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CONNECTION BETWEEN Co/MCM-48 CATALYST SYNTHESIS CONDITIONS AND PERFORMANCES IN THE STEAM REFORMING PROCESS THROUGH ARTIFICIAL NEURAL NETWORK

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Artificial neural network was used to decide an optimum Co/MCM-48 catalyst to obtain hydrogen through steam reforming of ethanol establishing the connection between catalyst synthesis conditions, catalyst characteristics and catalyst performances. Artificial neural network could predict the performances of Co/MCM-48 catalysts in terms of ethanol conversion and hydrogen yield. The optimal hydrogen yield was 61.77% and ethanol conversion 85.31%. The optimal catalyst was the one prepared for a stirring synthesis time of 15 h and 560^0C calcinations temperature which involves a higher thermal stability.

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1. Introduction

Hydrogen continues to be an important energy carrier for the future due to is low impact on the environment and its potential as a fuel for more efficient energy conversion.

In this way fuel cell oriented hydrogen production from ethanol reforming has attracted great interest. Ethanol especially can be easily produced in renewable form, from several biomass sources, and does not contribute to the global warming, releasing the same amount of carbon dioxide as that absorbed by the biomass.

Production of hydrogen by steam reforming of ethanol has been investigated over time by using different catalytic systems.

Kumar et al. [1] suggested that the nature of metal and support contributes the selection of path for hydrogen generation. The highly acidic nature of the support aided dehydration of ethanol whereas basic nature or addition of promoters inhibited dehydration and deactivation of catalysts by coke deposition.

Batista et al. [2] studied steam reforming of ethanol at 400^0C on Co/Al_2O_3 and Co/SiO_2catalysts with a cobalt content of 8 and 18% wt. respectively. The catalysts showed average conversion higher than 70% for the steam reforming of ethanol. The increase of ethanol conversion and reduction of the amount of liquid products were observed for the catalysts with higher cobalt contents.

Profeti et al. [3] investigated the performances of Co/Al_2O_3 promoted with small amounts noble metals (Pt, Pd, Ru, Ir) for steam reforming of ethanol. The better catalytic performances for ethanol steam reforming at 400^0C was obtained for the Co-Ru/Al_2O_3 catalyst, which presented an effluent gaseous mixture with the highest H_2 selectivity and reasonable low CO formation.Metal-supported catalysts have exhibited catalytic ability in steam reforming process. Overall supported cobalt catalysts exhibited excellent activity toward oxidation [4,5].

Sohn et al. [6] realized an overview of the research conducted on ethanol steam reforming using the Co/CeO_2 catalyst. The role of the support oxygen mobility and storage capacity of the Co/CeO_2 catalyst and how the addition of Co changes the oxygen vacanciesin the catalyst structure was discussed. They investigated how the synthesis parameters such as synthesis method,

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impregnation medium, choice of cobalt precursor, support morphology could affect the catalytic activity.

The synthesis of a new family of mesoporous molecular sieves with regular and constant pore diameter from 2 to 10 nm designated as M41S was reported in 1992 by the scientists at Mobil Oil Corporation. For all of that MCM-41 is the most utilizable silica in different type of applications [7-9] followed by SBA-15 in important processes like this studied ethanol steam reforming [10]. MCM-48 silica has been found to possess a bi continuous structure attractive for applications in adsorption, catalysis, chromatography, gas separation [11]. The use of new promoter species, such as Mn oxide with Co as the main catalytic ingredient on MCM-48 support was attempted for high hydrogen generation in ethanol steam reforming.

Lee et al.[12] examined hydrogen production by ethanol steam reforming over Mn/Co-Si-MCM-48 catalyst. The authors concluded that the catalytic performance varied according to the loaded metal oxide species and the presence or absence of Co ions in the Si-MCM-48 framework.

Su et al. [13] studied the hydrogen production from ethanol steam reforming over Ni-Zr loaded MCM-48. These Ni-Zr/MCM-48 catalysts exhibited significantly superior performances than Ni/MCM-48 catalyst, which were maintained for up to 60 h.

Despite of it all, even thought Co/MCM-48 catalyst seems to be active catalyst, the connection between catalyst synthesis conditions, catalyst characteristics and performance in the steam reforming of ethanol for hydrogen production have not been certain explained. In our previous work [14] we attempted to evaluate the optimum synthesis conditions of MCM-48 support for this kind of process.

