Application of Artificial Neural Networks and Adaptive Neuro-Fuzzy Inference Systems to Predict Activated Carbon Properties for Methane Storage

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ABSTRACT: BET surface area and micropore volume are important factors for improving methane storage in activated carbons (ACs). Specification and optimization of carbon structures are vastly examined by different researchers. However, because of complex relations between independent and dependent variables, the proposed statistical and mathematical models are not satisfactory. In this paper, the specifications of some ACs synthesized by chemical activation methods are predicted. The effects of parameters such as agent type, activation time, activation temperature, impregnation ratio and heating rate on the BET surface areas and micropore volumes of ACs are also analyzed. Two models of artificial neural networks and adaptive neuro-fuzzy interference systems are used. Later on, a number of data on other ACs reported by several researchers are used for the model validation. The obtained results from these two models are found to be satisfactory. The coefficients of determination for these models were 0.982 and 0.984, respectively. Through this modelling of AC production process, which was the main purpose of this study, the specifications of ACs may be obtained without spending extra time and expenses.

1. INTRODUCTION

In recent years, natural gas (also known as methane gas) has gained a lot of attention as a clean and affordable fuel for transportation due to various advantages, such as abundant reserves, reasonable price and being a clean fuel compared with the conventional fossil fuels (Perrin *et al*. 2004; Jhung and Chang 2009). Four various techniques suggested for methane (or natural gas) storage, namely, liquefied natural gas, compressed natural gas, adsorbed natural gas (ANG) and natural gas hydrate, have been considered to improve and modify the energy density (Ganji *et al*. 2007; Lino *et al*. 2008; Szargut and Szczygiel 2009; Kim *et al*. 2010; Bagheri and Abedi 2011). Among them, ANG on the porous materials, for example, activated carbon (AC) and zeolite, has the advantage of operating at low pressure and room temperature, allowing methane consumption comparable with the other conventional petroleum-based fuels (Pupier *et al*. 2005; Yang *et al*. 2005; Salehi *et al*. 2007; Esteves *et al*. 2008). Accordingly, it has been concluded that the proper ANG adsorbent should have the following features: (i) high adsorption capacity, (ii) high adsorption/desorption rates, (iii) being predominantly microporous with pores around 0.8 nm, that is, greater than the thickness of two methane molecules, to maximize the deliverability at ambient pressure; (iv) high packing density to ensure high storage capacity and high energy density on a volumetric basis; (v) low adsorption heat and high heat capacity to minimize changes in the vessel

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temperature during adsorption and desorption processes; (vi) good mass-transfer properties; (vii) being extremely hydrophobic and (viii) having reasonable price for the final user (Namvar-Asl *et al*. 2008a and b). ACs are regarded as versatile and fantastic adsorbents for high-performance gas storage. Their adsorptive properties, such as microporous structure, high surface area, and high degree of surface activity, are the most important and main features that make them suitable for various applications, for example, purification, decolourization, deodourization, separation, catalyst supports, battery electrodes, biomedical engineering, and also as appropriate adsorbents for methane storage (De la Casa-Lillo *et al*. 2002; Tamai *et al*. 2002; Lin and Teng 2003; Shen *et al*. 2003; Frackowiak 2007). The storing capacity of ACs depends on different parameters, such as pore size, pore-size distribution, surface area and molecular size of adsorbate (Lorenc-Grabowska and Gryglewicz 2007). Furthermore, different theoretical and statistical models are used to optimize the preparation of ACs.

Nowadays, due to the availability and reliability of data, theoretical modelling is more efficient than statistical modelling and diverse techniques of modelling are used. Artificial intelligence models, such as neural networks, fuzzy logic, and neuro-fuzzy models, are among such methods. The reason for combining neural networks with fuzzy systems is to take advantage of both statistical and theoretical methods. Neuro-fuzzy models are a combination of both neural networks and fuzzy models.

Neural networks have self-training ability, and fuzzy systems are close to human language. Because adaptive neuro-fuzzy interference system (ANFIS) is a powerful neural-fuzzy structure, which can solve non-linear problems (Al-Hinti *et al*. 2009; De Giorgi *et al*. 2011; Mohandes *et al*. 2011), it can be looked upon as an appropriate solution for non-linear predictions.

Artificial neural networks (ANNs) modelling only works with raw data, while human knowledge and experience play an important role in the ANFIS modelling. The latter method is used in this study based on the aforementioned advantage.

Neural networks and neuro-fuzzy structures have been widely used for various chemical engineering processes (Watanabe *et al*. 1989; Hoskins and Himmelblau 1992, 1998). However, neural networks have been applied only in few cases for predicting the specifications of ACs (Shahsavand and Ahmadpour 2005; Namvar-Asl *et al*. 2008a and b; Hashemipour *et al*. 2009), and ANFIS, which is used in this study, has not been applied for such an application. In addition, the parameters, which are effective in producing high surface area ACs, have been examined simultaneously through three-dimensional (3D) plots in this study.

2. LITRETURE REVIEW

Many studies have been performed on various methods of preparing ACs. Among them, chemical activation is a proper method to synthesize ACs with high surface areas for gas storage purposes (Bansal *et al*. 1988; Simitzis and Sfyrakis 1994; Ahmadpour and Do 1997; Lozano-Castelló *et al*. 2002). Recently, Ahmadpour *et al*. (2013) investigated methane storage in different ACs prepared with KOH and NaOH, and they achieved a high amount of storage equal to 176 vol/vol in comparison with previous studies. Celzard *et al*. (2007) proposed an advanced preparative strategy for the adsorptive storage of hydrogen. In their study, recent progresses in preparing suitable carbon structures are described and new routes for characterizing and correspondingly improving the micropore texture are explored. Rejifu *et al*. (2009) prepared activated carbon fibres (ACFs) with extremely high surface areas. In their results, ACF with the highest surface area showed excellent adsorptivity towards supercritical methane and hydrogen.

