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Hybrid training approach for artificial neural networks using genetic algorithms for rate of reaction estimation: Application to industrial methanol oxidation to formaldehyde on silver catalyst

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ABSTRACT

A novel reactor simulator for the methanol oxidation to formaldehyde on silver catalyst was presented in this paper, including an original kinetic model based on artificial neural networks. The neural network training was performed using genetic algorithms associated with standard back-propagation, in order to improve the training efficacy, eliminating the effect of random initial weights estimates. Experimental data for training (rates of reaction) were obtained from process data (conversion and selectivity), using a back-calculation procedure through a simplified deterministic model implemented in the reactor simulator. Process data are widely available at industrial plants or literature and the proposed approach improves the response time to train the neural network in cases where rigorous kinetic experimental work cannot be conducted due to resource limitations. The simulator containing the trained artificial neural network was successfully validated with literature and industrial data, especially at industrial operating conditions, where available deterministic kinetic models for this system have failed. The simulator presented here, as well as the procedure to train the neural net consist in a powerful tool for plant process engineers to optimize the formaldehyde silver reactor in a timely and economical fashion.

1. Introduction

Formaldehyde is one of the world's most important chemicals, basic building unit for a wide variety of substances [1]. Approximately 32 million metric tonnes of formalin, 37% solution basis, is produced worldwide per year [2], while the consumption has grown steadily over the past two decades due to increasing demand by the construction and automotive sectors for engineered products manufactured using formaldehyde-based resins.

Two processes are commonly employed for formaldehyde manufacture: the Silver and the Formox process [3,4]. In the former, methanol-rich methanol–air-stream mixture is passed through a simple silver catalyst fixed-bed at 600–700 °C. The Formox process differs in the nature of the catalyst (iron–molybdenum oxides), methanol concentration (oxygen-rich), bed temperature (300–400 °C) and bed configuration (multitubular reactor). The silver catalyzed route accounts for approximately 30–50% of the current world's capacity [5–7]. It consists basically in two parallel reactions: methanol oxidation (Eq. (1)) and methanol dehydrogenation (Eq. (2)), both taking place on the silver surface. The first reaction (oxidation) is responsible for approximately 50–60% of the formaldehyde produced. Formaldehyde is consumed in the reactor by further oxidation to carbon dioxide on the silver catalyst (Eq. (3)) and gas-phase decomposition to carbon monoxide above 650 °C (Eq. (4)).

$$CH_3OH + (1/2)O_2 \rightarrow HCHO + H_2O \qquad \Delta H = -159\,kJ/mol \qquad (1)$$

$$CH_3OH \leftrightarrows HCHO + H_2 \qquad \Delta H = +84\,kJ/mol \qquad (2)$$

$$HCHO + O_2 \rightarrow CO_2 + H_2O \qquad \Delta H = -514\,kJ/mol \qquad (3)$$

$$HCHO \rightarrow CO + H_2 \qquad \Delta H = +7\,kJ/mol \qquad (4)$$

Water plays an important role in increasing the selectivity towards the desired product [6,8–10]. The addition of water or not at reactor feed differ the two major variation of formaldehyde industrial process: *Water Ballast Process* and *Methanol Ballast Process*, respectively.

After more than a century since formaldehyde synthesis was developed, there is no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions [5,10–15]. In only a few reported studies in literature, attention has been paid to the way that by-products are formed. No single study covers the influence of temperature, methanol and oxygen concentrations, as well as residence time under industrial conditions [10,16]. The development of new models is costly,

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time consuming and they are not the focus of industrial personnel. Any attempt to obtain kinetic models applied to industrial conditions in a timely fashion would be a powerful tool for understanding and optimizing this process. In these cases, novel approaches like neural networks are efficient in predicting the rate of reaction, based on available data. Considering the potential market demand for formaldehyde and strong competition, there are significant economic incentives to improve the selectivity of the process [5,6,17]. Environmental pressure is also a driver in this case, once the carbon emissions generated by formaldehyde plants (carbon dioxide and carbon monoxide) will have to be reduced soon in order to comply with world's efforts against global warming.

Artificial neural networks (ANNs) are widely used for simulation of cases where deterministic models are not available or fail in fitting the data [18,19]. The model is known to be generic and it can be used for a variety of problems with minor adaptations [20]. The ANN learns the data pattern using an algorithm known as "training", where many data rows [input/output] are presented to the net until it fits the data. Details about the neural network algorithm features and training process may be found in [21–27].