Additionally, it cannot be ensured that these optimal synthesis conditions will be reached. However is essential to establish a method, which can take into account all catalyst properties in order to determine the optimum conditions.

ANN (artificial neural network) can be an important instrument for applications in process engineering. The application of ANN in catalysis and in chemical engineering has been reported in the literature.

Huang et al. [15]use the artificial neural network to simulate the relations between components of catalyst and aspects of catalytic performance, which include C_2 selectivity and conversion of methane.

Hou et al. [16] applied ANN to design a VSbWSn (P, K, Cr, Mo)/SiAl catalyst for acrylonitrile synthesis via propane. The conversion of propane and selectivity of acrylonitrile can be calculated as functions of the catalyst components by the ANN.

Watanabe et al. [17] use ANN to develop a catalyst for methanol synthesis from syngas. After training, the ANN can map the catalyst activity as function of catalyst composition and parameters for catalyst preparation.

2. Application of ANN in catalyst design

2.1. General details about the artificial neural network (ANN)

The artificial neural network is the tool that will be used in this paper to determine the connections between the properties and the performances of the catalyst, more precisely, to estimate the catalyst performances, knowing its characteristic properties' values. The obtained estimations will be use to calculate further the optimum values of the catalysts performances and, subsequently, to determine the catalyst properties that will lead to obtain the computed optimum performance.

The ANN is a computer algorithm that was inspired by the real, biological neural networks, especially the brain. Because it is a computer algorithm, it has input and output data. The input data is processed by a number of distinct units, simple abstractions, called *neurons*.

The neurons from the ANN are divided into three *layers*: the input layer, one or more hidden layers and the output layer. The input layer, which has a number of neurons equal to the number of inputs, has the purpose of receiving the input data and passing it to the neurons from the hidden layer. The purpose of the hidden layer is to receive the input data and to process them. After the process is complete, the results are passed to the output layers. The programmer chooses

the number layers and the number of neurons from the hidden layer. A larger number of neurons helps the neural network to solve more complex and/or large problems, but setting a high number of neurons for a specific problem,will produce unwanted effects. The same thing goes for the number of layers, with the mention that, in most cases, one layer of neurons is sufficient. The output layer's purpose is to receive the results of the hidden layer's computations and to store them. The number of neurons of the output layer is equal to the number of outputs.

To be able to compute the results, each of the neurons needs four parameters: an *input* (p), a *weight* (w), a *bias* (b) and a *transfer function* (f). The input is multiplied by the weight. The result of this multiplication is sent to a part of the neuron called *summer*, along with the bias. The result of this summation becomes the argument of the transfer function. The result of the transfer function is the output of the neuron, as it is shown in equation (1) [18]:

$$a=f(w) \tag{1}$$

In equation (1), *a* represents the output of the neuron.

The value of the output depends on the chosen transfer function. Typically, the transfer function is chosen by the programmer, so the value of the weight and the bias are adjusted according to some rules, so as the neuron input/output relationship meets some specific goal. These rules are called *learning rules*[18].

A very important property of the artificial neural network is its *learning* capacity. The learning process modifies the values of the weight the bias, according to some *learning rules*, known also as *training algorithms*. The purpose of the learning rule is to train the network to perform some task (estimation of some catalyst properties, in this case). There are three types of learning: *supervised learning*, *unsupervised learning* and *graded learning*.

Supervised learning is the most common type of learning used nowadays. In supervised learning, the learning rules are presented to a series of input-output pairs, which represent the correct behavior of the ANN. All these pairs form the *training database* and have the general pattern expressed below [16]:

$$(p_1, t_1), (p_2, t_2), \dots (p_n, t_n) \tag{2}$$

In the pattern (2), p is the network input and t is the corresponding correct output (known also as *target output*). In supervised learning, the weights and biases are adjusting so as the obtained outputs are as close as possible to the target outputs, for a given input. The training process is iterative. Like any other iterative process, a stop condition is needed, otherwise the ANN training would continue infinitely. This stop condition is called *performance index*. There are many performance indices, one of the most used being the mean squared error, where the error is defined as the difference between the target output and the computed output, for the same input.