The amounts of CH_4 and H_2 adsorbed were enhanced by 52% and 30%, respectively, as a result of re-activation.

As mentioned previously, various models have been suggested with the aid of artificial intelligence in chemical engineering area. However, only a few studies have been carried out on modelling and simulating the process of ACs production (Shahsavand and Ahmadpour 2005; Namvar-Asl *et al*. 2008a and b; Hashemipour *et al*. 2009). Shahsavand and Ahmadpour (2005) predicted the O_2/N_2 selectivity and the amount of methane uptake of ACs by examining various parameters, such as activation temperature, activation time, BET surface area (S_{BET}) and packing density with the purpose of reaching an optimum radial basis function neural network. Namvar-Asl *et al*. (2008a and b) examined the effect of different types of raw materials, chemical agents and heating rates on the micropore volume. Hashemipour *et al*. (2009) examined the prediction of iodine numbers with the help of activation time, activation temperature and the type of gas in physical activation using the feed-forward network. Okhovat and Ahmadpour (2012) applied different models to investigate the effects of different chemical agents on pore-size distributions of ACs and they found good agreements between the modelling and the experimental results. Sales *et al*. (2012) prepared different ACs for methane storage under compression and adsorption. In their studies, mathematical models were developed to predict temperature and pressure evolutions during the gas loading. Their results showed that models with considerable pore-size distributions were the most representative of experimental data for ACs.

Aghav *et al*. (2011) used ANN for predicting the competitive adsorption of phenol and resorcinol from aqueous solution by some carbonaceous adsorbent materials, such as AC, wood charcoal and rice husk ash. They illustrated that there was a good agreement between the ANN model and the experimental results.

Dutta *et al*. (2012) applied neural network to remove textile dye direct blue 86 using microwave-assisted AC. The Levenberg–Marquardt backpropagation method was used to train the ANN at various experimental conditions. Not only there was a good agreement between the modelling and experimental results, but also the developed network was found to be useful in predicting the adsorption capacity of an unknown material at any given experimental condition (Dutta *et al*. 2012).

A feed-forward ANN was investigated and tested for modelling of equilibrium data of hydrogen onto ACs by Kumar *et al*. (2010). The constructed ANN was found to be precise in modelling the hydrogen adsorption data for all inputs during the training process. The absolute percentage deviation between the experimental and the predicted data during both training and testing process was observed to be less than 5% for majority of the input conditions (Kumar *et al*. 2010).

In another study, Ghaedi *et al*. (2013) investigated a green approach for the synthesis of copper sulphide nanoparticles added on AC and its application for the removal of reactive orange 12. In their results, fitting the experimental equilibrium data demonstrated the suitability of Langmuir isotherm.

Karimi and Ghaedi (2013) simulated the influence of variables using ANN with subsequent of application of genetic algorithm for the optimization of effective variables for some prepared ACs. Their results showed a good agreement between experimental and theoretical results.

In the modelling of AC preparation process, the empirical rules are very important. This is a point that has been ignored in the previous studies. To incorporate such important rules into the modelling process, fuzzy inference system is needed. In this work, a fuzzy inference system is combined with a neural network to create a neuro-fuzzy system of ANFIS. We have used the experience of preparing various ACs in the form of fuzzy rules in our predictions, and listed the results along with those obtained by the neural networks. It is notable to mention that, to the best

of our knowledge, a fuzzy or a neuro-fuzzy system has not already been used to model the preparation process of ACs.

In addition, until now, there is no comparison between the performances of ANN and ANFIS in determining the features of ACs. Another advantage of this research is high accuracy of the predicting results when compared with those of similar studies (Shahsavand and Ahmadpour 2005; Namvar-Asl *et al*. 2008a and b; Hashemipour *et al*. 2009).

3. MODELLING

In this study, two artificial intelligence models are used to predict methane uptake by MATLAB. Initially, a neural network model is used to predict the data, and finally the work is completed by an ANFIS model. Several parameters including chemical agent ratio, activation time, activation temperature, impregnation ratio, heating rate, soaking time, CO_2 flow rate and nitrogen flow rate have effects on increasing the BET surface area and micropore volume of ACs. However, the first five parameters (i.e. agent ratio, activation time, activation temperature, impregnation ratio and heating rate) have been found to have the most important effects in comparison with the other parameters in preparation of various ACs. Therefore, these five inputs have been chosen for the models.

It is worth noting that the type of gas and its velocity are only important in the gas storage stage and do not have effects on the preparation of ACs. Therefore, these parameters are not considered in the modelling process. The model outputs are BET surface area and micropore volume. The procedure is shown in Figure 1.

3.1. Data Acquisition and Pre-Processing

In the ANN and ANFIS models, the experimental data are usually entered into the model at a random basis. In this study, to reduce the number of errors, 52 experimental data sets are classified into three groups: 30 as the training data, 12 as the validation data and the remaining 10 sets are used to test the model. In the ANN model, the training data sets are used for modifying and adjusting weights and biases, and in the ANFIS model, they are used for specifying the membership functions and establishing the rules. The validation data are used to establish both models and finally, the testing data are applied for testing. Because preparation and characterization of AC samples are expensive and time consuming, and due to diversity of raw

