SIMULATION OF THE SIEVE PLATE ABSORPTION COLUMN FOR NITRIC OXIDE ABSORPTION PROCESS USING NEURAL NETWORKS

Edward Rój, Marcin Wilk

Instytut Nawozow Sztucznych (INS), Pulawy, Poland

ABSTRACT

We present the modeling of the absorption column performance using feed-forward and radial basis function type neural networks. The input and output data for training of the neural networks are obtained from a rigorous model of the absorption column. The results obtained form the neural network models are compared with the results obtained mainly from the simulation calculations. The results show that relatively simple neural network models can be used to model the steady state behavior of the column. There are no essential preferences for the type of neural network applied for simulation purposes. Radial basis function based architecture is better in case of lower training data are available.

INTRODUCTION

Absorption column is one of the most important and expensive apparatus in nitric acid plant. Modern industrial nitric acid plants use mainly sieve plate absorption columns with weirs, Fig.1.
Absorption columns built about presently are over 6 m diameter and heights over 80 m. From the point of view of high capital costs and environmental protection regulation requirements the exact mathematical model of processes taking place in the column is indispensable. Ability of prediction of result of mass flow rate changes as well as temperature and pressure variations is useful in operational conditions for absorption column. In initial period of development of technology of nitric acid production the absorption columns were designed using experimental data collected from commercial plants. During growth of knowledge of basic theory of the process some calculations were made using graphic methods. Application of computers has allowed to develop more precise mathematical models of the absorption process and to perform fast and exact calculations of the columns. Problem of mathematical modeling of absorption columns was object of interest of many researchers and practitioners. The mathematical models for NOx absorption can be divided into two types:

- models applying an idea of plate efficiency used in mass transfer calculations,
- models applying mass transfer coefficients for mass transfer calculations on each plate.

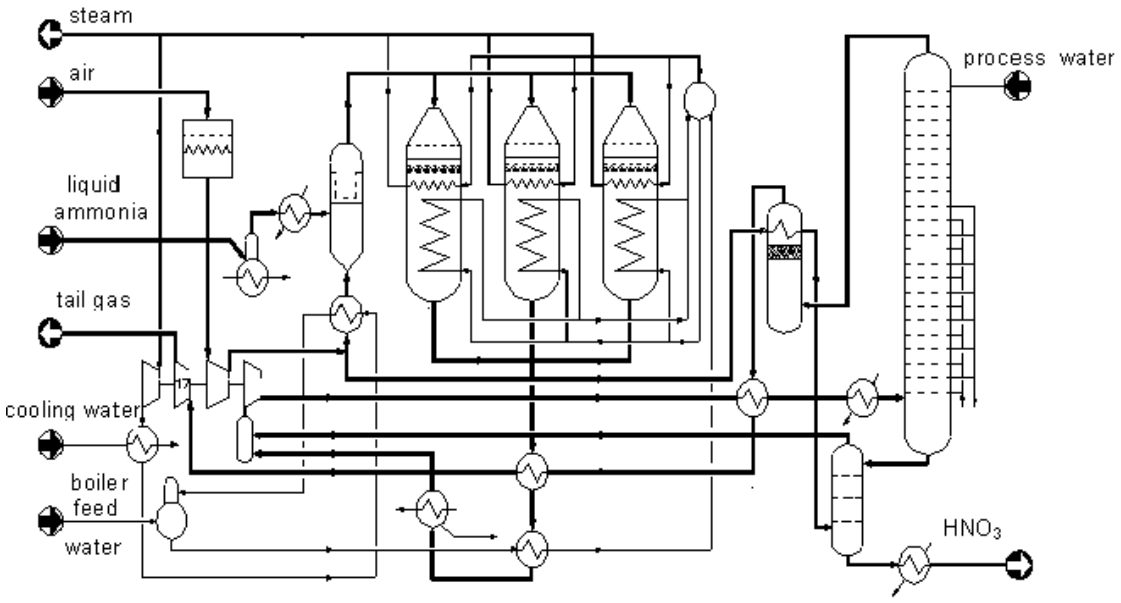

Fig. 1 Diagram of a nitric acid plant

One of the first model of the first type was Koukolik's and Marek's model [5] and Roudier's, Longeat's and Enjalbert's model.