One of the most used training algorithms is the Liebenberg-Marquardt algorithm. This algorithm is a version of the Newton's method and it is designed for neural network training for which the performance index is the mean squared error, which must be minimized. The training process continues as long as the computed mean squared error is higher than a preset value [18,19].

2.2 Multilayer feed-forward ANN configuration

The artificial neural network that is used in performance estimations is a multi-layer, feed-forward artificial neural network that was developed by using MATLAB software, version R2015a,using the "Neural Net Fitting" application. This application is a wizard which simplifies a lot the creation and the customization of the artificial neural network. In the end, the user has a fully functional network, which can be usedright away and/or save it for later, as a script file.

The artificial neural network that will be used has the following properties:

- It has one hidden layer, with 10 neurons;
- The training algorithm is Levenberg-Marquardt (which means that the performance index is the mean squared error);

- The training data are divided randomly, as follows: 70% of the data are marked as training data and the rest of 30% are distributed, evenly, between validation and testing data;

The training process is very important, because the quality of the estimations depends on the quality of the data from the training database.

3. Experimental

3.1 Synthesis of catalysts

Three preparations stirring time were uses for catalyst synthesis: 2h, 9h and 15h. The preparation procedures used for these synthesis methods are described in detail elsewhere [20].

3.2 Catalysts characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 Advance diffractometer with CuKα radiation in the 2θ range of 1-10^0 at scanning rate of 1^0/min. Specific surface area and pore size were measured using an automatic QuantachromeAutosorb Gas Sorption system. The morphology of the sample was examined using a scanning electron microscope Quanta.

3.3 Catalytic activity tests

The steam reforming of ethanol was carried out under atmospheric pressure in a fixed bed reactor. The catalyst was loaded between two layers of glass beads inside the reactor and the reaction temperature was measured by a thermocouple and controlled by a digital temperature controller. Ethanol was delivered to the reactor chamber by means of a HPLC pump controlled at the desired flow rates. Prior to reaction, the catalyst was reduced in situ by hydrogen at 550^0C for 6h. The products were analyzed on-line using a Varian gas chromatography equipped with capillary columns Pora Plot and a TCD detector. Helium was used as carrier gas. The reductions were carried out at atmospheric pressure and reaction temperature of 400^0C. The product mixture during reaction was passed through a condenser to separate the gaseous and liquid products for analysis.

The catalysts were evaluated for their performance in the reforming of ethanol. The criteria used were ethanol conversion and hydrogen yield.

$$X_{EtOH} = \frac{n_{EtOH\ in} - n_{EtOH\ out}}{n_{EtOH\ in}} \times 100 \quad (3)$$

$$\eta_{product} = \eta_{H_2} = \frac{g_{H_2}}{g_{mpreal}} \cdot 100 = \frac{\%H_2 \cdot g_{gas}}{g_{mpreal}} \quad (4)$$

where:

X_{EtOH} - ethanol conversion
n_{EtOHin} – moles of ethanol in of reactor
$n_{EtOHout}$ – moles of ethanol out of reactor
η_{H2}- yield of hydrogen
g_{H2}- mass of hydrogen
g_{gas} - mass of gas produced in the experiments, g
g_{mpreal} - real raw mass, g
% H_2 –weight percent of H_2 obtained by chromatographic analysis of gas fraction (produced in reactor)

3.4. Linear –interpolation methods

For process development, the study of optimization of parameters may not always be likely because of limited experimental results. Linear interpolation is a method of curve fitting using linear polynomials to construct new results points within the range of a discrete set a known data points.

In our case the pore volume, pore size and BET surface area which involves the part of characterization of the catalyst, were corresponding to outputs section. The synthesis time and the calcinations temperature during support preparation play the role of inputs section.
Hydrogen production, the ethanol conversion and hydrogen yield formed the output section.