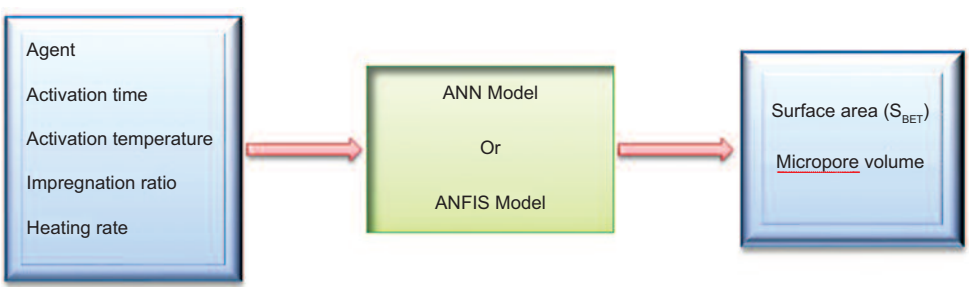

Figure 1. Block diagram of the calculation procedure.

materials, the experimental data are extracted from the literature. Table 1 lists the data of cellulose-based ACs (Ahmadpour and Do 1997; Hayashi *et al*. 2000; Vernersson *et al*. 2002), and Table 2 lists the data of coke-based ACs formerly reported in the literature (Ahmadpour and Do 1996; Hsu and Teng 2000; Lozano-Castelló *et al*. 2001; Qiao *et al*. 2006).

4. ANN

ANN is a powerful network, which implements complex functions in various fields. The most applied multi-layer neural networks are known as error backpropagation networks. These networks are proved to have excellent prediction capacities and classification tasks.

4.1. Model Specification

The factors that determine the accuracy of models are related to the structures of models as well as their specifications and characteristics. The structures and specifications of the ANN and ANFIS models are as follows:

The basic parameter of a multi-layer perceptron (MLP) neural network is the artificial neuron shown in Figure 2, which performs simple mathematical operations on its inputs. The input of the neuron consists of variables $y_1, \ldots, y_n$ and a bias term. On the result obtained, a known activation function (α) performs a pre-specified (non-linear) mathematical operation (Shahsavand and Pourafshari Chenar 2007).

The MLP networks may contain many neurons ordered in layers. The neurons in the hidden layers do the actual processing, whereas the neurons in the input and output layers only distribute and gather the signals. Although many hidden layers can be used, one hidden layer networks are more popular for practical applications due to their simple structures. During the training phase, the network output is compared with a desired output. The error between these two signals is used to adapt the weights (Shahsavand and Pourafshari Chenar 2007).

Multi-layer networks with the error backpropagation algorithm are used for data modelling. There are three layers for the model, namely, an input layer, a hidden layer and an output layer. A large number of layers are allocated for the internal structure of the network. The distinction between these layers is the number of neurons of the input layers, the number of neurons in the output layers, transfer function of layer 1 and transfer function of layer 2. Table 3 illustrates the number of neurons and transfer functions used.

As seen in the table, the number of neurons in layers 1 and 2 varies between 6 and 16. Considering the output of the models, the number of neurons in the third layer is one. In addition, different transfer functions are examined for these cases. The transfer functions for the input and hidden layers are tansig, logsig, satlin and satlins. Purelin is applied for the transfer function of the output layer. Finally, the error backpropagation algorithm is used for the network training.

A fuzzy inference system is a system introduced by Zadeh, which uses if–then rules. This system is able to model quantitative parameters of quality aspects and human knowledge without using a precise qualitative analysis. Fuzzy modelling techniques can be categorized as follows: (i) linguistic (Mamdani) models, (ii) Takagi–Sugeno models and (iii) the relational equation models.

In the Mamdani fuzzy inference systems, the antecedents and consequences are totally fuzzy sets, and in the Takagi–Sugeno models, just one linear function is used in the consequent part. A way for creating a fuzzy model is to state the expert knowledge as fuzzy rules.

The ANFIS model is developed by combining neural networks and fuzzy inference systems. In fact, this model benefits from the generalization capacity and self-learning characteristic of a

TABLE 1. Collected Data of Cellulose-Based ACs from the Literature (Ahmadpour and Do 1997; Hayashi *et al*. 2000; Vernersson *et al*. 2002)

No.	Agent	Activation time (min)	Activation temperature (°C)	Impregnation ratio (R)[a]	Heating rate (°C/minute)	S_{BET} (m^2/g)	Micropore volume (cm^3/g)
1	H_3PO_4	60	400	150	3	1089	0.55
2	H_3PO_4	60	450	150	3	1104	0.56
3	H_3PO_4	60	500	150	3	1151	0.56
4	H_3PO_4	60	550	150	3	1001	0.45
5	H_3PO_4	60	400	200	3	688	0.35
6	H_3PO_4	60	450	200	3	733	0.37
7	H_3PO_4	60	500	200	3	1114	0.56
8	H_3PO_4	60	550	200	3	907	0.45
9	H_3PO_4	60	500	250	3	841	0.42
10	H_3PO_4	0	500	200	3	1333	0.67
11	H_3PO_4	15	500	200	3	1312	0.66
12	H_3PO_4	30	500	200	3	1309	0.65
13	H_3PO_4	60	500	100	10	721	0.29
14	H_3PO_4	60	600	100	10	1038	0.43
15	H_3PO_4	60	700	100	10	942	0.38
16	H_3PO_4	60	800	100	10	800	0.32
17	H_3PO_4	60	900	100	10	674	0.27
1	$ZnCl_2$	60	500	100	10	1033	0.41
2	$ZnCl_2$	60	600	100	10	1034	0.53
3	$ZnCl_2$	60	700	100	10	816	0.33
4	$ZnCl_2$	60	800	100	10	711	0.3
5	$ZnCl_2$	60	900	100	10	714	0.29
6	$ZnCl_2$	60	500	100	5	1795	0.77
7	$ZnCl_2$	120	500	100	5	1661	0.74
8	$ZnCl_2$	180	500	100	5	1624	0.71
9	$ZnCl_2$	60	600	100	5	1540	0.65
10	$ZnCl_2$	60	700	100	5	1301	0.57
11	$ZnCl_2$	60	500	23.5	5	711	0.31
12	$ZnCl_2$	60	500	50	5	895	0.4
13	$ZnCl_2$	60	500	75	5	1375	0.6
14	$ZnCl_2$	60	500	125	5	1950	0.78
15	$ZnCl_2$	60	500	150	5	2007	0.79
16	$ZnCl_2$	60	500	200	5	2500	0.87
17	$ZnCl_2$	60	500	300	5	2550	0.85
18	$ZnCl_2$	60	500	500	5	1480	0.84
1	KOH	60	600	100	10	770	0.31
2	KOH	60	700	100	10	1273	0.51
3	KOH	60	800	100	10	1531	0.6
4	KOH	60	900	100	10	1369	0.55
5	KOH	60	700	100	5	1157	0.54
6	KOH	60	600	100	5	628	0.29
7	KOH	60	800	100	5	1169	0.53
8	KOH	60	700	23.5	5	757	0.33
9	KOH	60	700	50	5	895	0.4
10	KOH	60	700	200	5	1080	0.5
11	KOH	60	700	500	5	1550	0.73