The models are simplified and temperature and pressure distribution is assumed at each sieve plate. The plate's efficiency was calculated using also simplified relationships. Other models belonged to the same type were developed later by Sobotka [7], Holma and Sohlo [8], Carta and Pigford [9] and Guiterrez-Canasa [10]. They had similar limitations relying on lack of pressure drop calculations for gas passing over the plates and heat balance calculations for NOx oxidation in area among the plates. In the second type models the way of calculation of NOx oxidation was similar to the first type but mass transfer rate calculations were performed in a different way. Emig et al [11] assumed constant mass transfer coefficients for the whole column. Equlibrium partial pressure of gas phase was calculated using Henry's constant. However, this model did not involved pressure losses and heat balance between the plates. A model of similar degree of accuracy was presented by Counce and Perona [12]. A novel approach has been used in models developed by Wiegand, Scheibler and Thiemann [13] from Uhde firm and Pradhan and Suchak [14]. The authors have used commonly known equations cited in literature or elaborated by themselves to calculate reaction rate and equlibrium data in gas phase between the plate area and in liquid phase as well. Pressure drop and heat balance models were also incorporated into their calculations.

In INS Pulawy a model of sieve plate column has been developed basing on plate efficiency strategy. Comparing another models, the developed model is significantly complex. Using the model a simulation calculations of heat and mass transfer can be done for each plate of the column. Of course, the model can be applied to any sieve plate column. The model has been tested using data collected from different nitric acid industrial plants. Positive results allowed to use the model to design a column for a new commercial plant [15,16]. Furthermore, simulation results obtained with the model allowed to design a new type of absorption column. Moreover, to speed up

calculations a neural model approach has been applied. The new approach will assure to apply the model for optimization of a nitric acid plant performance. The neural network based model can be easily adopted to the existing environment using available data collected from the computer based data acquisition systems.

MATHEMATICAL MODEL

In the nitric acid plant the mixture of ammonia and air is passed over catalyst gauze. Among many reactions the a major one:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad \text{(I)}$$

The gas stream leaving the ammonia oxidation reactor is cooled in a heat exchanger. If its temperature is below a determined limit than NO is transformed into NO_2, and N_2O_4 and a condensate appears as well. Some part of nitric oxides react with condensing water forming a solution of weak nitric acid which concentration depends on time of contact and amount of the condensed water. The condensate is then fed with a pump on a proper plate of the absorption column. In the absorption column the different reactions can occur in gas and liquid phase from which the most important are:

- Oxidizing of nitric oxide to nitric dioxide and dimerization to N_2O_4

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{(II)}$$

$$2NO_2 \leftrightarrow N_2O_4 \quad \text{(III)}$$

- Reaction of dioxide and tetroxide with water

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \quad \text{(IV)}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \quad \text{(V)}$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad \text{(VI)}$$

Besides, gas is bubbled through a pool of liquid where water vapor condenses. The cool gas stream consisting of (NO, NO_2, N_2O_4), O_2, H_2O and small amount of N_2O, CO_2 and Ar is introduced at the bottom of the column. Besides, one of the sieve plate is supplied with acid condensate formed in the condenser. The last plate is fed with a water allowing to obtain a stream of nitric acid of desired concentration. Heat transfer coils filled with water are placed in the pool of liquid over the plates. They are designed to remove the heat liberated during oxidation of NO and formation of NO_2, N_2O_4 and HNO_3. Model for the absorption column has been developed using the following assumptions:

- gas and liquid phases are ideally mixed in the pool of liquid over the plate,
- there are not concentration and temperature gradients in the pool of liquid,
- HNO_2 decomposes to HNO_3, NO and H_2O in the pool of liquid,
- gas and liquid phases flow in a plug flow type,
- heat losses to environment are negligible,
- reaction heat is exchanged by the heat transfer coils,
- temperature of gases leaving the pool of liquid and the liquid temperature are the same,
- chemical reactions proceed in the empty sections without heat exchange with environment.