The classical ANN training methods, as back-propagation (BP), have been improved by the association of new techniques, as genetic algorithms (GA). The training session starts with GA, which performs a global search on the net weights range, refining an initial random set of weights to obtain a better estimate, more probable to be close to the global optimum. The BP algorithm then assumes the training, refining the solution provided by GA to approach the optimum solution. GA have been successfully used to solve optimization problems involving multiple parameters, where many local optima may exist and there is a need to perform a wide search on the variables range [28–30]. Details about GA may be found in [22,31–36].

In this work, the ANN was trained using an association of GA and BP as a training algorithm. Experimental kinetic data correlating rate of reaction with associated conditions (composition, temperature and pressure) is required to train the ANN, but this kind of data is not usually available on industrial processes, which measure and collect only macroparameters as conversion and selectivity. Due to several limitations [5,10–15], particularly for the formaldehyde process, there is little kinetic data reported in literature and the best works available deal only with macroparameters. In this sense, we employed an alternative approach to back-calculate the rate of reactions from these macroprocess parameters, as described in [25], according to the steps described below.

Initially, a simplified deterministic kinetic model was inserted into the reactor simulator. A set of data points which correlated conversion, selectivity and operational conditions (temperature, pressure and feed composition) was taken into consideration and, for each of these process data points, the simplified model parameters were adjusted until the conversion and selectivity calculated by the simulator fit the experimental ones. Once each individual point was fit, the rate of reaction profile through the catalytic bed calculated by the simulator was saved with the associated local operational conditions (partial pressures and temperature profiles), also provided by the simulator. This simplified kinetic model fit had to be done individually for each single data point and it was only valid for that data point, but after repeating the same procedure for all available experimental points, a huge set of rate of reaction data may be obtained [25]. It is important to mention that the reactor profiles obtained through this procedure is the goal, for further use on ANN training, and not the singular parameters of the simplified model. This procedure has been successfully applied by the authors as detailed in [25] and it is not supposed to replace rigorous experimental work to obtain the kinetics of a reaction, but it represents a quick approach to generate required data to simulate the process, in cases where there are limited resources for kinetic experimentation.

The ANN was trained, using the back-calculated rates of reaction and the association GA + BP as a training algorithm and, finally, the optimum set of weights was stored in a data file. The trained ANN is in fact the kinetic model and it was then able to estimate the rate of reactions for the whole range of input variables. Rates for the methanol oxidation to formaldehyde on silver catalyst back-calculated from process information obtained in literature [14] and industry were used to exemplify the procedure. The hybrid simulator, using a deterministic model for the catalytic fixed-bed and ANN to calculate the rate of reactions, was employed to estimate conversion and selectivity at selected conditions, in order to compare simulated values with experimental ones, for validation purposes. Many cases were successfully tested, and the procedure proved to be an effective tool for the simulation of this process.

To the best of our knowledge, this is the first time ANN is used to model the kinetics of the methanol oxidation to formaldehyde on silver catalyst. The simulator equipped with the trained ANN was able to successfully estimate industrial conditions, where deterministic models available in literature failed. The back-calculation of kinetic data from macroprocess information, using a simplified deterministic kinetic model with the simulator, was used for the first time with this process as well.

The association of GA and BP for ANN training has been extensively reported in literature and proved once more to be a good approach to improve training efficacy.

2. Formaldehyde reactor simulator

The formaldehyde fixed-bed reactor was simulated based on mass balance (Eq. (5)), derived from the equation of continuity [37] on cylindrical coordinates, considering plug-flow tubular model, molecular diffusion, mechanical dispersion and steady-state operation [38,39]. Calculations and industrial observations indicated that, for practical ends, the reactor (fixed-bed) operates isothermally [25,40,41]. The pressure drop in the bed is small enough to consider the pressure constant in the simulations [25]. Fig. 1 shows a scheme of a typical silver reactor.

$$D_L.\frac{\partial^2 C}{\partial z^2} + D_R.\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}.\frac{\partial C}{\partial r}\right) - V_Z.\frac{\partial C}{\partial z} + \nu_A.R_V = 0 \quad (5)$$

where "C" is the substance concentration (kg/m^3); "r" is the distance from the reactor central line (m); "z" is the distance from the reactor inlet (m); "D_L" and "D_R" are the axial and radial hydrodynamic dispersion coefficients, respectively (m^2/s); "V_Z" is the axial velocity (m/s); "ν_A" is the stoichiometric coefficient for the studied substance (dimensionless) and "R_V" is the rate of the reaction per reaction volume (kg/m^3 s). The hydrodynamic dispersion coefficient is the sum of molecular diffusion coefficient and the mechanical dispersion coefficient.