Note: Test data for the predicted model.

[a]R= Agent(g) × 100/precursor(g).

TABLE 2. Collected Data of Coke-Based ACs from the Literature (Lozano-Castelló *et al*. 2001; Hsu and Teng 2000; Ahmadpour and Do 1996; Qiao *et al*. 2006)

No.	Agent	Activation time (min)	Activation temperature (°C)	Impregnation ratio (R)[a]	Heating rate (°C/minute)	S_{BET} (m^2/g)	Micropore volume (cm^3/g)
1	$ZnCl_2$	60	500	425	30	756	0.33
2	$ZnCl_2$	60	600	425	30	822	0.39
3	$ZnCl_2$	60	700	425	30	680	0.34
4	$ZnCl_2$	60	800	425	30	663	0.32
5	$ZnCl_2$	60	500	100	5	1100	0.48
6	$ZnCl_2$	180	500	100	5	990	0.45
7	$ZnCl_2$	60	600	100	5	814	0.36
8	$ZnCl_2$	60	700	100	5	763	0.38
9	$ZnCl_2$	60	800	100	5	600	0.23
10	$ZnCl_2$	60	500	150	5	1300	0.54
11	$ZnCl_2$	60	500	200	5	1400	0.56
1	KOH	60	800	400	5	2454	1.25
2	KOH	60	800	500	5	2759	1.28
3	KOH	60	800	600	5	2906	1.39
4	KOH	60	800	700	5	2750	1.30
5	KOH	60	600	425	30	1768	0.75
6	KOH	60	700	425	30	2269	0.99
7	KOH	60	800	425	30	3281	1.57
8	KOH	60	700	300	5	2758	0.72
9	KOH	60	700	400	5	3290	0.81
10	KOH	60	700	500	5	3183	0.73
11	KOH	60	800	200	5	2085	0.96
12	KOH	30	700	200	5	1784	0.8
13	KOH	120	700	200	5	2111	0.91
14	KOH	60	700	200	5	3290	1.45

Test data for the predicted model.

[a]R= Agent(g) × 100/precursor(g).

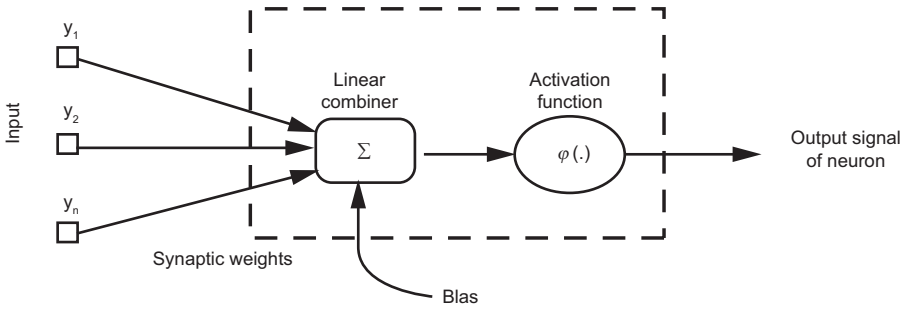

Figure 2. Schematic representation of a projection-based neuron.

neural network along with the knowledge representation by fuzzy logic. The ANFIS structure consists of five layers, which are depicted in Figure 3. The first hidden layer is used to map the input variable relative to each membership function. In the second layer, the T-norm agent is used for the antecedent of rules.

TABLE 3. Characteristic of ANN Models Used in This Work

Transfer function of layer 2	Neuron of layer 2	Transfer function of layer 1	Neuron of layer 1
Tansig Logsig Satlin Satlins	6–16	Tansig Logsig Satlin Satlins	6–16

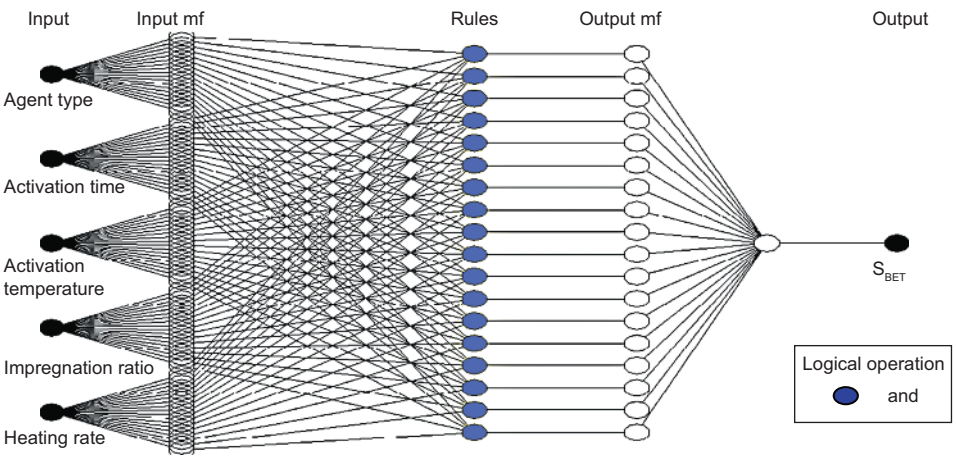

Figure 3. Structure of the proposed ANFIS model for predicting BET surface area of ACs.

