Estimation Relationships for Ethanol Conversion and Hydrogen Yield Using Neural Network for Ethanol Steam Reforming on Co/Al_2O_3 Catalyst

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An artificial neural network has been developed for estimation of ethanol conversion and hydrogen yield function of reaction conditions in ethanol steam reforming process based on Co/Al_2O_3. Ethanol (8% and 10% vol) was considered as raw material for hydrogen production by steam reforming. For this investigation, we have created an artificial neural network to describe the complex relationship between ethanol steam reforming and the Co/Al_2O_3 catalyst used in the process. To test the estimation accuracy of the created neural network, a set of input data, whose outputs are already known was used. For these input data, the output data are calculated and then compared with the known outputs.

Keywords: ethanol, steam reforming, artificial neural network, catalyst

Along with the increasing demand for zero carbon emission process, considerable attention has been paid to transform the biomass-derived compounds into hydrogen-rich gas. Among such compounds, bioethanol obtained by biomass fermentation is of particular interest because of the increasing availability of raw material, ease of handling in the liquid state, high hydrogen content, and low toxicity. Production of hydrogen by steam reforming of ethanol has been performed over time by using different catalytic systems. The most effective process for hydrogen production from ethanol is this steam reforming reaction $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$. Hydrogen has been considered as the least polluting fuel that can be used in an internal combustion engine or a fuel cell for electricity generation. Steam reforming of ethanol is an attractive route to produce hydrogen because of the zero carbon emissions as well as the easy-handling and the less toxic property of ethanol [1-3]. The steam reforming of ethanol is catalyzed by a cobalt based catalyst although the composition of the catalyst is still far from optimum and often the optimum catalyst so far as the selectivity is concerned is not necessarily the best overall catalyst. The design of catalysts on the basis of the mechanism of the reaction needs a lot effort and money and the rate of success not all that high. Metal-supported catalysts have exhibited catalytic ability in steam reforming process. Overall supported cobalt catalysts have been shown to have excellent activity toward oxidation [4,5]. Although, Co-containing catalysts have been less studied than Pt or Ni, it has been revealed that Co/Al_2O_3 shows considerable activity for the CH_4/CO_2 reaction, the Fischer-Tropsch reaction and the steam reforming of ethanol [6].

In recent years, Artificial Neural Networks (ANN) had been applied to the design of heterogeneous catalysts and a number of reports have been published in the literature [7-11].

An ANN is a computer algorithm, which is designed to simulate the functioning of biological neural networks, especially the brain. An ANN consist in a number of nodes (called neurons), which are distributed into layers. To estimate the desired output, the neurons are interconnected. These connections are mathematically represented by transfer functions. These transfer functions have weights, which signify the strength of the signal flowing into the nodes. In general, having provided the input, the algorithm sets the weights so that the output is within the acceptable error limit of the experimental output (supervised learning). If a network has been trained correctly, it can predict the response of a corresponding system towards a new set of inputs that are not in the ANN's training database [12].

The purpose of the present work is to design and train a neural network to be able to predict the performance of Co/Al_2O_3 catalyst for the steam reforming of ethanol. The developed ANN is able to estimate hydrogen production and ethanol conversion performance, having as input data the following catalyst parameters: temperature (°C), feedstock ethanol content (% vol.) and feedstock flow (mL/min).

Experimental part

Chemicals and reagents

The following chemicals were used for catalyst synthesizing: Al_2O_3 for support was purchased from National Institute of Research and Development for Chemistry and Petrochemistry Bucharest, and the metallic precursor for the impregnation process, respectively $Co(NO_3)_2 \cdot 6H_2O$ (98%), was purchased from Sigma Aldrich. For the steam reforming tests, a mixture of distilled water and ethanol (Chemical, 98%) was used as a feedstock.

Catalytic tests

The ethanol reforming experimental program was carried out in a continuous system, using a micro pilot unit containing a stainless steel fixed bed reactor. The unit was equipped with a control panel which provides: regulation and registration of the reactor's temperature and indicates the temperature along the catalytic bed.