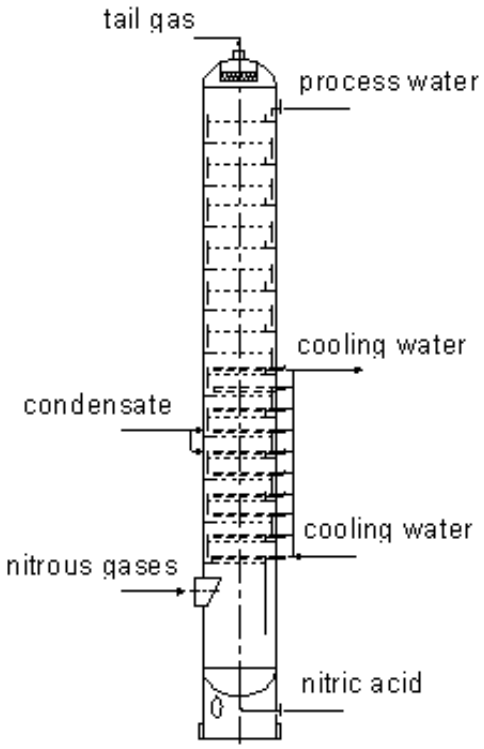

Fig. 2. A commercial nitric acid column

Model for sieve plate

The following reaction occurs in the liquid phase:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad \text{(VII)}$$

The extent of the reaction depends on plate construction features, composition of gas mixture entering the sieve plate and nitric acid concentration formed on the plate. Efficiency of the plate is defined a distance of NO_x partial pressure and its equilibrium pressure. The equilibrium pressures of NO and NO_2 have been calculated using Zhidkov and Skorcov relationship [17].

$$\log K_1 = \log \frac{p_{NO}}{p_{NO_2}^3} = 6{,}5235 - \log \frac{8{,}5}{8{,}5 - c_{HNO_3}} + 2{,}2215 \log \frac{100}{c_{HNO_3}} -$$
$$- 0{,}05618 c_{HNO_3} - 0{,}05618 c_{HNO_3} - 0{,}004854 (T - 273{,}15) + \qquad (1)$$
$$+ 0{,}01666 \cdot 10^{-3} (T - 273{,}15) c_{HNO_3}$$

Having calculated the equilibrium pressures of NO and NO_2 the theoretical extent of NO_x transformation was calculated using the equations:

$$y = 1 - \frac{pnr^i (p^i - pnp)}{pnp (p^i - pnr^i)} \qquad (2)$$

$$pnr^i = p_{NO} + p_{NO_2} \qquad (3)$$

$$pnp = \frac{p^{i-1}\sum_{jj=NO}^{N_2O_4} G_j^{i-1}}{\sum_{j=NO}^{Ar} G_j^{i-1}} \quad (4)$$

Pressure of gas over the plate was calculated using equation

$$p^i = p^{i-1} - \Delta p \quad (5)$$

Pressure drop over the plate was calculated using Hunt relationship [16]. The amount of nitric acid formed on the plate is a function of the plate efficiency, theoretical ratio of NO_x reaction and amount of the NO_x entering the plate:

$$x_{HNO_3} = \eta y \sum_{j=NO}^{N_2O_4} G_j^{i-1} \quad (6)$$

$$\eta = 1 - \exp(A \frac{\left(1 + \frac{c^i_{HNO_3}}{100}\right)^{1,49}}{\left(w_g^i\right)^{0,546}\left(p_{NO}^{i-1}\right)^{0,0483}\left(T^i\right)^{1,248}}) \quad (7)$$

The composition of nitric acid solution flowing off the i-th plate can be described by the following relationships:

$$L^i_{HNO_3} = L^{i+1}_{HNO_3} + x_{HNO_3} \quad (8)$$

$$L^i_{H_2O} = L^{i+1}_{H_2O} + y_{H_2O} - 0,5x_{HNO_3} \quad (9)$$

$$y_{H_2O} = G^{i-1}_{H_2O} - \frac{p^i_{H_2O}\left(\sum_{j=NO}^{N_2O_4} G^i_j + \sum_{j=O_2}^{Ar} G^i_j\right)}{p^i - p^i_{H_2O}} \quad (10)$$