$$O_i^2 = \omega_i = \mu_{Ai}(x)\mu_{Bi}(y) \qquad (i=1,2) \tag{1}$$

where μ_{Ai} is the membership grade of x in A_i fuzzy set and μ_{Bi} is the membership of y in fuzzy set of B_i. The third hidden layer makes the rules strengths normal. Next, the fourth hidden layer comes, which determines the consequents of the rules.

$$O_i^3 = \omega_i^n = \frac{\omega_i}{\omega_1 + \omega_2} \qquad (i=1,2) \tag{2}$$

$$O_i^4 = \omega_i^n f_i = \omega_i^n (p_i x + q_i y + r_i) \qquad (i=1,2) \tag{3}$$

In equations (2 and 3), r_i, q_i and p_i are adaptive parameters of the fourth layer and are entitled *consequent parameters*. Finally, the last layer determines the related output (or global output) by calculating the total number of all received signals to this layer.

$$O_1^5 = \sum_{i=1}^{2} \omega_i^n f_i = \frac{\omega_1 f_1 + \omega_2 f_2}{\omega_1 + \omega_2} \qquad (i=1,2) \tag{4}$$

TABLE 4. Characteristic of the ANFIS Model Used in This Work

Characteristic	Type
Defuzification	Weight average
And method	Prod
OR method	Probor
Train method	Hybrid algorithm

ANFIS uses two algorithms of error and backpropagation and a hybrid method for training the adaptive neuro-fuzzy network. In the first stage, the input patterns are propagated and the parameters of consequents are measured using the iterative minimum squared method algorithm. However, the parameters of the premises are regarded fixed. Second, the input patterns are propagated again, and within each iteration, the backpropagation learning algorithm is applied to modify and improve the parameters of the premises, while the consequents remain fixed.

In this study, the fuzzy clustering algorithm method is used to reach the optimized fuzzy rules. The subtractive clustering method is an expansion of the mountain clustering method (Yager and Filev 1994). When there is no obvious idea on how many clusters should be there for a given set of data, subtractive clustering can be regarded as a fast, one-pass algorithm for estimating the number of clusters and the cluster centres in a set of data. The subtractive clustering method assumes that each datum is a potential cluster centre and estimates the likelihood of each data point being distinguished as the cluster centre, based on the density of the surrounding data points.

4.2. ANFIS Structure

The features of the created ANFIS structure are addressed in Table 4. This includes the operator types in the training structure and the learning method. Training the model leads to a multi-layer fuzzy neural network illustrated in Figure 3. It shows the diagram for the internal layers of the ANFIS model.

In Figure 3, the selected ANFIS structure has five inputs (agent type, agent ratio, activation temperature, activation time and nitrogen flow) and one output (BET surface area). A Gaussian function is used as the membership function for all inputs and the hybrid learning is used to have a fast identification of the parameters. Based on the data presented in Tables 1 and 2, the created rules through clustering, which are used in the ANFIS model, are divided into three main groups. The first group, which contains clusters 1–6, is related to carbons activated with H_3PO_4 from low to high amounts of various parameters. The second group is related to carbons activated with $ZnCl_2$ and consists of clusters 7–12 and the third group is related to carbons activated with KOH and contains clusters 13–18.

5. RESULTS AND DISCUSSION

5.1. Predicted Specifications for ACs Produced from a Cellulose-Based Precursor

Different ANN and ANFIS structures are trained to find the proper model. Three types of errors [mean square error (MSE) of training, MSE of validation and MSE of testing] besides the coefficient of determination (R^2) are used to indicate the accuracy of the models.

5.2. ANN Results

In modelling the process of AC preparation with the ANN method, two models with better results and accuracy are chosen. Table 5 shows the specifications of these two models. In Figure 4, the amounts of error for training, validation and test data for both models are illustrated. The best values of correlation coefficients (R) for predicting surface area (S_{BET}) and micropore volume are 0.99347 and 0.95736, respectively (Figure 5).

TABLE 5. Specifications of Two ANN Models

	Neuron of layer 1	Transfer function of layer 1	Neuron of layer 2	Transfer function of layer 2	Training method
Model 1	9	Tansig	14	Logsig	Trainlm
Model 2	7	Tansig	14	Logsig	Trainlm