After the test pressure is done, the inert gas was introduced to activate the catalyst at an appropriate temperature and pressure of the activation process, in this case 550°C for 6 h. After that, the temperature of the reactor was adjusted to the wanted reaction temperature namely 350, 400 and 450°C respectively. The feedstock was an aqueous solution of ethanol to the concentration of 8% and 10 vol% ethanol. After stabilization of the process the composition of the gas phase was determined (hydrogen,

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methane, ethane, ethylene, carbon dioxide, carbon monoxide), using a Varian chromatograph.

The process performance was assessed by the conversion of ethanol and hydrogen yield.

The formulas used to calculate the conversion of ethanol and hydrogen yield was as follows:

$$X_{EtOH} = \frac{n_{EtOH_{in}} - n_{EtOH_{out}}}{n_{EtOH_{in}}} \times 100 \quad (1)$$

$$\eta_{product} = \eta_{H_2} = \frac{g_{H_2}}{g_{mpreal}} \cdot 100 = \frac{\%H_2 \cdot g_{gas}}{g_{mpreal}} \quad (2)$$

where:

X_{EtOH}- ethanol conversion

η_{H2}-yield of hydrogen

g_{gas}- mass of gas produced in the experiments, g

g_{mpreal}-real raw mass, g

$\%H_2$–vol % of H_2 gas obtained by chromatographic analysis.

Neural network

Hydrogen production and the ethanol conversion can be estimated using different methods. One of the estimation methods is the ANN.

An ANN is a computer algorithm, which is designed to simulate the functioning of human brain. The most important advantages of ANN for assessment of research data are:

- Flexibility. The inputs and outputs can be chosen according to the available experimental data.

-Data reusability. The new input data that was used to estimate the output parameters can be used in training, improving the ANN's estimation precision.

- Quickness. Because today's ANN algorithms are the result of over 50 years of study, they are very well optimized. This means that the time needed for estimation is very small. It mostly depends on the machine's hardware configuration.

An ANN consist in a number of nodes (called *neurons*), which are distributed into layers. There are three types of layers:

- input layer. This layer's purpose is to acquire the input data from an outside source. One neuron is assigned to each of the input variables, which means that the number of neurons the input layer has is equal to the number of input variables;

- hidden layer. This layer does all the required processing to reach the desired result. The number of neurons from the hidden layer is chosen by the ANN user. There is not a strategy to choose the optimum number of neurons. Trial-and-error and experience are the main criteria in this case. The number of neurons increases with the problem complexity. However, too many neurons for the problem complexity can lead to the unwanted phenomenon of overfitting;

- output layer. The output layer displays the result of the processing done by the hidden layer. Like the input layer, the number of neurons the output layer is equal to the number of output variables.

Because the neural network is a computer algorithm, it has input and output data. In this paper, the input data that were temperature (°C), feedstock ethanol content (% vol.) and feedstock flow (ml/min) while the output data are ethanol conversion (%) and hydrogen yield (%).

The correct use of an ANN is a two-step process:

- creating and configuring the neural network.

- training the ANN.

Creating and configuring the neural network was made using the Neural Fitting app of the MATLAB R2015a program, which will shortly be referred to as MATLAB. MATLAB is a wide-known software program developed by Mathworks [13]. The Neural Fitting app is an interface wrapper of the MATLAB neural network functions, making the creation and the use of the neural network much easier.

Results and discussions

Hydrogen production and the neural network approach

The values obtained for the ethanol conversion and hydrogen yield, for Co/Al_2O_3 catalyst prepared and tested in the ethanol reforming reaction, are presented in table 1 and 2, respectively.

The data from tables 1 and 2 were gathered and saved into the training database, according to the MATLAB specifications. The final training database had 12 rows and 3 columns for the input data, respectively 12 rows and 2 columns for the output (target) data. A sample of the input data from the training database is presented in table 3. The left column represents the temperature, the middle column represents the feedstock ethanol content and the right column represents the feedstock flow.

A sample of the target data, corresponding to the data from table 3, is presented in table 4. In table 4, the left column represents the ethanol conversion (%), while the right column represents hydrogen yield (%).

The next step was the configuration and training of the ANN. This step was done with the aid of the Neural Fitting app. The neural network has 10 neurons in the hidden layer and was trained using the Levenberg-Marquardt algorithm.

