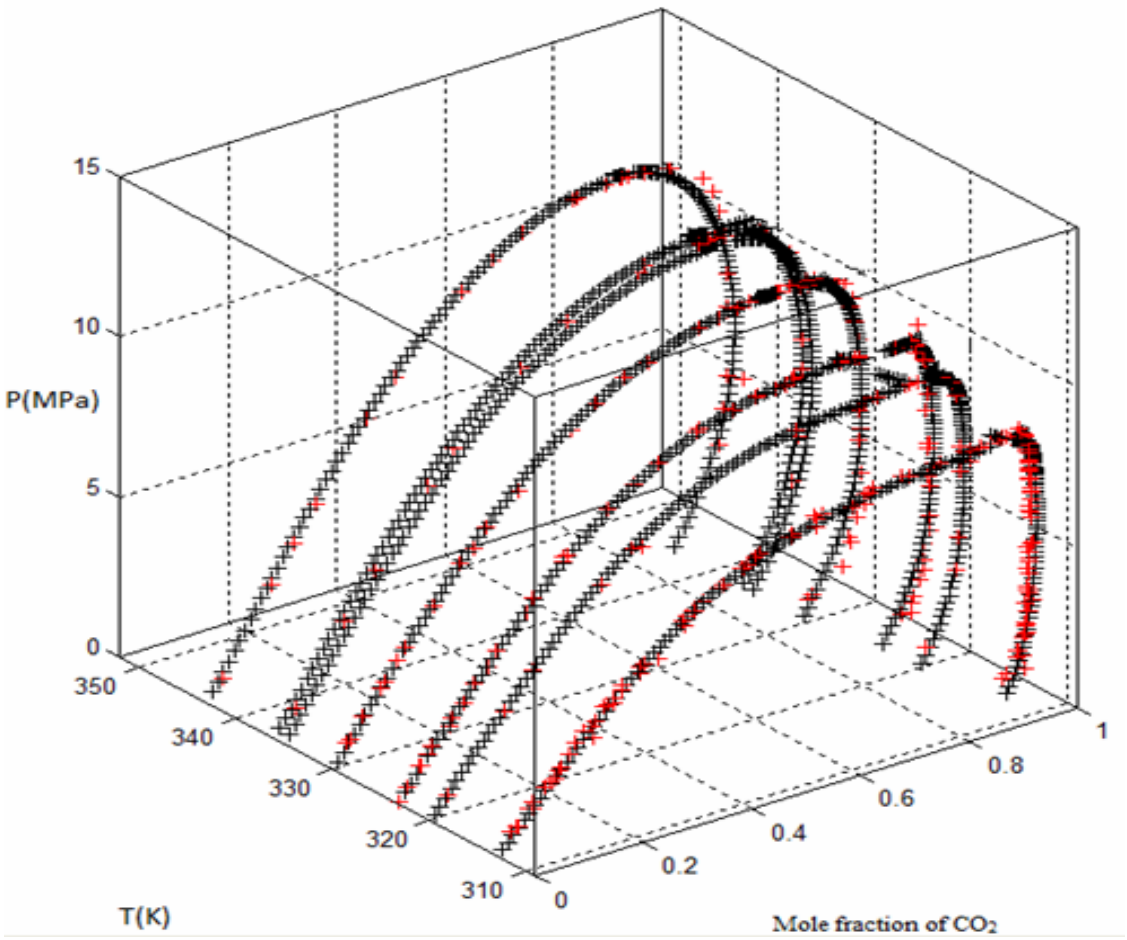

Fig. 7: Vapor liquid equilibria of carbon dioxide-methanol system, comparison between ANN results (black plus sign) with experimental data (red plus sign) at 310K to 350K.

Experimental

Vapor-Liquid Experimental Data

In this paper, carbon dioxide – methanol experimental data of Joung *et al.* [9] and Seuianu *et al.* [10] have been used for developing an ANN model. These data are presented in Table-1 and Table-2.