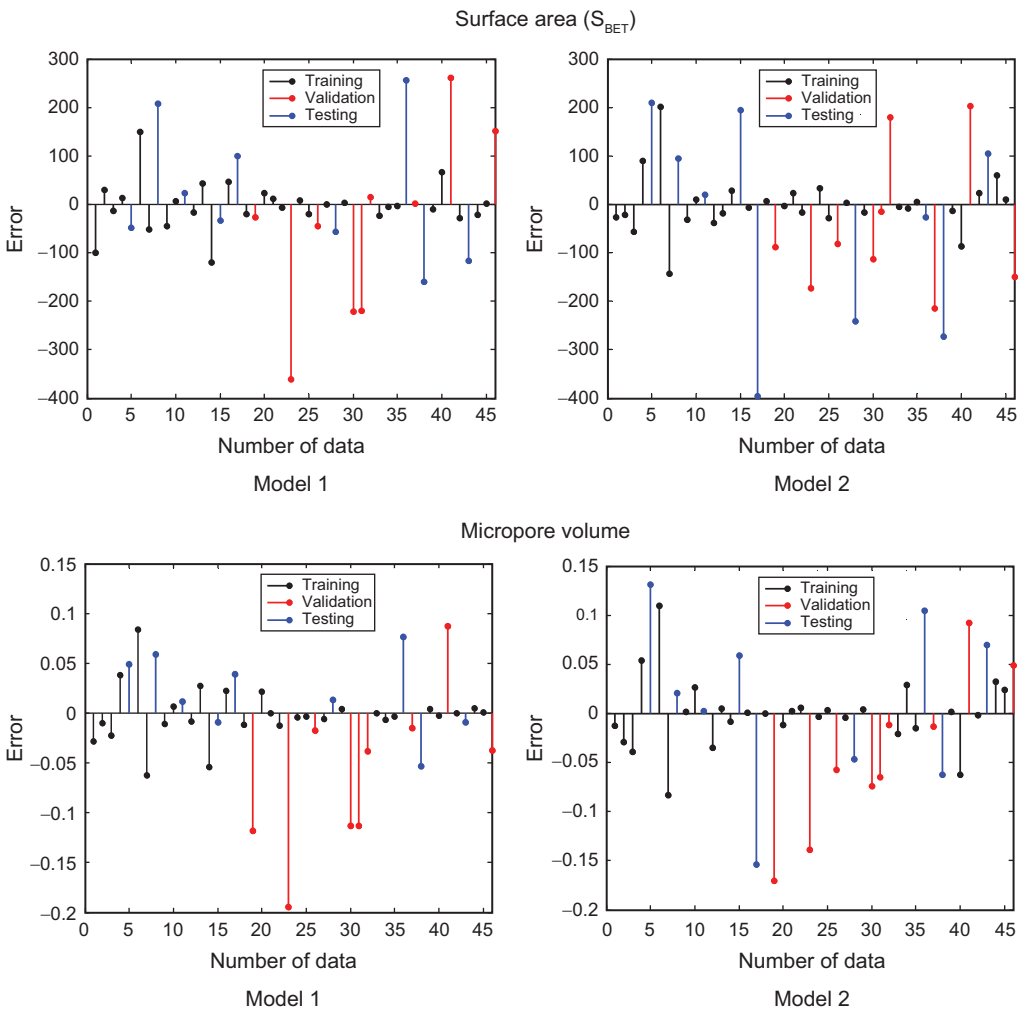

Figure 4. Amounts of error for training, validation and test data.

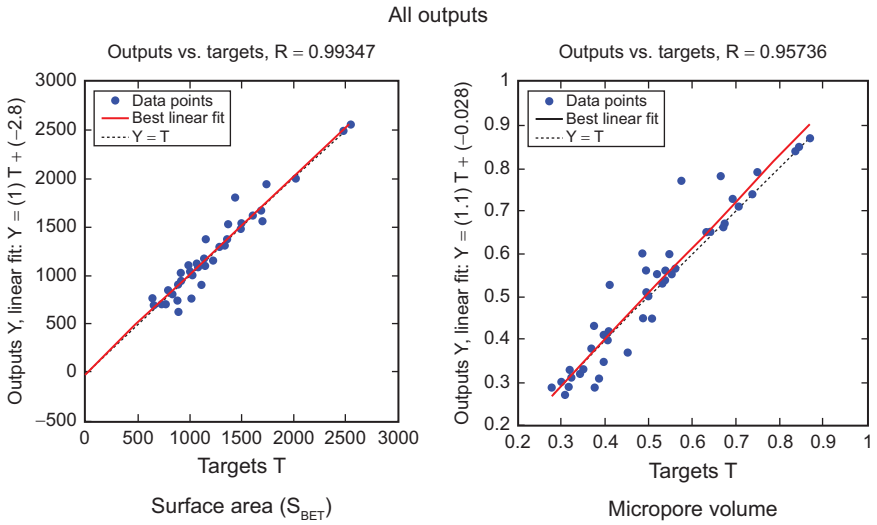

Figure 5. Trend of all outputs values versus targets for both models.

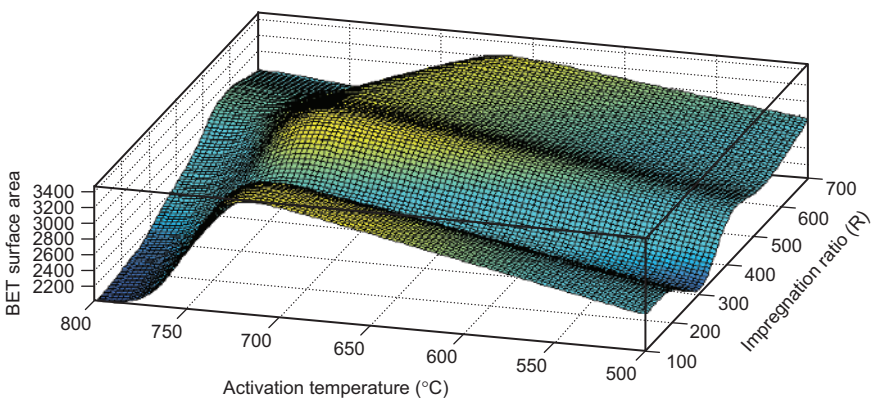

Figure 6. S_{BET} versus activation temperature and KOH impregnation ratio at an activation time of 60 minutes and heating rate of 5 °C/minute.