The composition of solution flowing off the plate being supplied with condensate can be calculated as follows:

$$L^i_{HNO_3} = L^{i+1}_{HNO_3} + x_{HNO_3} + L^k_{HNO_3} \quad (11)$$

$$L^i_{H_2O} = L^{i+1}_{H_2O} + L^k_{H_2O} + y_{H_2O} - 0,5x_{HNO_3} \quad (12)$$

Model for empty space between plates

In empty space the following reactions occur: NO oxidation and NO_2 formation and dimerization of NO_2 and formation of N_2O_4. The rate of NO oxidation can be calculated using the equation:

$$-\frac{dp_{NO}}{dt} = kp^2_{NO}p_{O_2} \quad (13)$$

Constant k can be calculated as follows:

$$k = 97,402\exp\left(42,982 + 1,323\cdot 10^{-2}T - 3,943\cdot 10^{-6}T^2 - 7,5\ln T\right) \quad (14)$$

using the equations (13) and (14) the degree of oxidation α can be calculated as a ratio of partial pressure of NO_2 and NO. The equilibrium extent of dimerization rate of NO_2 was calculated using the relationship:

$$K_p = \frac{2p^iG^i_{NO_2}(1-\beta)^2}{\beta\left(1 - 0,5G^i_{NO_2}\right)} \quad (15)$$

$$\ln K_p = 7{,}0505 - \frac{6198}{T} + 1{,}75\ln T + 0{,}011T - 1{,}64 \cdot 10^{-5} T^2 \qquad (16)$$

Inlet gas phase composition at i+1 plate can be calculated using the equations:

$$G_{NO}^{i+1} = (1-\alpha)\left(G_{NO}^{i-1} + 0{,}5x_{HNO_3}\right) \qquad (17)$$

$$G_{NO_2}^{i+1} = (1-\beta)\left(G_{NO_2}^{i-1} + 2G_{N_2O_3}^{i-1} - 1{,}5x_{HNO_3} + \alpha\left(G_{NO}^{i-1} + 0{,}5x_{HNO_3}\right)\right) \qquad (18)$$

$$G_{N_2O_4}^{i+1} = 0{,}5\beta\left(G_{NO_2}^{i-1} + 2G_{N_2O_3}^{i-1} - 1{,}5x_{HNO_3} + \alpha\left(G_{NO}^{i-1} + 0{,}5x_{HNO_3}\right)\right) \qquad (19)$$

$$G_{O_2}^{i+1} = G_{O_2}^{i-1} - 0{,}5\alpha\left(G_{NO}^{i-1} + 0{,}5x_{HNO_3}\right) \qquad (20)$$

$$G_{H_2O}^{i+1} = G_{H_2O}^{i-1} - y_{H_2O} \qquad (21)$$

$$G_{N_2}^{i+1} = G_{N_2}^{i-1};\ G_{N_2O}^{i+1} = G_{N_2O}^{i-1};\ G_{CO_2}^{i+1} = G_{CO_2}^{i-1};\ G_{Ar}^{i+1} = G_{Ar}^{i-1} \qquad (22)$$

Having obtained the gas phase composition then the heat effect of the NO oxidation reaction and NO_2 dimerization was calculated at the inlet of plate i+1. During absorption process there is heat liberated. The heat is removed by a cooling coil system immersed in the pool of liquid. Heat balance for the i-th plate can be presented as follows:

$$\sum_{j=NO}^{Ar} G_j^{i-1} H_j^{i-1} + \left(L_{HNO_3}^{i+1} + L_{H_2O}^{i+1}\right) H_{HNO_3+H_2O}^{i+1} - \\ - \sum_{j=NO}^{Ar} G_j^{i} H_j^{i} - \left(L_{HNO_3}^{i} + L_{H_2O}^{i}\right) H_{HNO_3+H_2O}^{i} - \qquad (23)$$
$$- k_c^i F^i \Delta T^i = 0$$

For the plate where a condensate is fed the mass balance should be completed with an enthalpy of the stream. Heat transfer coefficients have been calculated using data obtained by Hellmer and Jozwiak [18, 19].