The mass balance differential equation was solved numerically using the Crank–Nicholson algorithm [42,43], a semi-implicit method known to be intrinsically stable. The physical properties of pure substances and mixtures were calculated [44] at each step of Crank–Nicholson method, according to the actual local conditions, as a function of temperature and pressure.

The simulator contains a sub-routine with the ANN algorithm to calculate the rate for the three reactions of interest in this process: formaldehyde formation (Eq. (1) + Eq. (2)), oxidation (Eq. (3)) and gas-phase decomposition (Eq. (4)), using the trained weights stored in a data file. For every step of the numerical method, the simulator

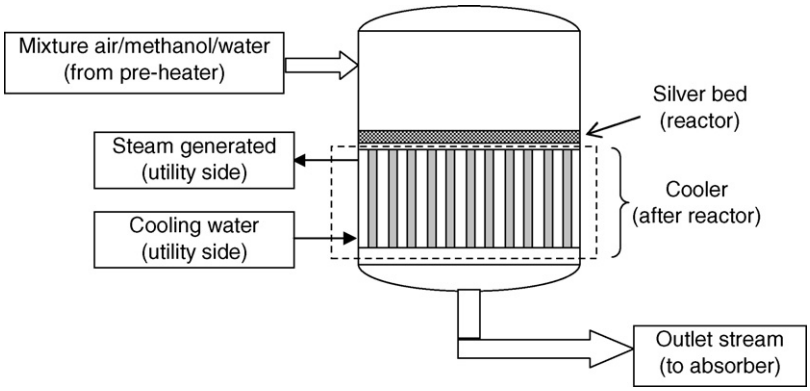

Fig. 1. Scheme of a typical silver reactor, showing the fixed-bed and the downstream cooler.

provides to the ANN the local conditions (temperature and partial pressures) and it calculates the rates for the three reactions.

Fig. 2 shows a flow diagram with the complete procedure. The inputs to the network are bed temperature (K); total pressure (atm); partial pressures of methanol, oxygen, water, hydrogen, formaldehyde, carbon dioxide and carbon monoxide. The number of neurons at hidden layer was varied to obtain the optimum configuration. The hybrid simulator containing the ANN as well as the sub-routines for ANN training using GA and BP were written by the authors in Fortran® code.

3. Results and discussion

Experimental process data obtained in literature [14] and industrial data were used to exemplify the procedure and train the ANN.