Although a detailed description of the experimental apparatus was presented by both authors groups, the authors briefly explain the measurement method of VLE data by Seuianu *et al* [10]. Here as it carried out recently. The main part of the experiment apparatus was a visual cell with two sapphire windows and variable volume. The internal loop of the equipment includes an equilibrium cell that was evacuated with a vacuum pump. The cell was charged with methanol; after that, it was heated to the experimental temperature and was pressurized with carbon dioxide to the experimental pressure. The mixture in the cell was stirred for a few hours. Then samples of the liquid and vapor phase were collected by depressurization and expansion into glass traps, by using manually operated valves. The amount of carbon dioxide in each phase was obtained by expansion in a glass bottle of calibrated volume [10].

ANN Structure

In this paper, the calculations were done by the bubble P method. In this method, pressure and the mole fractions of the components in vapor phase, at given temperature and liquid phase mole fraction, are obtained. So, the ANN architecture contains two inputs, temperature and liquid mole fraction, and two

outputs, pressure and vapor mole fraction. In order to obtain accurate ANN results, the parameters that influence the ANN performance such as number of hidden layers, number of hidden layer's neuron and learning rate were optimized. Choosing a suitable number of neurons in the hidden layers is very important aspect in the neural networks. Using too many neurons will raise the training time and may leads to the over fitting problem. On the other side, using smaller number hidden neurons increases the probability of learning algorithm becoming trapped in a local minimum [18]. Selection of the optimal ANN parameters was performed by systemically changing its value in the training step. Another important parameter in ANN design is the type of transfer functions. Different transfer functions, including hardlim, tansig, logsig, poslin, satlin and purelin, were employed for neurons in the different layers. These transfer functions were examined in each layer separately and with respect to the mean squared error of the testing data the best transfer functions were chosen. Finally, tansig for hidden layers and purelin for output layer gave the best performance compared to other activation functions. A network with a architecture that depicted in Fig. 8 was found to yield the most accurate results after several configurations were examined with different number of hidden layers each having different number of neurons in them.

The weights and biases which determine the employed ANN in the present study were presented in Table-3.

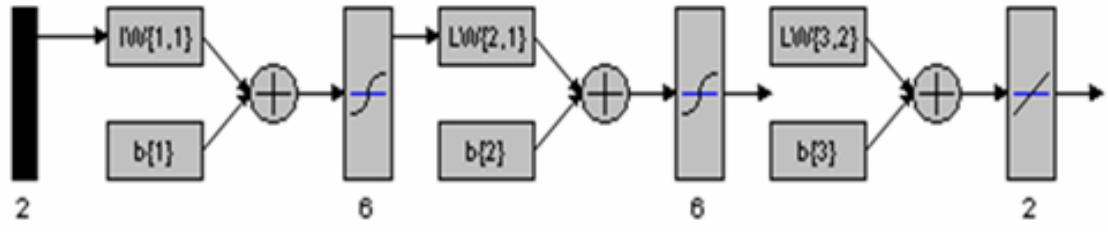

Fig. 8: Schematic of the current multi-layer feed forward neural network model.

Table-1: Vapor–liquid equilibrium data for CO_2 (1)–methanol (2) system obtained by Joung *et al*. [7].