Using the above equations a software for nitric acid column simulation has been developed. The software was tested for the industrial plant performance conditions. Quite good results have been obtained comparing the experimental results Fig. 3.

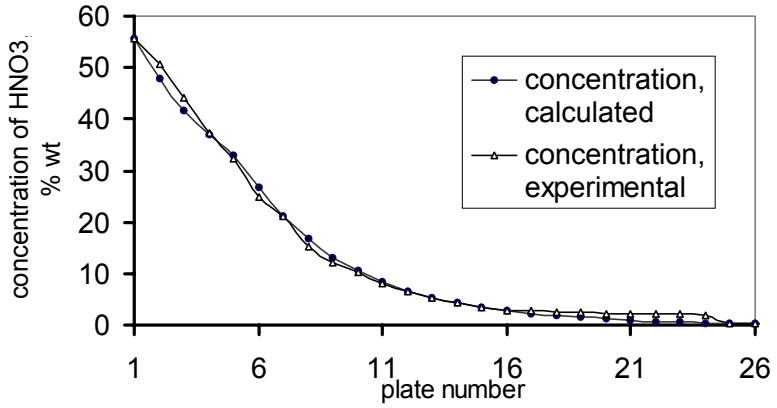

Fig.3. Simulation of a commercial nitric acid column – concentration of HNO_3 vs. plate number

For simulation and control purposes it is sometimes necessary to calculate quickly the desired output data. To meet the needs a neural approach has been applied.

NEURAL NETWORKS

Neural network (nn) approaches have been proposed as useful and powerful tools for process modeling and simulation by a number of researchers [20]. One of the main features of the neural networks is the potential to perform nonlinear system identification on the basis of historical or currently collected data. After being trained on a number of examples of a relationship, they can often induce a complete relationship that interpolates from the examples in a sensible manner. Neural networks with feed-forward or radial basis function (RBF) architecture can approximate with arbitrary precision, static nonlinear functions.

Feed-forward neural networks

Neural networks are parallel structures of activation elements often of the same type [21]. Signals are propagated from the input nodes to the hidden nodes via weighted connections. The signals from the hidden nodes feed forward to the output nodes. Computation via a transfer function occurs only in the hidden and output nodes. The weights of a network contain representational information and are the decision variables adjusted during training. Feed-forward networks have been usually trained using a backpropagation algorithm [22]. The backpropagation algorithm is a first order gradient descent based method (an optimization technique) that can adjust the network weights minimizing the mean squared error between the network outputs and target outputs for a set of training data. The feed forward networks perform a static nonlinear mapping of the input to output space.

RBF networks

Another technique enabling to accomplishment a nonlinear mappings of input signals into output signals is RBF network [23]. The RBF architecture comprises only three layers: input layer, hidden layer and output layer. The transfer function in the input units is unity if the inputs themselves are properly scaled. The transfer function in the second layer is radial basis activation function, and the output layer transfer function is usually linear or sometimes nonlinear type. Training of the network requires two steps. First, the centers c_i of hidden layer neurons activation functions should be chosen and the activation function widths σ_j should be set. Then the output synaptic weights can be computed solving the matrix equation:

$$\Phi w = d \qquad (24)$$

where Φ - is the interpolation matrix, w – is the vector of synaptic weights of an output layer neuron, d – is a vector of the output patterns.

$$\Phi = \begin{pmatrix} \varphi_{11} & .. & .. & \varphi_{1n} \\ \varphi_{21} & .. & .. & \varphi_{2n} \\ .. & .. & .. & .. \\ \varphi_{p1} & .. & .. & \varphi_{pn} \end{pmatrix};\ w = \begin{pmatrix} w_1 \\ w_2 \\ \\ w_n \end{pmatrix};\ d = \begin{pmatrix} d_1 \\ .. \\ .. \\ d_p \end{pmatrix}$$

$$\text{and } \varphi_{ij} = \varphi(x_i, c_j) = \exp\left(-\sqrt{\sum_{s=1}^{k} (x_{is} - c_{js})^2} / \sigma_j \right)$$