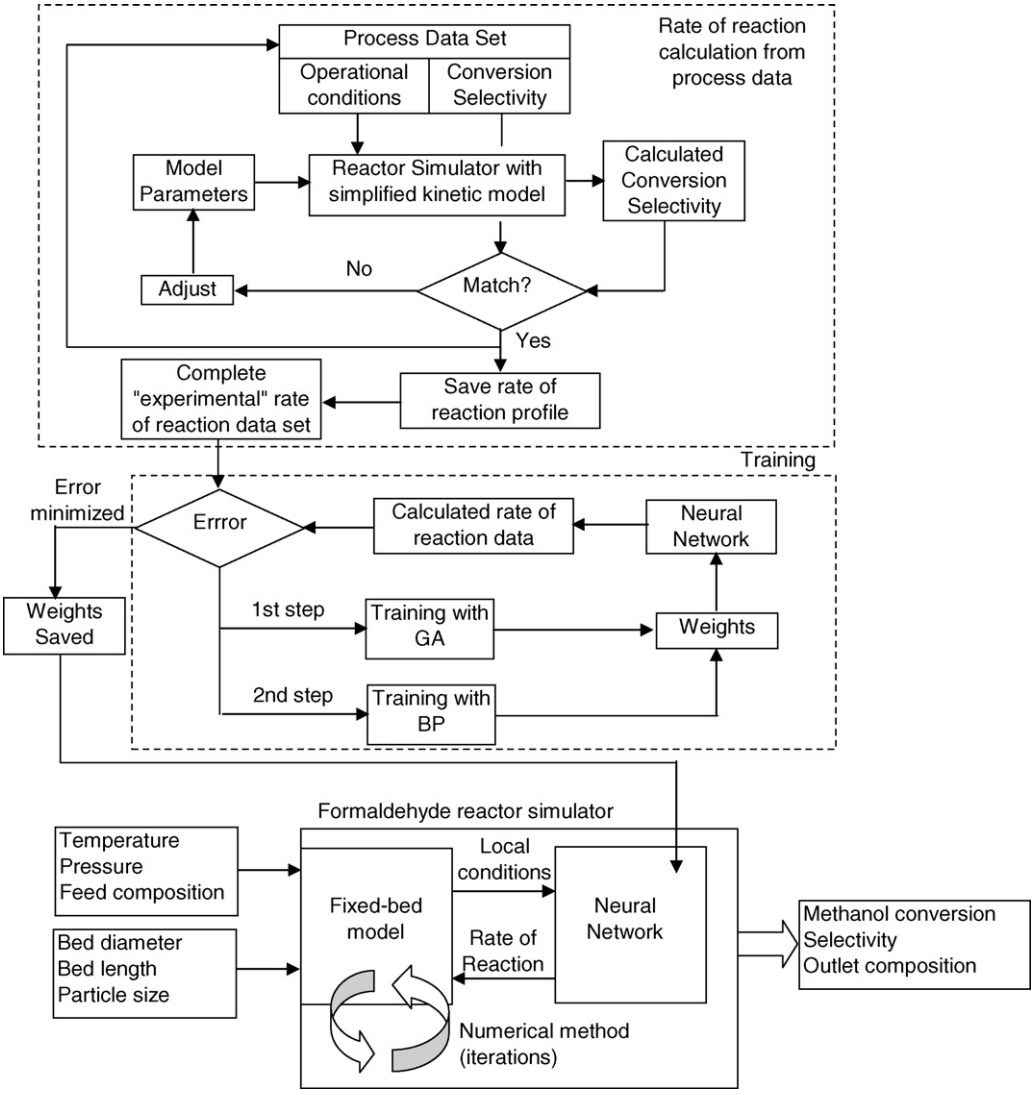

Fig. 2. Flow diagram with the complete procedure for back-calculation, ANN training and reactor simulation.

Table 1
Sample of the rate of reaction set of data (nitrogen partial pressure completes total pressure).

Rate of reaction (kmol/m³ h)			Process conditions–partial pressures (atm)						
R_{HCHO}	R_{CO_2}	r_{CO}	CH_3OH	O_2	H_2O	HCHO	CO_2	H_2	CO
5.9715E+02	4.2389E+01	4.8627E+02	4.09E−02	2.44E−02	7.87E−02	2.47E−02	1.90E−03	3.27E−02	1.17E−02
4.6233E+02	1.6475E+01	2.1465E−01	6.36E−02	3.13E−02	7.00E−02	1.73E−02	3.79E−04	9.22E−03	2.88E−06
1.5812E+02	1.9595E+01	1.0479E+00	2.66E−02	2.04E−02	8.59E−02	4.98E−02	2.83E−03	2.93E−02	8.85E−05
5.9728E+01	1.7348E+01	1.4351E+00	1.12E−02	1.50E−02	9.25E−02	6.14E−02	5.50E−03	3.94E−02	2.73E−04
6.6853E+01	1.4969E+01	1.3753E+01	8.90E−03	1.52E−02	9.33E−02	6.33E−02	3.82E−03	4.06E−02	2.16E−03
5.7087E+01	1.7234E+01	1.4452E+00	1.07E−02	1.48E−02	9.26E−02	6.17E−02	5.63E−03	3.97E−02	2.83E−04
2.3453E+02	1.7311E+01	9.5235E+00	2.76E−02	2.12E−02	8.55E−02	4.95E−02	1.66E−03	2.81E−02	5.38E−04
2.3148E+01	1.1270E+01	7.4406E+01	2.61E−03	1.27E−02	9.43E−02	4.76E−02	5.10E−03	6.31E−02	2.11E−02
8.6629E+01	2.1837E+01	4.7030E−02	2.09E−02	1.74E−02	8.83E−02	5.21E−02	5.85E−03	3.49E−02	7.30E−06
2.6341E+02	2.4674E+01	5.3329E−05	7.27E−02	3.35E−02	6.60E−02	8.60E−03	5.53E−04	5.13E−03	6.96E−10

3.1. Literature data simulation

Waterhouse et al. [14] performed experimental work with a fixed-bed microreactor, filled with silver catalyst, using water at feed (Water Ballast Process). They ran experiments with molar feed composition $CH_3OH/O_2/H_2O/He$ of 2.25/1.00/1.70/20.00, total pressure of 1.1 atm and space velocity of $1.25 \times 10^5\ h^{-1}$, varying the bed temperature. A set of 670 data points that correlate rate of reaction with local temperature and partial pressures of the reactants were back-calculated [25] from Waterhouse's study and used for the ANN training. Table 1 brings a small sample of this set of data.