Table 1. Original experimental results used for linear interpolation

	Results 1		**Results 2**			**Results 3**	
Catalyst name	Stirring time	Calcinations temperature	BET surface	Pore size	Pore volume	Ethanol conversion	H_2 yield
MC1	2h	520^0C	920.20	2.42	0.61	30.0	18.0
MC2	2h	560^0C	946.60	2.58	0.61	61.0	35.0
MC3	2h	600^0C	961.00	2.50	0.59	61.5	35.4
MC4	9h	520^0C	940.11	2.70	0.62	41.0	34.0
MC5	9h	560^0C	958.71	2.61	0.62	73.3	50.1
MC6	9h	600^0C	1002.10	2.54	0.61	80.0	52.0
MC7	15h	520^0C	1300.00	2.88	0.69	41.0	52.3
MC8	15h	560^0C	1028.95	2.68	0.69	86.3	62.0
MC9	15h	600^0C	1000.40	2.52	0.60	82.0	60.0

The results 1, 2 and 3 from table 1 are the original experimental data. These results are not enough to create the neural network in order to find the connection between results. Two ways were adapted in this case: the linear interpolation and drawing a line of best fit thought the experimental results set.

4. Results and discussions

4.1 Neural network application for the characteristics of Co/MCM-48 catalyst

The developed artificial neural network was used to estimate the catalyst properties in two distinct cases:

- The input data are calcination temperature and synthesis stirring time and the output data are BET surface, pore size and pore volume;
- The input data are calcination temperature and synthesis stirring time and the output data are ethanol conversion and hydrogen yield.

In both cases the same neural network is used, the only thing that is changed being the training databases. To ease the understanding of the estimation and optimization processes, the neural networks are treated as distinct, thus named *Neural Network 1* (NN1) and *Neural Network 2* (NN2).

A schematic approach of the two estimation processes is presented in Fig. 1.

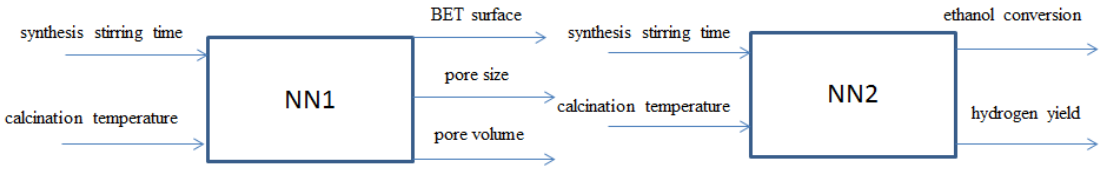

Fig. 1. The input and the output data of the two types of estimations made by the ANN
Neural network one NN-1

For this neural network, the training database has two inputs and three outputs, which means that the input layer has two neurons and the output layer has three. The structure of this neural network is presented in figure 2.

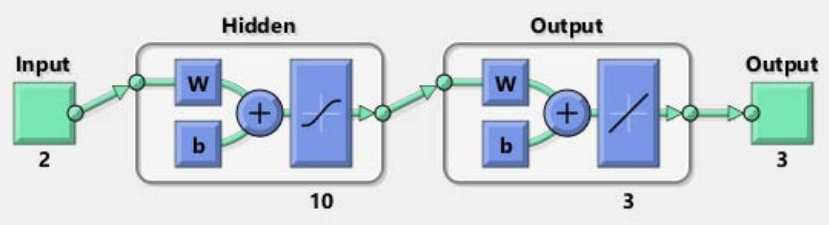

Fig. 2. The structure of NN1

In figure 2 the basic elements of the neurons can be seen: the weight, the bias (marked with *w* and *b* respectively), the summer (marked with a plus sign) and the transfer function that is being used: the hyperbolic tangent sigmoid for the hidden layer and the linear function for the output layer.

The hyperbolic tangent sigmoid transfer function (implemented in MATLAB as the *tansig* function) has the following expression [16]:

$$tansig(x) = \frac{2}{1+e^{-2n}} + 1 \tag{5}$$

The linear function (implemented in MATLAB as the *purelin* function) has the following expression [21]:

$$purelin(x) = x \tag{6}$$

The choice of the linear function as transfer function for the output layer is obvious: the alteration of the result, in this stage, is not desired. The hyperbolic tangent sigmoid transfer function that is used in the hidden layer is the default transfer function for the Neural Net Fitting Application, but it can be modified by editing the generated script.

Because of the large number of data from the training database and because a large proportion of the training data was obtained by linear interpolation, the data from the training database are highly correlated, which means that the training efficiency is high. This fact is proved by the error histogram, which shows that the majority of the errors, defined as the difference between the target data and the output data, are very small. The error histogram is presented in figure 3.