Temperature	Ethanol 8%, 1ml/min	Ethanol 8%, 3 ml/min
350^{0}C	77.14%	74.24%
400^{0}C	81.54%	79.57%
450^{0}C	87.92%	86.29%
Temperature	**Ethanol 10%, 1ml/min**	**Ethanol 10%, 3 ml/min**
350^{0}C	79.40%	77.52%
400^{0}C	82.32%	80.31%
450^{0}C	89.24%	88.55%

Table 1
ETHANOL CONVERSION ON Co/Al_2O_3 CATALYST

Table 2

HYDROGEN YIELD ON Co/Al_2O_3 CATALYST

Temperature	Ethanol 8%, 1ml/min	Ethanol 8%, 3 ml/min
350^{0}C	60.30%	60.09%
400^{0}C	59.86%	59.59%
450^{0}C	59.72%	59.15%
Temperature	**Ethanol 10%, 1ml/min**	**Ethanol 10%, 3 ml/min**
350^{0}C	61.12%	60.91%
400^{0}C	60.71%	59.96%
450^{0}C	59.87%	59.74%

Table 3

SAMPLE OF THE INPUT DATA FROM THE TRAINING DATABASE

350	8	1
350	8	3

Table 4

SAMPLE OF THE TARGET DATA FROM THE TRAINING DATABASE

77.14	60.3
74.24	60.09

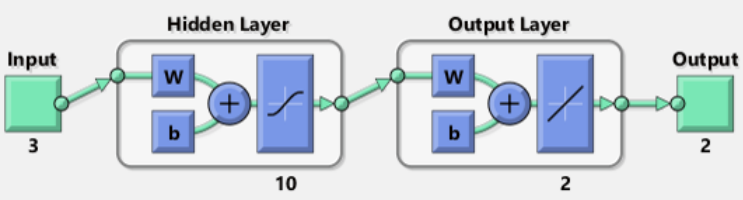

Fig. 1. Neural network architecture, which contains 3 neurons in the input layer, 10 neurons in the hidden layer and 2 neurons in the output layer

The ANN obtained using the Neural Fitting app had the architecture presented in figure 1.

From figure 1 it can be seen that the input layer has 3 neurons, because 3 input variables are used: temperature, feedstock ethanol content and feedstock flow. The hidden layer has 10 neurons, as it was mentioned before. Finally, the output layer has 2 neurons, because the neural network is required to estimate two parameters: hydrogen yield and ethanol conversion performance.

To check the training efficiency, the error histogram and the training data regression analysis were used. The error histogram shows how close to 0 are the error outputs. When more outputs are close to 0, the more efficient is the training. The error histogram for ANN training is presented in figure 2.

Figure 2 shows that most of the errors are near the 0 value (between -1.595 and 1.338), which means that the training was efficient.

The training data regression analysis is another evaluation method. It shows the correlation level of calculated data from the training database. The result of this analysis is quantified as a number, R factor, which is between 0 and 1. If R=0, then the data are completely random, if R=1, then the data are perfectly correlated.

The results of regression analysis for training data are presented in figure 3.

The results presented in figure 3 show a fair correlation of the data from the training database. In this case, the values of the R factor along all the types of data are very similar: about 0.99, despite the low number of data. The reason for this result is that the data are well correlated, although the statistical variation is high.

To determine the estimation precision of the ANN, the input data from the training database will be used. To

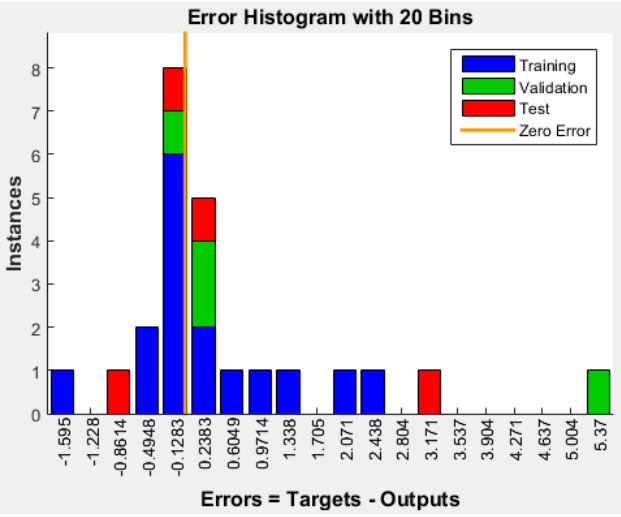

Fig. 2. Error histogram of the neural network training. Excepting the few outliers, most of the errors are close to the 0 value