The training session starts with GA as the algorithm to adjust the ANN weights. It develops as follows: (1) initial population is chosen randomly – each individual of the first generation is characterized by a random set of ANN weights; (2) every individual of the population was evaluated – the ANN was run for all "*N*" experimental inputs, calculating the outputs, using the weights associated to each individual. The calculated outputs were compared to the experimental rates; (3) the individuals of the population were ranked according to the lower "*E*" (neural network error) values; (4) the lowest "*E*" value of the population (best individual) was copied to the next generation (elitism); (5) the best parents were chosen to generate the children, using the crossover operators described in literature [22,31,33–36]; (6) the same procedure is repeated for the second generation and the algorithm is run for a defined number of cycles. The final set of weights (chromosome of the best individual of the last generation) is saved in a data file.

The GA features used in this work were: population size of 50–150 (typical: 100); best 20 individual selected as parents; 1000–5000 generations (typical: 3000); real chromosome code; 50% probability for single-point and uniform crossover, each [34]; 6.6% probability of creep mutation; and 3.4% probability of jump mutation. The best population size in the cases studied here was found to be 100, considering 3000 generations. These values were defined as default after several GA studies performed by the authors with different applications [25]. After finishing the GA training (1 h, Pentium-4, 2.66 GHz, 480 MB RAM), the BP algorithm starts from the solution provided by GA, stored in a data file. The BP continues according to the classical method, reducing the error "*E*" until it lies below a certain limit established by the user. When the training is finished, the final set of weights is stored in a data file and the ANN is used to calculate the rate values for a new set of data (validation).

On the validation step, the calculated rates were compared to the experimental ones (formation, oxidation and decomposition of formaldehyde, respectively). The results are shown in Figs. 3–5, where the rate of reaction calculated by the ANN was plotted against the experimental values extracted from Waterhouse et al. [14], both normalized between 0 and 1, for the three reactions stated above. High correlation coefficients (0.9985; 0.9976 and 0.9988, respectively) were obtained and calculated points concentrated along identity line, as shown on the graphs, indicating that the neural network could successfully fit the experimental data simultaneously for the three rates. The good fit was confirmed through the "*F*" test (*F*-value of 489, which is overwhelmingly sig-

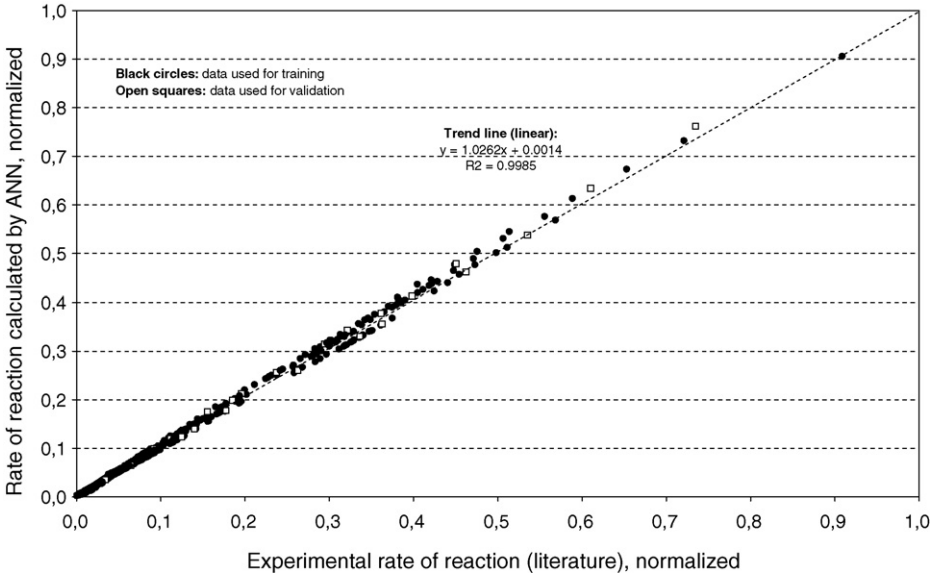

Fig. 3. Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (*x*-axis) and rates calculated by the ANN (*y*-axis) for the formaldehyde formation reaction (Eq. (1) + Eq. (2)).