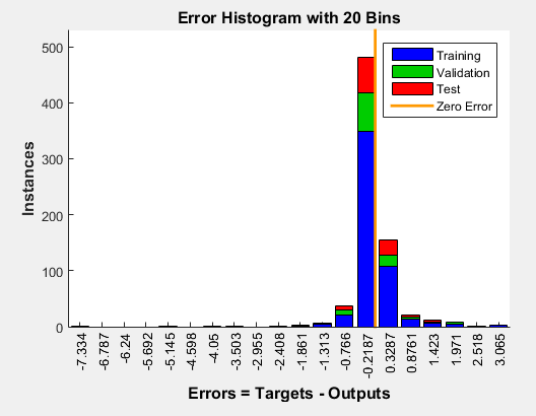

Fig. 3. Error histogram of NN1 training

Another criterion in evaluating the training efficiency is the data regression analysis. The result of this analysis is represented as a number, between 0 and 1, noted with R. The closest the value of R is from 1, the more efficient the training was. The results of the regression analysis are presented in figure 4. Because the regression analysis and the error histogram evaluate the same

process, the neural network training, the presented results will always be the same, the only difference being the presentation form.

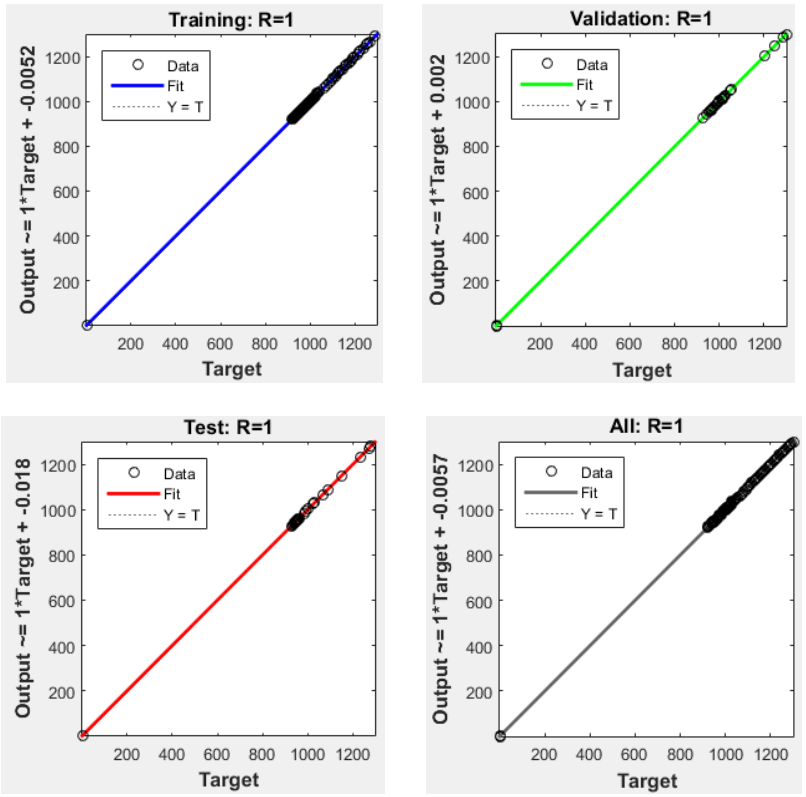

Fig. 4. Regression analysis of NN1 training

Neural network two NN-2

NN2 is fairly similar to NN1, the only difference being that another training database is being used, because the outputs are different. In NN2, the inputs are the same to NN1, but the outputs are the ethanol conversion and the hydrogen yield.

Because NN2 has two outputs, it means that the input layer has two neurons, the middle layer has ten neurons and the output layer has two neurons as well. The transfer functions for both hidden and output layer are the same as NN1.

The structure of NN2 is presented in Fig. 5.