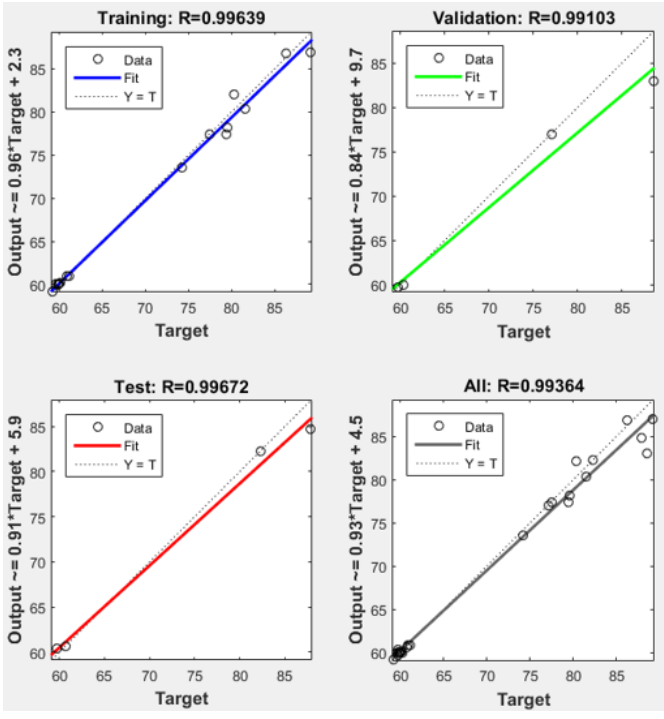

Fig. 3. Data regression analysis for training, validation, test data and overall training database

accurately determine the estimation precision, the following factors must be taken into account:

- the random factor. It appears when the training data is divided into the three categories. As a consequence, the ANN will show different results after each training, for the same input data;

- the low amount of data from the training database. A consequence of this factor is that the training may not be as efficient as it could be, given more data. There are two ways of offsetting this consequence: retraining the ANN or (preferred) training the ANN with a larger database. Because the latter option is not available, the former option will be used.

As a consequence of the influence of the two factors mentioned above, the author's opinion is that the best way to determine the estimation precision is to iteratively use and re-train the ANN, having the same input data, for a specified number of times and taking into account the average of the outputs from each iteration. Increasing the number of iterations increases the chances to obtain an accurate estimation, but it also increases the duration needed to obtain the desired answer.

The evaluation criteria for the estimation precision will be the relative error, computed with the following formula:

$$RE(\%) = (D-M)/D*100$$

In the above formula, D is the determined value of the property and M is the average value of the same property.

Increasing the number of iterations for the same input data, as specified above, decreases the influence of the random factor, which reduces the relative error. The number of iterations needed to evaluate is given by the highest relative error that is considered acceptable in a certain situation. If the relative error that is considered acceptable is high, the number of iterations is low and vice-versa.

For this experiment, there were taken into account the obtained estimations after 3, 10 and 20 iterations. The obtained values of the outputs are presented in table 5.

In table 6, the relative errors (%) for the data from table 5 are presented.

In tables 5 and 6, H signifies the hydrogen yield (%) and E signifies the ethanol conversion (%).

From table 6 it can be see that increasing the number of iterations leads, in a vast majority of the cases, to the decrease of the relative error, as it was expected. The cases in which the relative error does not decrease with the increase of the number of the iterations are possible because of the variance in separating the training data into the three categories. Most of the relative errors vary between -3 and 3%, so the author's opinion is that the presented method is reliable and the optimum number of iterations, in this case, is 10.