The vector w can be simply computed as:

$$w = \Phi^{-1} d \qquad (25)$$

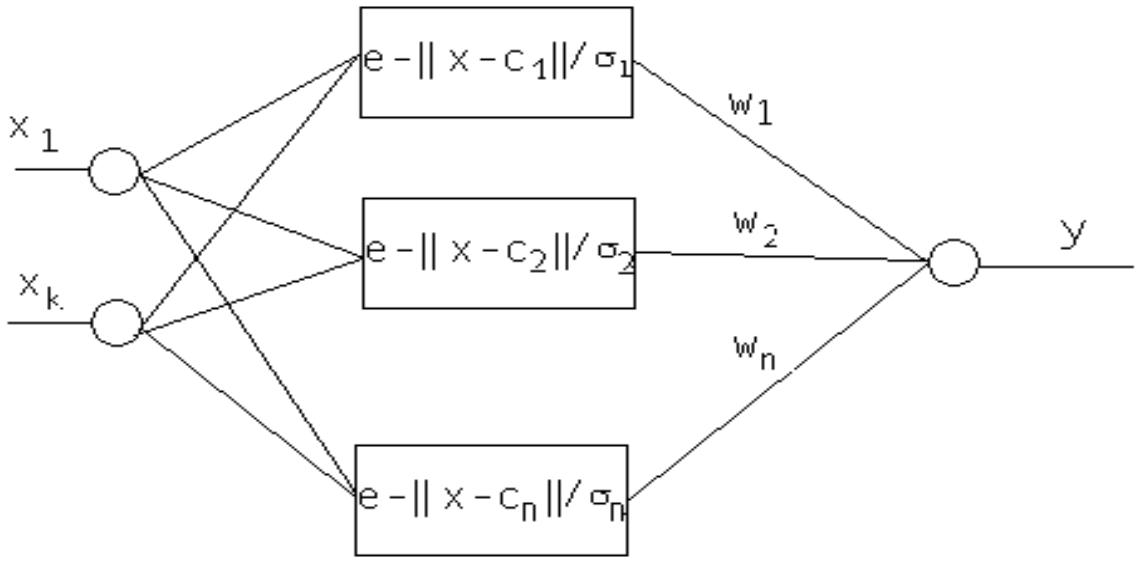

Fig. 4. Architecture of a RBF neural network

MODELING OF A SIEVE PLATE COLUMN USING A NEURAL NETWORKS

The developed model of the sieve plate absorption column has been used as a reference model providing data for training the feed-forward and RBF neural networks. Some input and output data for neural network training are listed below. An absorption column model may be presented according to the below diagram, Fig. 5. Input variables cover gas stream G consisting of nitrous gas components (NO,NO_2,N_2O_4,O_2,H_2O,N_2), condensate stream g_k at concentration c_k and temperature t_k, process water w_{hg} at temperature t_w and cooling water temperature, t_{wc}. Output variables cover tail gas stream G_{out} consisting of the following components: NO_x,O_2,H_2O,N_2 (where NO_x=NO+NO_2), nitric acid stream G_{HNO3} at concentration c_{HNO3}. Another parameters as nitric acid temperature and cooling water temperature are not included in the figure. For practical purposes the most interesting absorption column output is nitric acid production G_{HNO3} and its concentration c_{HNO3} as well as NO_x emission. These components are strongly dependent on gas load G and its parameters T and P and process water flow rate w_{hg} as well as condensate flow rate g_k and its concentration c_k. In Fig. 7. there is a simulation results of NO_x emission for the above mentioned parameters as a function of G and P.