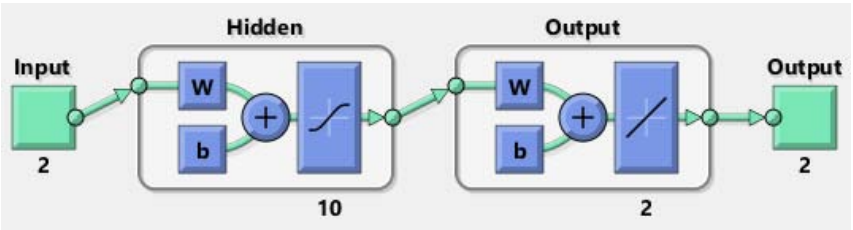

Fig. 5. The structure of NN2

The training process of NN2 is similar to NN1. The obtained error histogram is presented in Fig. 6.

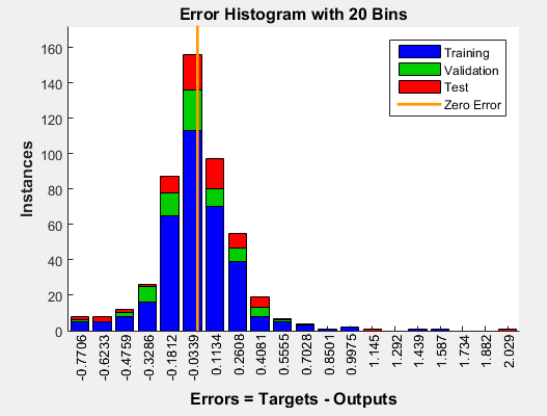

Fig. 6. Error histogram of NN2 training

The results of the regression analysis of the training data are presented in figure 7.

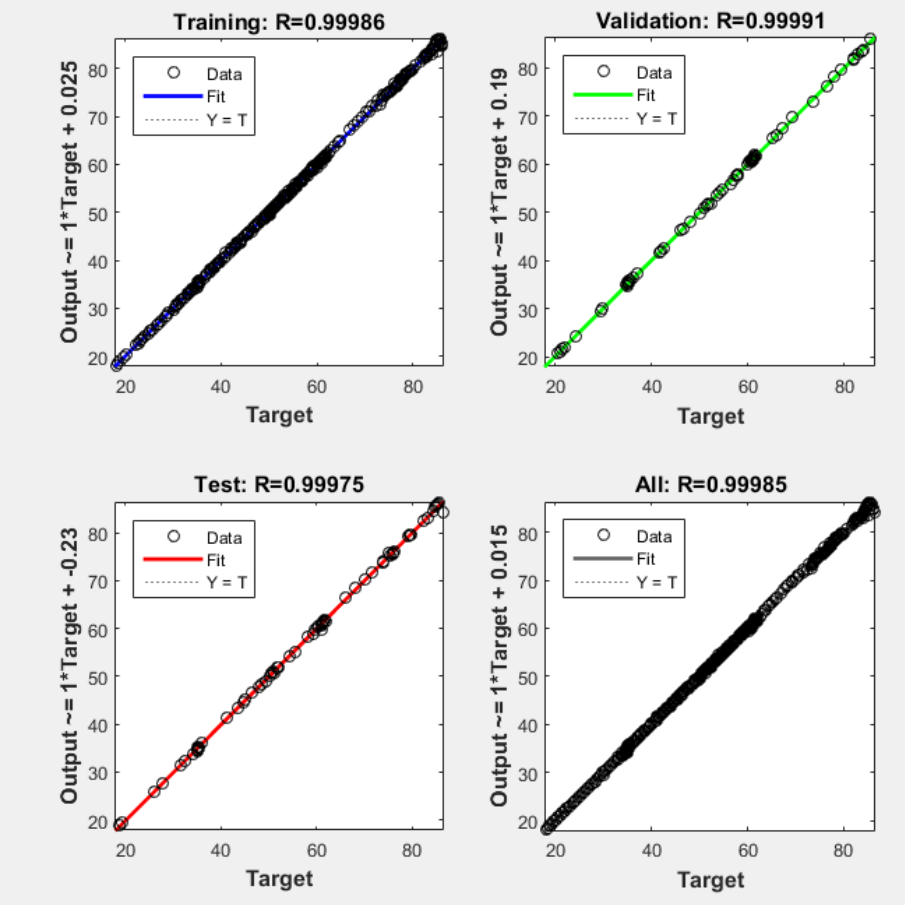

Fig. 7. Regression analysis of NN2 training

The results presented in figures 6 and 7 are similar to the results from figures 3 and 4. Also, the results from figures 6 and 7 are not surprising; because of the way the training data were obtained.