5.3. ANFIS Results

The following information is obtained from the analysis of 3D plots of ANFIS modelling done on AC with cellulosic base. Figure 6 shows S_{BET} versus activation temperature and impregnation ratio. This figure is plotted for KOH agent for an activation time of 60 minutes, when the heating rate is 5 °C/minute. As it can be seen, with an increase in temperature between 700 and 750 °C, S_{BET} also increases, but at higher temperatures, S_{BET} declines. This is because by increasing the temperature, the formation of salt ions in pores reaches its highest limit; after preparation of carbon and washing the sample, it produces the highest number of micropores. When the temperature exceeds this limit, some of the micropores will deform, which leads to the decline of S_{BET}.

As depicted in Figure 6, at the temperature of 800 °C, the best impregnation ratio that leads to the highest S_{BET} is 600. The reason is that the penetration of KOH agent into the pores is maximized in this ratio and, consequently, the micropores reach their largest volume resulting in

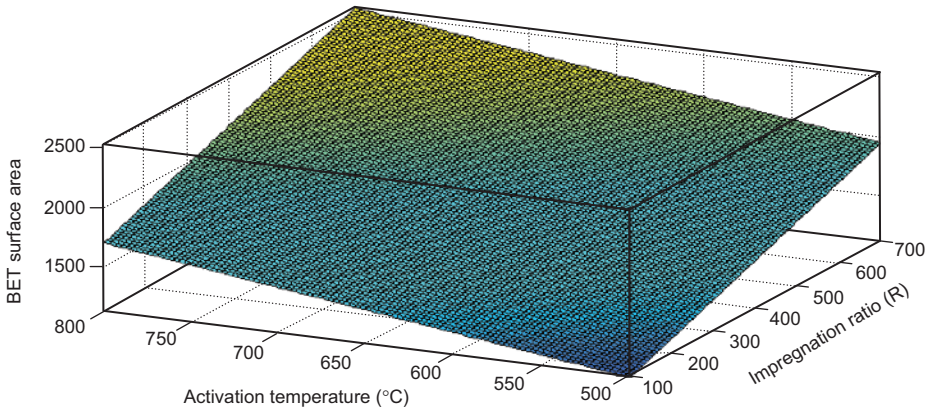

Figure 7. S_{BET} versus activation temperature and KOH impregnation ratio at an activation time of 60 minutes and heating rate of 30 °C/minute.

high amount of surface area. In other temperatures, the trends predicted by the model are different. In the temperature range below 750 °C, with an increase in impregnation ratio, the trends of S_{BET} changes are in the way that with an increase in impregnation ratio up to 300, the S_{BET} declines, then if the impregnation ratio reaches to the range of 300–450, S_{BET} increases as well. Eventually, when the impregnation ratio exceeds 450, there will be no effect on S_{BET}. This can be justified as follows: in impregnation ratios below 300, KOH is not able to create micropores, but when the impregnation ratio increases, potassium gradually penetrates into the structure and creates micropores. However, when impregnation ratios are greater than 450, increase in the impregnation ratio will have no effect on the volume of micropores, and consequently, there will be no more increase in the surface area.

In Figure 7, the condition is same as Figure 6 with a difference that the heating rate is 30 °C/minute. It is obvious that with a rapid increase in temperature and upon approaching the activation temperature, there is no time for pores to become larger in size. Consequently, the volume of the produced pores increases, and further increase in temperature and impregnation ratio results in enhancement of surface area for different ratios and temperatures.

Figure 8 shows the behaviour of carbons activated with $ZnCl_2$ agent at the fixed conditions of 60-minute activation time and heating rate of 5 °C/minute. As shown in the figure, with an increase in activation temperature between 500 and 550 °C, S_{BET} reaches its maximum value, and beyond this limit it decreases. The reason is that $ZnCl_2$ as a chemical substance makes mainly mesopores, which are medium-sized pores. Therefore, with an increase in temperature, the volume of mesopores increases as well, and as a result, the total volume of pores and S_{BET} decline.

In the temperature range of 500–600 °C, with an increase in $ZnCl_2$ and impregnation ratio, because the activation temperature of Zn is low, it creates small volume mesopores. Thus, the active surface area increases. However, in temperatures above 800 °C, due to the rapid reaction of $ZnCl_2$ with the raw material, bigger mesopores are created which decrease surface areas.

Maintaining the conditions of Figure 8, and increasing the heating rate from 5 to 30 °C/minute, different results are obtained (Figure 9). For an agent ratio of 300, for an increase in temperature to 700 °C, S_{BET} increases, as there is not enough time for creating mesopores. However, at 700 °C,

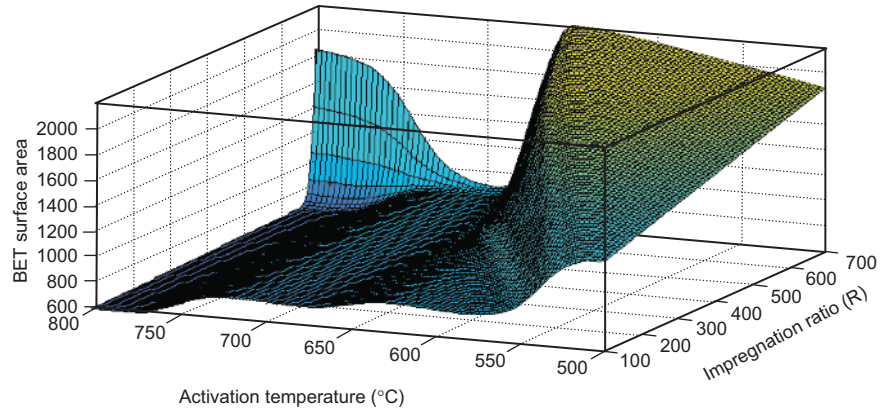

Figure 8. S_{BET} versus activation temperature and $ZnCl_2$ agent ratio at an activation time of 60 minutes and heating rate of 5 °C/minute.