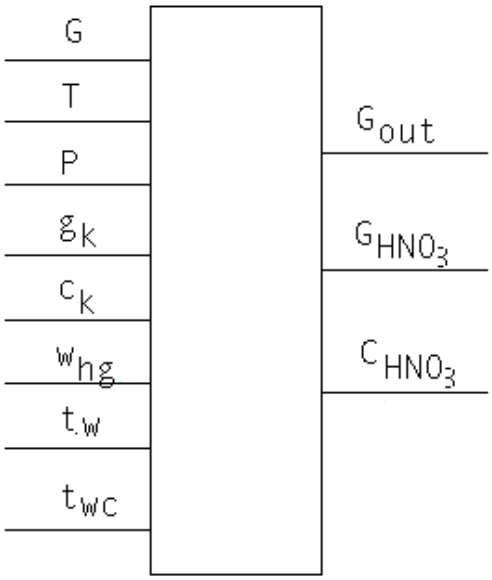

Fig.5. Absorption column model

Architecture determination

feed forward network

This task in system modeling corresponds to the determination of the architecture of the multilayered perceptron (MLP) type network, that is, the number of input variables, which gives the number of input layer nodes, the number of hidden layers, and the number of nodes in each of the hidden layers. The final step is the determination of the output layer nodes corresponding to the number of output variables. There are no definitive methods for deciding a priori the number of layers and units in the hidden layers. The one hidden layer is usually sufficient to model any continuous function. The number of nodes is related to the complexity of the nonlinear function which can be generated by the neural network. One approach to selecting the number of hidden layer nodes involves randomly splitting the data into two subsets, using one of the sets for training and the other for testing the output results. If the average error on the training subset is significantly less than the testing subset, over-fitting is indicated and the number of nodes should be reduced. One of the possible procedure is to start with a small number of nodes and increasing the number of nodes until there is no significant increase in modeling accuracy gained by increasing the number of nodes. The weights of the neural connections are determined by using a backpropagation algorithm.

radial base function network

The radial based function architecture is constructed on the base of clustering methods allowing to determine the c_i and σ values . After positioning and sizing the nodes, the second layer weights, which appear linearly in the calculation of the network output, must be determined. These parameters can be estimated usually by solving the appropriate optimization problem.

Model validation

Model validation is usually the final step of any identification procedure. If the system under test is nonlinear then well known covariance tests covering autocorrelation or cross-correlation tests, developed for linear systems, provide incorrect information. So that extended tests can be applied to validate the neural network models. If the modeling data are noise-free, the neural network test can be performed using noise corrupted input signals. A standard error of estimates defined as:

$$\varepsilon = \sqrt{\frac{\sum_{k=1}^{N}(y_{mk} - y_{sk})^2}{\sum_{k=1}^{N} y_{sk}^2}} \qquad (26)$$

ε is a measure of quality of any developed model.

Results

feed-forward neural network

A set of about 4000 data values have been obtained as a result of simulations carried out using the developed absorption column model. The data were divided into two equal subsets. One of the subset was used as the training data set and on other one as the testing set. Using the incremental procedure mentioned above the number of nodes in the hidden layer was obtained. The number of nodes in the hidden layer required to model the system adequately is determined as 14. This results in all overall network with 8 nodes in the input layer, 14 nodes in the hidden layer and 3 nodes in the output layer. This results in a total 168 weights including bias connections. The activation function is of sigmoid type as :

$$f(x) = \frac{1}{1 + \exp(-x)} \qquad (27)$$

RBF network

The same set of training data as mentioned above has been used to position the nodes c_i and to determine the widths σ_i. A result of the calculations is a number of nodes which is 40. This results in a total 40 weights.

CONCLUSIONS

The work demonstrates that the nonlinear absorption column model can be approximated using feed-forward and RBF type neural networks. The comparison of the responses of the nonlinear simulations with the responses of the identified models indicates very good agreement. The identified model can be used for simulation and optimization purposes. RBF based models require less training data comparing the MLP based models.