4.2. Hydrogen production with neural networks

4.2.1 Using the neural networks to obtain optimal operation and catalyst conditions for maximum ethanol conversion or hydrogen yield

The neural network trained with the two distinct training databases are used to determine the optimal catalyst conditions so as to obtain maximum ethanol conversion or hydrogen yield.The next step is to use the obtained results so as to determine the optimum performance for the studied catalyst. Precisely, the goal is to determine the maximum ethanol conversion and the maximum hydrogen yield. Once those are determined, the next step is to find out the stirring time and calcination temperature needed to obtain the maximum value of the properties.

The optimization procedure is described in figure 8. This procedure involves setting up the initial values for the stirring time and for the calcination temperature, then using the ANN to estimate the ethanol conversion and the maximum hydrogen yield. After each estimation, the values of the two properties are increased following the some rules. The estimations stop when both catalyst properties reached their maximum value.

The notations used in figure 8 are as follows:

- ST – stirring time;
- CT – calcination temperature;
- Step – the amount with which CT increases after every iteration;
- i – counter;
- Res – the result of the ANN estimation (abbreviation from *Result*);
- EC/ ECM – ethanol conversion/ maximum ethanol conversion;
- H2Y/ H2YM – hydrogen (H_2) yield/ maximum hydrogen yield;
- OSTE/ OSTH – optimum stirring time for ethanol production/ for H_2 yield;
- OCTE/ OCTH – optimum calcination temperature for ethanol production/ for H_2 yield;

As it can be seen in figure 8, the entire optimization process is iterative, simple and straightforward. It involves a number of estimations, using the artificial neural network, for certain values of the stirring time and calcination temperatures. Thus, the stirring times take the values of 2, 9 and 15, successively, and the calcination temperatures vary from 520 to 600, with the step of 10. The chosen value for the step was arbitrary, so it can be modified.

Because the artificial neural network estimates two outputs at the same time, they are represented as an array of two numbers. The first number represents the ethanol conversion and the second number is the hydrogen yield. This explains the*Res* [1]and*Res* [2]notations.*Res* [1] signifies the first element of the array and, obviously, *Res* [2] signifies the second element.

Another important thing needs to be mentioned: it is not possible to determine both optimum values for a catalyst *at the same time*. So, the interpretation of the given results becomes a problem of choice: if, at a given time, the optimum ethanol conversion is desired, then one type of catalyst will be produced; if the optimum hydrogen yield is desired, then another type of catalyst will be produced.

By running the algorithm presented in figure 8, we obtain the results from table 2.

Table 2. Optimum values for ethanol conversion and hydrogen yield

Property	Optimum value	Catalyst properties for the optimum value	
		Stirring time (h)	Calcination temp. (°C)
Ethanol conversion (%)	85.31	15	570
Hydrogen yield (%)	61.77	15	560

From table 2, it can be seen that the optimum values for the desired properties can be obtained when the stirring time used for the catalysts synthesis is 15 hand the calcination temperature is around 560–570°C, depending on the desired property. This result is expected, because the maximum values for these properties, presented in table 1, are close to the optimum values at 15 h stirring time, the calcination temperature being in the 560-600°C range.