Basic hardware and software requirements. Variations of the basic requirements

For a user to be able to reproduce the experiment presented in this paper, the basic requirements are a computer (PC or laptop) with MATLAB software installed. The MATLAB version that was used was R2015a, but any MATLAB version that supports apps is fine as well. For complete experiment repeatability to be achieved using MATLAB, two steps must be performed:

- ANN creation, customization and training;

- Repeatedly using the above ANN to estimate the desired properties.

MATLAB provides two ways for a user *to create, customize and train the ANN* he will use for estimation. The first method is to code the desired ANN using MATLAB language. This method is more suited for the advanced users because it requires both programming and artificial

Table 5

THE ESTIMATED VALUES FOR HYDROGEN PRODUCTION AND ETHANOL CONVERSION AFTER 3, 10 AND 20 ITERATIONS

Determined values		Estimated values after 3 iterations		Estimated values after 10 iterations		Estimated values after 20 iterations	
H	E	H	E	H	E	H	E
77.14	60.3	73.35	60.97	77.14	60.33	77.72	60.25
74.24	60.09	74.17	60.23	73.68	60.29	77.94	59.86
81.54	59.86	81.29	60.72	83.46	59.98	81.87	60.01
79.57	59.59	81.63	59.73	81.25	60.16	79.17	59.64
87.92	59.72	85.63	59.69	87.33	59.75	85.31	59.67
86.29	59.15	85.62	59.9	85.95	59.34	84.18	59.18
79.4	61.12	81.14	61.02	78.35	61.04	80.67	60.68
77.52	60.91	79.41	60.9	77.42	60.61	76.4	60.63
82.32	60.71	82.41	60.47	82.2	60.17	83.3	60.18
80.31	59.96	79.85	59.88	80.96	59.97	82.97	60.33
89.24	59.87	93.97	59.65	88.85	59.85	87.24	60.11
88.55	59.74	87.7	59.55	86.88	59.67	85.25	59.62

Table 6

THE RELATIVE ERRORS RE FOR HYDROGEN PRODUCTION AND ETHANOL CONVERSION AFTER 3, 10 AND 20 ITERATIONS

Determined values		RE(%) for 3 iterations		RE (%) for 10 iterations		RE (%) for 20 iterations	
H	E	H	E	H	E	H	E
77.14	60.3	2.33	-1.11	0	-0.05	-0.75	0.09
74.24	60.09	0.09	-0.24	0.76	-0.33	-4.99	0.38
81.54	59.86	0.31	-1.44	-2.35	-0.2	-0.4	-0.25
79.57	59.59	-2.6	-0.24	-2.11	-0.96	0.5	-0.09
87.92	59.72	2.6	0.06	0.67	-0.05	2.96	0.08
86.29	59.15	0.78	-1.27	0.39	-0.32	2.44	-0.05
79.4	61.12	-2.2	0.17	1.32	0.12	-1.6	0.73
77.52	60.91	-2.43	0.01	0.14	0.49	1.44	0.47
82.32	60.71	-0.11	0.4	0.14	0.89	-1.2	0.87
80.31	59.96	0.57	0.14	-0.81	-0.01	-3.31	-0.61
89.24	59.87	-5.3	0.37	0.44	0.04	2.24	-0.4
88.55	59.74	0.96	0.32	1.89	0.12	3.73	0.21

intelligence knowledge. The main advantage of this method is that the user can control every detail of the ANN and can optimize it according to the particular problem he has. The second method is to use the *Neural Network Fitting* app. This app creates the script to manage the ANN automatically; all the user needing to do is to save the script in a file, to be used later. However, because the app is created for the users with below average programming and artificial intelligence knowledge, it's impossible to fine tune the resulting ANN without learning the language, to manually modify the resulting script. Neither method is superior, long term, because they have the same goals, taking different paths.

In this paper, the ANN was created, customized and trained using the *Neural Network Fitting* app. More info on how to use this app is provided in the MATLAB help. It suffices to mention the parameters that were used to create the ANN from this paper:

- Inputs: temperature, feedstock ethanol content and feedstock flow, stored in a file according to MATLAB requirements;

- Targets: hydrogen yield and ethanol conversion performance, stored in a file according to MATLAB requirements;

- Sample dividing: 70% training data, 15% validation data and 15% testing data;

- Number of neurons in the hidden layer: 10;

- Training algorithm: Levenberg-Marquardt;

At the end of the training process, the app offers the possibility to save the created ANN into a file.