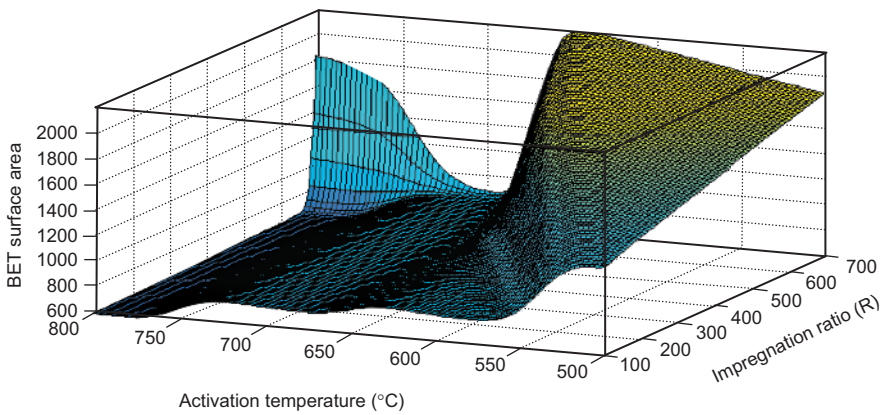

Figure 9. S_{BET} versus activation temperature and $ZnCl_2$ agent ratio at an activation time of 60 minutes and heating rate of 30 °C/minute.

due to high temperature and high heating rate, $ZnCl_2$ produces more mesopores in comparison with those at lower temperatures, and consequently, S_{BET} and volume of mesopores decline.

Figure 10 shows the effect of activation time on ACs surface area, maintaining activation temperature at 500 °C and heating rate at 5 °C/minute for $ZnCl_2$ agent. Changing the S_{BET} in this figure can be justified considering that with activation times of less than 2 hours, the amounts of micropore and mesopore formation are almost equal, and thus the surface area does not change noticeably. However, after 2 hours of activation, with an increase in the burning rate, the volume of mesopores increases. Moreover, change of many pores from micro to meso causes the microporosity to diminish. These two factors decrease S_{BET}.

5.4. ANFIS Prediction for ACs Produced from a Cellulose-Based Precursor

The data of BET surface areas for ACs produced from a cellulosic base are plotted against their values obtained from the model and shown in Figure 11. The figure illustrates high accuracy of the proposed model in predicting S_{BET} values.

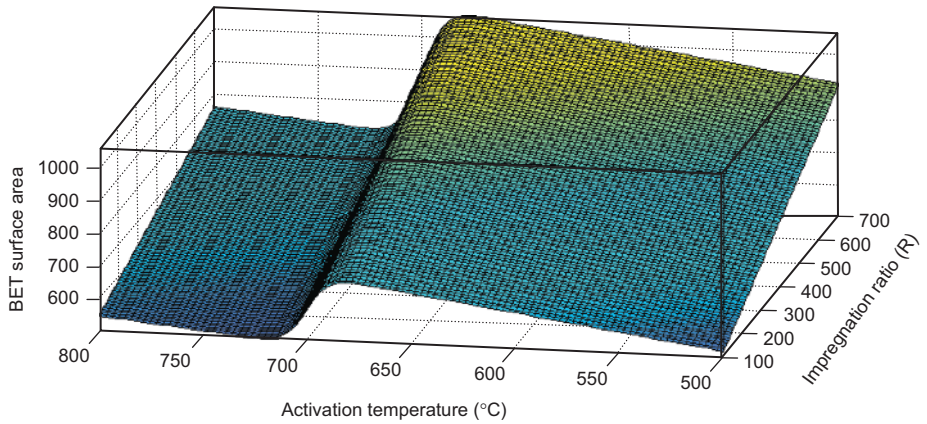

Figure 10. S_{BET} versus activation time and $ZnCl_2$ agent ratio at an activation temperature of 500 °C and heating rate of 5 °C/minute.

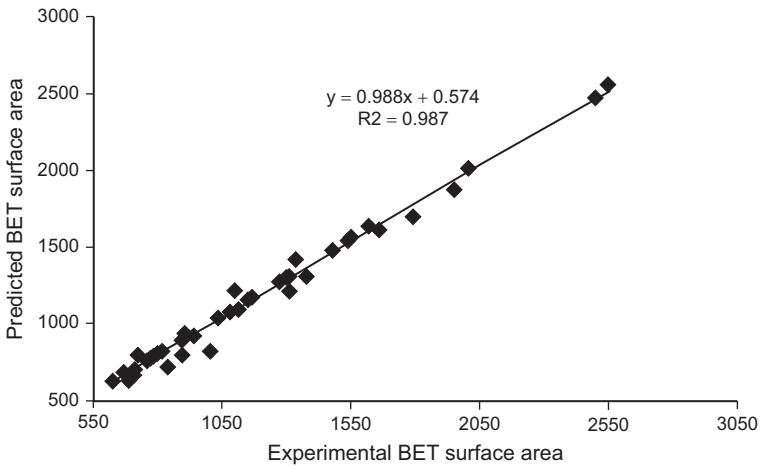

Figure 11. Comparison of the predicted and real S_{BET} data for ACs produced from a cellulose-based precursor.

6. CONCLUSIONS

In this study, ANFIS and neural networks are used to numerically assess the effective parameters in AC preparation process. At first, all effective parameters are analyzed, and then five more important parameters including agent type, activation time, activation temperature, impregnation ratio and heating rate are selected. Then, modelling is done with the aid of neural networks and ANFIS for producing ACs with coke and cellulosic bases. The accuracy of the models in predicting the specifications of produced AC is considerable. It is also demonstrated that the methods applied in this work are far better than the popular statistical methods. This study can be a new approach for economical production of ACs without spending time and expenses for doing extra tests between the applied ranges of parameters. This kind of modelling can also be helpful for other similar cases.

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