T(K)	P(MPa)	x(-)	y(-)	T(K)	P(MPa)	x(-)	y(-)
313.15	0.69	0.0424	0.0977	335.65	0.84	0.0336	0.8592
313.15	2.73	0.1479	0.9781	335.65	3.08	0.1208	0.9502
313.15	3.78	0.2199	0.9832	335.65	4.41	0.1768	0.9620
313.15	5.60	0.3546	0.9857	335.65	6.52	0.2760	0.9671
313.15	6.57	0.4555	0.9846	335.65	7.44	0.3247	0.9664
313.15	7.84	0.7651	0.9757	335.65	9.32	0.4471	0.9583
313.15	7.93	0.8218	0.9743	335.65	10.28	0.5330	0.9466
313.15	7.99	0.8968	0.9745	335.65	11.15	0.6651	0.8948
313.15	8.06	0.9147	0.9688	335.65	11.25	0.6762	0.8901
313.15	8.10	0.9298	0.9635	335.65	11.44	0.7759	0.8250
313.15	8.12	0.9350	0.9452	335.65	11.45	0.7925	0.8059
313.15	8.15	0.9351	0.9351	335.65	11.46	0.7940	0.7940
320.15	0.60	0.0326	0.9150	342.80	0.67	0.0247	0.7999
320.15	2.69	0.1371	0.9717	342.80	3.13	0.1145	0.9403
320.15	3.70	0.1913	0.9778	342.80	4.20	0.1553	0.9510
320.15	5.72	0.3166	0.9815	342.80	5.23	0.1961	0.9559
320.15	6.50	0.3750	0.9804	342.80	7.37	0.2909	0.9586
320.15	8.14	0.5505	0.9738	342.80	8.40	0.3427	0.9574
320.15	8.62	0.6757	0.9662	342.80	10.41	0.4664	0.9432
320.15	8.85	0.8053	0.9484	342.80	11.10	0.5234	0.9312
320.15	8.88	0.8287	0.9441	342.80	11.64	0.5806	0.9108
320.15	8.93	0.8791	0.9010	342.80	12.23	0.6792	0.8498
320.15	8.95	0.8860	0.8860	342.80	12.21	0.6719	0.8526
				342.80	12.37	0.7311	0.8026
330.00	0.78	0.0346	0.8857	342.80	12.39	0.7603	0.7720
330.00	2.24	0.0960	0.9537	342.80	12.40	0.7610	0.7610
330.00	3.12	0.1342	0.9610				
330.00	5.17	0.2365	0.9717				
330.00	6.07	0.2845	0.9725				
330.00	8.90	0.4836	0.9647				
330.00	9.42	0.5382	0.9584				
330.00	10.22	0.6779	0.9438				
330.00	10.48	0.7401	0.8777				
330.00	10.55	0.7694	0.8619				
330.00	10.57	0.8215	0.8572				
330.00	10.59	0.8243	0.8243				

Table-2: Vapor–liquid equilibrium data for CO_2 (1)–methanol (2) system obtained by Seuianu *et al*. [8].

T(K)	P(MPa)	x(-)	y(-)	T(K)	P(MPa)	x(-)	y(-)
293.15	0.79	0.0582	0.9842	310.15	0.48	0.0254	0.9404
293.15	1.55	0.1185	0.9932	310.15	1.56	0.0846	0.9788
293.15	2.42	0.1884	0.9951	310.15	2.15	0.1303	0.9835
293.15	3.1	0.2572	0.996	310.15	2.73	0.1609	0.9857
293.15	3.77	0.351	0.9967	310.15	3.22	0.1933	0.9872
293.15	5.03	0.6079	0.9969	310.15	3.68	0.219	0.9878
293.15	5.72905	1	1	310.15	4.09	0.2556	0.9884
				310.15	4.6	0.2859	0.9894
298.15	0.5	0.0337	0.9595	310.15	5.14	0.3241	0.9892
298.15	0.6	0.0375	0.9725	310.15	5.18	0.3282	0.989
298.15	0.99	0.0654	0.9815	310.15	5.78	0.3984	0.9888
298.15	1.1	0.0715	0.9835	310.15	6.24	0.4416	0.9884
298.15	1.48	0.0989	0.9883	310.15	6.82	0.5905	0.9871
298.15	1.58	0.1092	0.9888	310.15	7.12	0.6474	0.9864
298.15	1.75	0.1257	0.9892	310.15	7.16	0.6502	0.9856
298.15	2.01	0.1394	0.9898	310.15	7.21	0.7183	0.9852
298.15	2.3	0.1662	0.9904	310.15	7.33	0.7491	0.9844
298.15	2.68	0.1925	0.9912	310.15	7.58	0.9624	0.9826
298.15	3.06	0.2252	0.992	310.15	7.6	0.9683	0.983
298.15	3.35	0.2438	0.9924				
298.15	3.56	0.2722	0.9926	323.15	1.03	0.0383	0.9298
298.15	3.79	0.2814	0.9927	323.15	2.2	0.0982	0.9693
298.15	3.86	0.2946	0.9929	323.15	3.86	0.1784	0.982
298.15	4.29	0.3444	0.993	323.15	5.12	0.2479	0.9772
298.15	4.53	0.3721	0.9931	323.15	6.11	0.3049	0.9793
298.15	4.55	0.3769	0.9931	323.15	7.19	0.3839	0.9739
298.15	4.67	0.3869	0.9931	323.15	8.74	0.5514	0.9731
298.15	4.92	0.4315	0.993	323.15	9.3	0.6632	0.9532
298.15	4.99	0.4446	0.9929	323.15	9.48	0.725	0.9447
298.15	5.15	0.4755	0.9928	323.15	9.51	0.8154	0.8478
298.15	5.18	0.4784	0.9928				
298.15	5.56	0.5547	0.9929				
298.15	5.61	0.5675	0.993				
298.15	5.68	0.6283	0.9929				
298.15	5.81	0.6809	0.9928				
298.15	5.86	0.6892	0.9928				
298.15	5.98	0.8281	0.9936				
298.15	5.99	0.8285	0.9938				
298.15	6.43425	1	1				