To *repeatedly use the above ANN to estimate the desired properties*, a MATLAB script is required. MATLAB programming knowledge is a benefit, because the user can program and customize its own script. However, it is not mandatory, because the authors can provide, for free, the source for the script, along with all the needed assistance.

The algorithm that was used for estimation, expressed using the logical scheme, is presented in figure 4:

The notations used in figure 4 are the following:

- Inputs - Number of input variables;

- Outputs- Number of output variables;

- Data - Number of experimental data;

-Evals -Number of evaluations;

-i, j - counters;

- Avg – Matrix that stores the averages of the estimated properties;

- Errors - Matrix that stores the estimation errors of the properties;

- Sum - Matrix that stores the sum of the estimated properties values;

The requirements presented above can suffer a few variations. The main variation is that it's not mandatory to use MATLAB to be able to estimate the catalyst properties using the artificial neural network. Any software designed to create, customize and train an ANN is suitable. In this case, it's the user responsibility to acquire any necessary knowledge regarding using and/or programming the software.

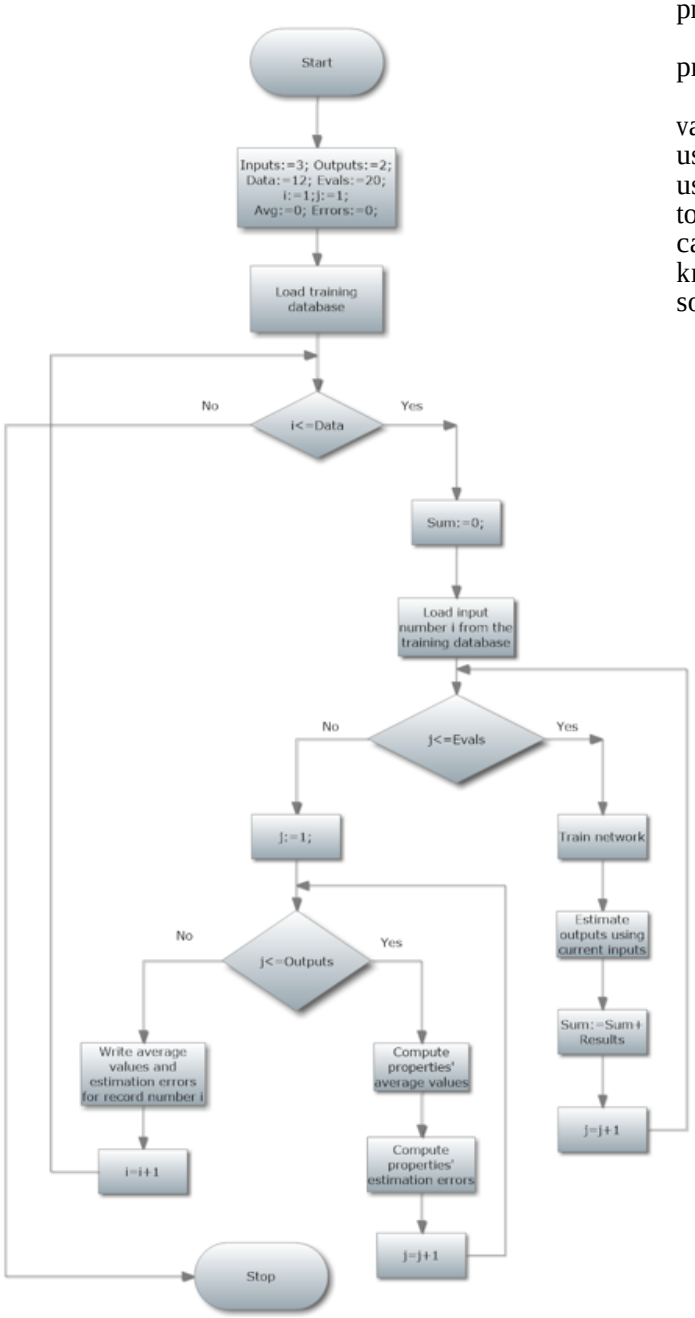

Fig. 4. Logical scheme of the estimation algorithm

Another significant variation is that the algorithm presented in figure 4 can be modified according to user's needs.