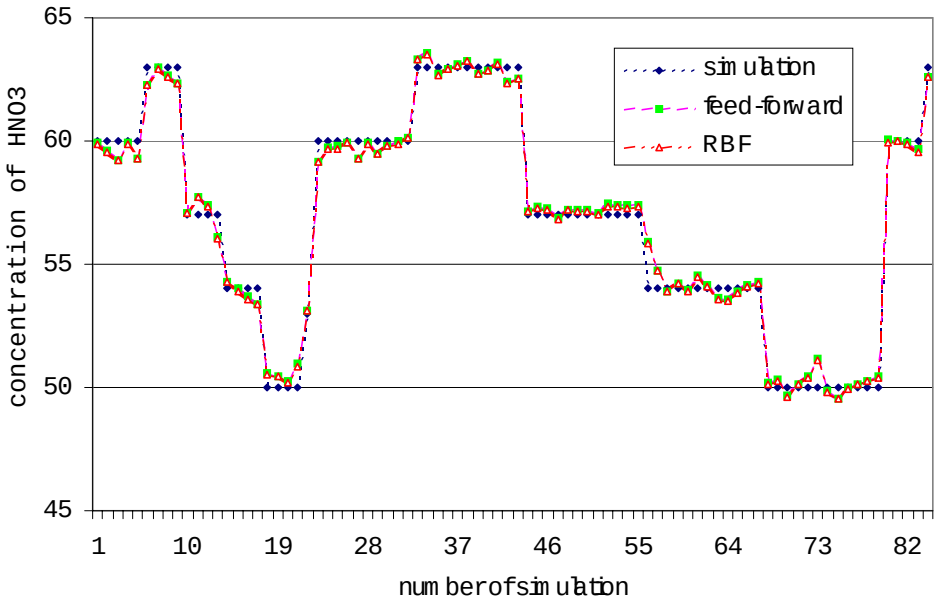

Fig. 6. Comparison of simulated data and calculated using feed-forward and RBF networks.

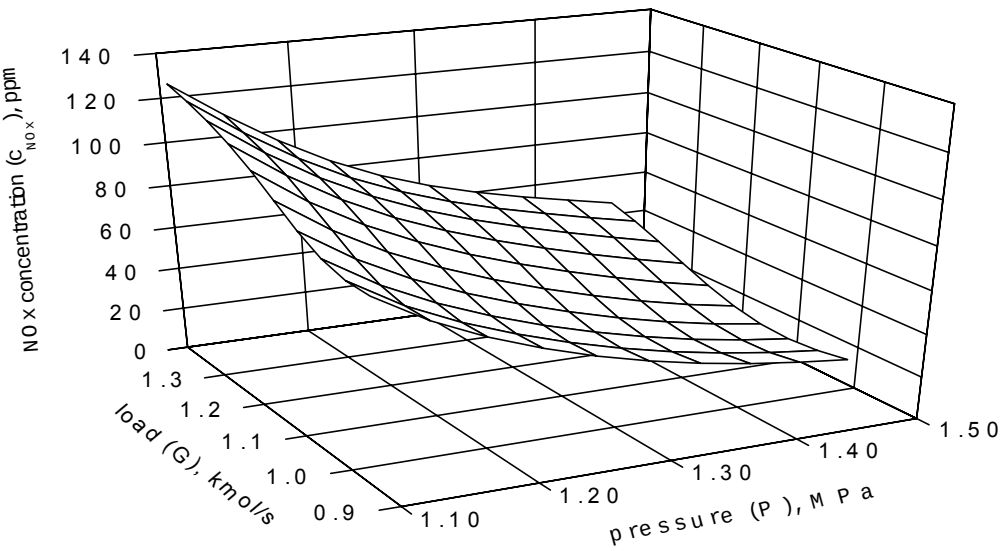

Fig.7. Plot of NOx concentration in tail gas as a function of gas flowrate, G, and absorption column pressure, P.

NOMENCLATURE

A – constant,
c_{HNO_3} – HNO_3 concentration in bulk liquid, wt %.
F – area, m^2.
G – component of gas phase, kmol/s,
H – enthlapy, kJ/kmol,
k – rate of NO oxidation, $MPa^{-2}s^{-1}$,
k_c – heat transfer coefficient, $W/(m^2K)$,
K_p – equilibrium constant of dimerization of NO_2,
L – component of liquid phase, kmol/s,
p_{NO} – partial pressure of NO, MPa,
p_{NO_2} – partial pressure of NO_2, MPa,
p, P – pressure, MPa,
T – temperature, K,
w_g – gas velocity , m/s,
y_m,y_s – nn model and target data,
α – degree of NO oxidation,
β – degree of NO_2 dimerization,

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Nitric acid, absorption column, neural network, simulation, RBF network