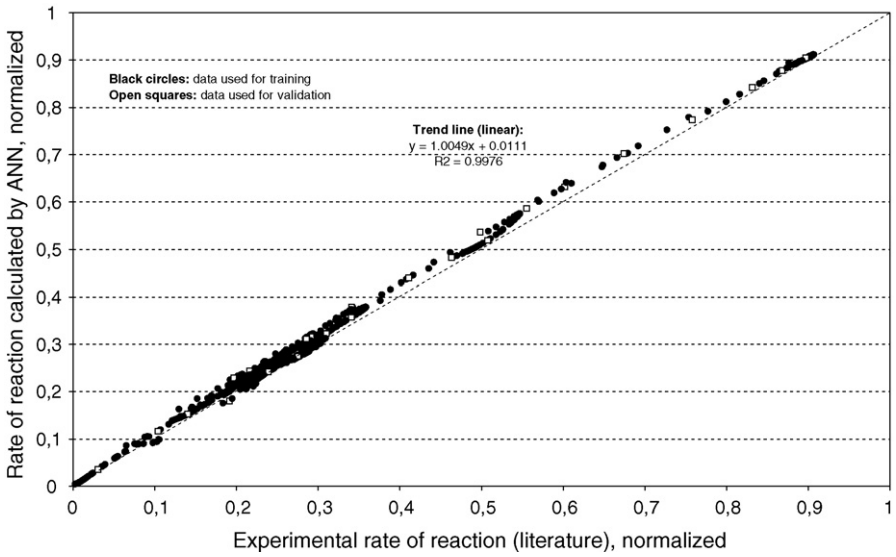

Fig. 4. Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (*x*-axis) and rates calculated by the ANN (*y*-axis) for the formaldehyde oxidation reaction (Eq. (3)).

nificant when compared to the *F*-distribution [45], demonstrating the success of the ANN model to fit the experimental rates). Black circles refer to data used for training the ANN. Part of the data set was reserved to feed the trained ANN, for validation purposes. The open squares indicate the validation set of data, comparing the experimental rates with the calculated ones and confirming the good ANN training.

The optimum number of neurons at hidden layer was identified as 12. The ANN configuration set for this case has 169 weights to be fit and 670 experimental points, which is a possible case under the mathematical point of view, with significant number of points compared to the number of parameters to be fit. Sha [46] provided a valuable discussion about the mathematical aspects of ANN training. The training statistics are: training time of 5 h (Pentium-4, 2.66 GHz, 480 MB RAM) and 1,677,943 iterations.

It is important to guarantee that the data set covers a significant range of the variables to have a good ANN training, otherwise, the model could fail on the generalization test and might be restrict to the narrow range of the parameters represented by the experimental data. One of the risks of ANN training is the over-learning, when the net fits perfectly the data used for training, but it becomes unable to deal adequately with new data. This issue was verified with two validation steps: the trained ANN was employed to calculate rates at conditions not used for training and the results were compared to experimental ones; the hybrid simulator, with the trained ANN was used to simulate different scenarios, including extrapolation and conditions not used to back-calculate the rates for training. Both validation steps were succeeded and the ANN passed on the generalization test.

The process conditions reported by Waterhouse et al. were then estimated using the reactor simulator equipped with the trained ANN. Fig. 6 shows Waterhouse's [14] experimental points and the results of the simulator, which was able to properly fit the experimental points on a wide temperature range (350–750 °C) and principally on the range of 600–700 °C, where most industrial plants are operated. It can predict correctly the abrupt change on

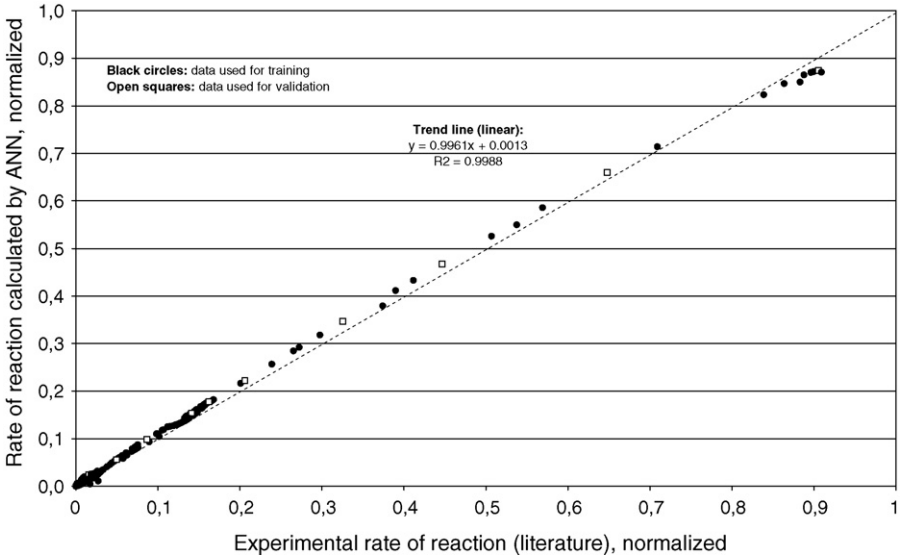

Fig. 5. Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (*x*-axis) and rates calculated by the ANN (*y*-axis) for the formaldehyde decomposition reaction (Eq. (4)).