Conclusions

High hydrogen yields obtained through the bioethanol reforming on the proposed catalytic systems represent a great economic advantage because it allows the use of the bioethanol obtained from biomass, a renewable source of feedstock.

The ANN is very useful tool to estimate the catalytic conditions for a chemical process and its main advantages are quickness and flexibility. The artificial neural network has been used to estimate the ethanol conversion and hydrogen yield function of reaction condition in ethanol steam reforming process using Co/Al_2O_3 catalyst. According to our calculations the optimum number of iterations was 10, because the relative error (RE) varied between -2.35 and + 1.89, the smallest interval obtained from the three tested scenarios. The presented estimation method can be adapted by availability of experimental data and/or user's wish.

Our next step will consist in finding the optimum parameters (temperature, pressure, feedstock flow and ethanol content) for maximum hydrogen yield obtained by steam reforming of ethanol on Co/Al_2O_3 catalyst.

References

1. L.ZHANG, W.LI, J. LIU, C.GUO, Y.WANG, J.ZHANG, Ethanol steam reforming reactions over Al_2O_3/SiO_2-supported Ni–La catalysts, Fuel **88**, 2009, p. 511–518;

2.GHITA, D., STANICA EZEANU, D., CURSARU,D., ROSCA, P., Pt supported catalysts for steam reforming reaction, Rev. Chim. (Bucharest), **63,** no. 12, 2012, p. 1296

3. GHITA, D., STANICA EZEANU, D., CURSARU,D., ROSCA, P.,Hydrogen Production by Steam Reforming of Bioethanol over Pt Based Catalysts, Rev. Chim. (Bucharest), **67**, no. 1, 2016, p.145

4.MIHAI, S., NEGOIU,M., Synthesis and Characterization of Ni(II), Pt(IV), Pd(II), Co(II), Au(III), Cu(II) Complexes with Mixed Ligands, Rev. Chim. (Bucharest), **60**, no. 3, 2009, p. 222

5. NEGOIU, M., MIHAI, S., NEAGOE, S.,PANTEA, O.,Combinaii complexe ale Co(II), Cd(II), Pd(II), Rh(III) si Pt(IV) cu tiuram, Rev. Chim. (Bucharest), **58**, no. 10, 2007, p. 866

6. GHITA, D., STANICA EZEANU, D., ROSCA, P., CURSARU, D., Performances of Al_2O_3 Supported Catalyst for Steam Reforming Process, Rev. Chim. (Bucharest), **65**, no. 11, 2014, p. 1395-1398;

7. Z.Y. HOU, Q.L. DAI, X.Q. WU, G. T.CHEN, Artificial neural network aided design of catalyst for propane ammoxidation Artificial neural network aided design of catalyst for propane ammoxidation Artificial neural network aided design of catalyst for propane amoxidation**,** Applied Catalysis A, **161**, 1997, p. 183;

8. K. HUANG, F.Q. CHEN, D.W. LU, Artificial neural network-aided design of a multi-component catalyst for methane oxidative coupling, Applied Catalysis A: General, **219**, 2001, p. 61;

9. D. MATEI, B. DOICIN, D. L. CURSARU, Pd/SBA-15 mesoporous catalyst for ethanol steam reforming. A neural network approach, Digest Journal of Nanomaterials and Biostructures, **11**, nr. 2, 2016, p. 443 - 451;

10. K. HUANG, X.L. ZHAN, F.Q. CHEN, D.W. LU, Catalyst design for methane oxidative coupling by using artificial neural network and hybrid genetic algorithm, Chemical Engineering Science, **58**, 2003, p. 81;

11. Y. LIU, D. LIU, T. CAO, S.HAN, G.XU, Design of CO_2 hydrogenation catalyst by an artificial neural network, Computers Chemical Engineering, **25**, 2001, p. 1711;

12. S. JOOYA, F. GOBAL, Artificial neural network aided design of a multi component catalyst for the steam reforming of methanol, Indian Journal of Chemistry, **44**, 2005, p. 64-66;

13. *** www.mathworks.com

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