Table-3: The (2-6-6-2) ANN parameters.

	Hidden layers parameters											Output layer parameters		
	Hidden layer 1				Hidden layer 2									
n_i	IW(1,1)		b_1	m_j	IW(2,1)						b_2	m_j	IW(3,2)	
	Input1	Input2	Bias for n_i		n_1	n_2	n_3	n_4	n_5	n_6	Bias for m_i		Output 1	Output2
n_1	-0.02369	3.1222	3.2803	m_1	0.42994	1.4731	0.15366	0.3497	0.91645	-0.05061	-3.0162	m_1	1.2627	0.45493
n_2	-1.6928	1.9523	1.9527	m_2	0.12015	1.0343	-0.83241	-0.74035	0.48741	0.27313	-1.462	m_2	-0.20695	-1.2467
n_3	-2.2359	-0.50053	1.5598	m_3	-0.08415	-0.05737	-0.88943	-1.37	-0.51051	-1.677	-0.32962	m_3	0.947	0.017953
n_4	-1.0299	-0.16127	-0.27328	m_4	-0.28459	0.89202	-0.52923	0.093624	-0.23566	1.2698	1.1375	m_4	0.7249	-0.20299
n_5	-0.15004	2.6085	-1.0389	m_5	0.2927	0.40379	-0.02365	-2.061	-0.77261	-0.81854	0.61566	m_5	1.0671	1.0526
n_6	-2.4411	0.76482	-3.4252	m_6	1.092	-1.461	0.51779	-0.44063	2.3218	0.40433	1.8187	m_6	0.29054	-0.10898
											Bias for output layer		-0.72559	-0.92346

Conclusion

In this paper, the vapor liquid equilibrium data for the binary system of carbon dioxide + methanol were modeled with ANN. The experimental data set was divided into three parts: 60 % for training to adjust the parameters of the models, 20 % for validation to prevent the overtraining and 20 % for testing set to test the model. The Best neural network result has been obtained with two hidden layer network, with 6 neurons. The high accurate results between the network prediction and the corresponding experimental data prove that modeling of phase equilibrium processes using ANN is a satisfactory method. The ANN results were compared also with the results obtained by cubic equations of state in the literature. The comparison showed that unlike cubic equation of state that cannot predict the critical region of carbon dioxide + methanol VLE data, the ANN predictions were in satisfactory agreement with the literature data. As obtaining the VLE data near critical point is very difficult than low pressure region, ANN can be taken into account for obtaining the required data in this region without need to any extra experiment.

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