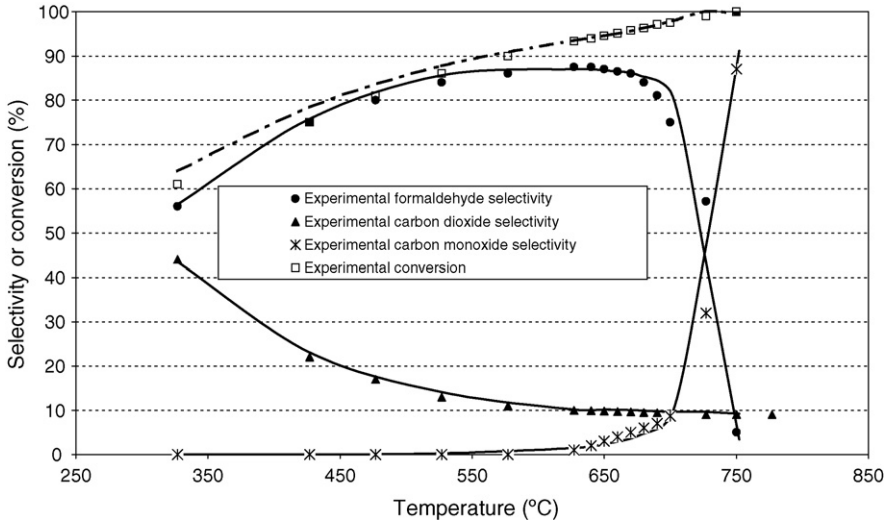

Fig. 6. Simulation of experiments from Waterhouse et al., varying bed temperature. Points are experimental measurements for the selectivity towards formaldehyde, carbon dioxide and carbon monoxide, as well as methanol conversion. Solid lines represent simulated values for selectivity; dashed line represents simulations for conversion.

the kinetics above 650 °C, where decomposition of formaldehyde to carbon monoxide becomes relevant, which is extremely important for the reactor optimization. Some deviation from experimental points for formaldehyde selectivity is still observed in the range 700–730 °C, above industrial operation range, with small impact on practical use of the simulator.

Selectivity towards formaldehyde increases with bed temperature up to 650 °C and then starts to decrease, with a dramatic drop above 700 °C, due to the gas-phase decomposition of formaldehyde to carbon monoxide. Selectivity towards carbon dioxide decreases consistently with increasing temperature. On the other hand, the higher the temperature, the higher the carbon monoxide selectivity, showing a quick increase above 700 °C. These trends are very important to understand and optimize the Silver process, and the proposed approach has proven to allow the ANN to capture correctly these relationships.

Waterhouse's [14] experiments were run at near industrial conditions, where many laboratory studies had failed, which they attributed to differences in catalyst, bed construction, reactor design and testing conditions. In accordance with industrial practices, Waterhouse et al. identified the importance of water presence at feed for achieving high formaldehyde yields.

3.2. ANN training with industrial data

Industrial data from an operating Silver plant in Brazil were studied according to the same procedure. Actual process information was extracted from the plant, based on Water Ballast Process, with molar feed composition $CH_3OH/O_2/H_2O/N_2$ of 2.60/1.00/0.46/3.76 (air is the carrier gas), total pressure of 1.2 atm, space velocity of $6.1 \times 10^6\ h^{-1}$, and temperature set-point of 625 °C. A set of 4050 data points which correlate rate of reaction with local temperature and partial pressures of the reactants were back-calculated from plant process data and used for the ANN training, performed in the same fashion as explained above. The optimum number of neurons at hidden layer was also found to be 12 in this case. The number of experimental points is significantly bigger than the number of fitting parameters.

The rate of reaction calculated by the trained ANN was plotted against the experimental values from the industrial Silver plant. Due to space limitations, the graphs are not shown, but high correlation coefficients were obtained: 0.9985 for formaldehyde formation, 0.9910 for formaldehyde oxidation and 0.9967 for formaldehyde decomposition. Calculated points also concentrated along the identity line, indicating that the neural network could successfully fit the actual experimental data from the plant, even containing noise normally encountered in an industrial plant (instrument errors, unregistered deviations, record errors, measurement lags and normal oscillations from set-points). The good fit for the validation set of data (not used for training) confirmed the successful ANN fit. The complete analysis may be found in [25].