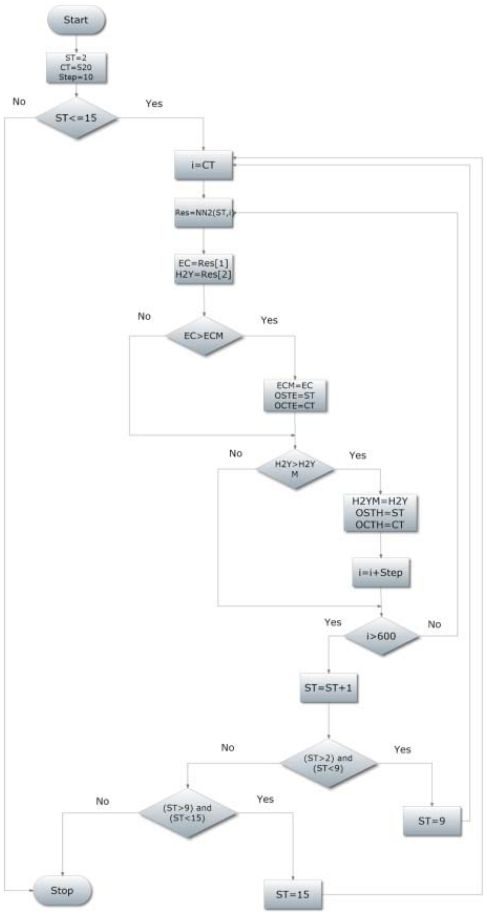

Fig. 8. The utilized optimization algorithm

4.2.2 Verification with ANN

There are many ways to scrutinize the accuracy of ANN prediction. In this paper, two practical ways will be considered. The first way is to interpret the training database regression analysis (figures 4 and 7) or the error histograms (figures 3 and 6) and draw the appropriate conclusions. The second way is to use the artificial neural network to predict the desired properties, using input data for which the outputs are already known. Then, the predicted and the known output values are compared.

To determine the artificial neural network estimation accuracy using the second method, the data presented in table 1 were used. For each of the inputs presented in that table, the values for the 5 properties were estimated then compared to the determined valued from table 1. Because the data from the training database were strongly correlated, the authors believe that only one estimation is enough to reflect the estimation capacity of the neural network, if the data were less strongly correlated, more estimations for the same input would be needed, the value taken into account being the average of the estimations.

In table 3, the determined and the estimated values for BET surface, pore size and pore volume are presented.

Table 3. Estimated and determined values for BET surface pore size and pore volume

		Determined values			Estimated values		
Stirring time	Calcinations temperature	BET surface	Pore size	Pore volume	BET surface	Pore size	Pore volume
2h	520^0C	920.2	2.42	0.61	920.3	2.48	0.61
2h	560^0C	946.6	2.58	0.61	946.55	2.56	0.60
2h	600^0C	961.0	2.50	0.59	961.24	2.54	0.60
9h	520^0C	940.11	2.70	0.62	940.07	2.66	0.62
9h	560^0C	958.71	2.61	0.62	959.26	2.62	0.62
9h	600^0C	1002.1	2.54	0.61	1000.1	2.54	0.60
15h	520^0C	1300.0	2.88	0.69	1299.3	2.84	0.71
15h	560^0C	1028.95	2.68	0.69	1032.2	2.68	0.66
15h	600^0C	1000.4	2.52	0.60	1000.9	2.56	0.61

From table 3 it can be noticed that the difference between the determined and the estimated values, most of the times the difference is under 1. This is another evidence that the artificial neural network is efficiently trained, so its estimations are accurate.

In table 4, the same estimations are made, but for the ethanol conversion and hydrogen yield.

Table 4. Estimated and determined values for ethanol conversion and hydrogen yield

		Determined values		Estimated values	
Stirring time	Calcination temperatures	Ethanol conversion	H_2 yield	Ethanol conversion	H_2 yield
2h	520^0C	30.0	18.0	29.92	18.00
2h	560^0C	61.0	35.0	60.42	34.53
2h	600^0C	61.5	35.4	61.42	35.32
9h	520^0C	41.0	34.0	41.18	34.01
9h	560^0C	73.3	50.1	72.88	49.83
9h	600^0C	80.0	52.0	79.84	52.15
15h	520^0C	41.0	52.3	41.52	52.22
15h	560^0C	86.3	62.0	85.16	61.93
15h	600^0C	82.0	60.0	82.18	60.17

Similar to table 3, the estimated and the determined values from table 4 are very close to each other. Again, this proves that the training was efficient and the estimations are accurate.

5. Conclusions

ANN has been used to design an optimum Co/MCM-48 for the production of hydrogen by steam reforming of ethanol. ANN could predict hydrogen production performance of various preparation type conditions in terms of ethanol conversion and hydrogen yield. Specifically, on catalyst design, ANN was used to determine the optimum catalyst conditions for obtaining good hydrogen production. The optimal hydrogen yield was 61.77% and the ethanol conversion85.31%. The optimal catalyst was the one synthesized at stirring time of 15 h and calcination temperatures of 560–570^0C.

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