Papes Filho [25] compared the training efficacy using only standard BP and the hybrid approach (GA + BP), concluding that the later is definitely superior for achieving better fit.

Process simulations for industrial conditions with the ANN have demonstrated the ability of the neural net in estimating conversion and selectivity close to industrial measurements. Fig. 7 shows some of the comparison results, where simulations were performed with different operating temperatures. Industrial points (black symbols) lie only on the temperature range limited to the operational conditions (620–680 °C), in this sense, literature data (open symbols) from Waterhouse et al. [14] spread on a wider temperature range (580–720 °C) were plotted on the same graph in order to provide a clearer picture of the trends for the reader. Simulated data (lines) perfectly matched the industrial data, validating the simulator for plant use. The simulated trends were very consistent to the literature data. Some deviation from simulation and literature data was observed in this case, once ANN training was performed using only industrial data. Depending on the catalyst quality and reactor geometry, some differences might be perceived on the performance of different silver reactors. In this sense, the simulator must be fit (or the ANN must be trained) for each case, using the proper experimental data. The trends provided by the simulator will be very similar, but individual values might vary depending on the reactor.

It is worthwhile mentioning that this proposed approach allows dealing even with data obtained when the regimen is not kinetic but rather mass-transfer controlled which may occur in some industrial operating conditions. This is very suitable in cases where the focus of the project is more practical (process control or optimization) than theoretical (kinetic study), when the process reaction rates may be back-calculated from the operational data and measured reactor temperature profiles. The procedure is not supposed to replace experimentation and rigorous modeling, but it is a first step to model and simulate a process to take fast decisions about

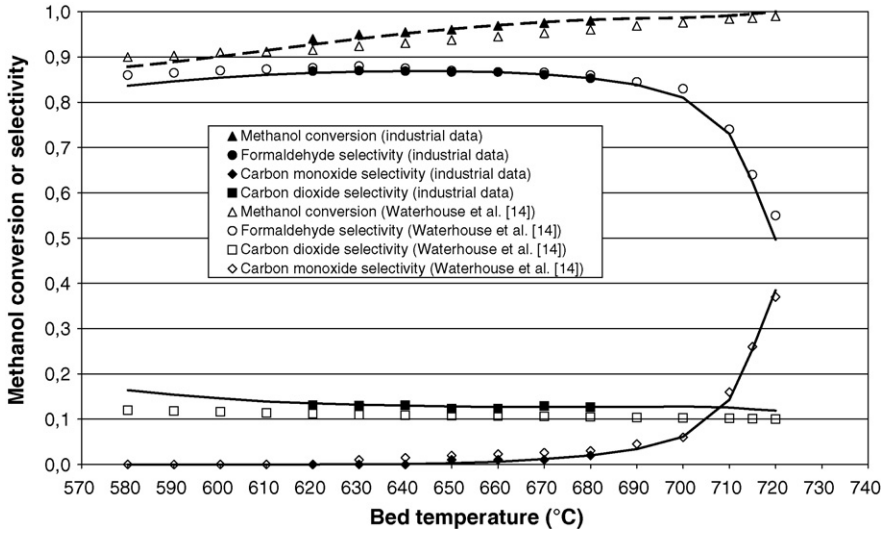

Fig. 7. Effect of temperature on methanol conversion, selectivity towards formaldehyde, carbon dioxide and carbon monoxide. Simulations were performed in this work, according to the base industrial operational conditions, varying the bed temperature. Industrial (black symbols) and literature (open symbols [14]) data were plotted for comparison. Solid lines refer to simulated selectivity. Dashed line refers to simulated conversion.

safe conditions, operational policies and economical aspects. The hybrid simulator and the ANN training approach presented in this work proved to be effective in simulating the Silver process with existing available data. In this sense, it represents an effective tool to understand this process, aiding operators and engineers in foreseeing abnormal situations and allowing anticipation of corrective actions. The system may also be used for process optimization, helping process engineers to define best operational policies to reduce costs, improve throughput and minimize carbon emissions [25].

The presented approach was truly used to simulate an operating industrial Silver formaldehyde reactor and the outputs guided process engineers to define new operational set-points which lead to significant improvement on reaction selectivity to formaldehyde in a Brazilian formaldehyde plant. Consequently, significant value was added to the process while production costs and the carbon emissions decreased.

4. Conclusions

A novel simulator for methanol oxidation to formaldehyde on silver catalyst was presented in this work. A novel kinetic model based on artificial neural networks was inserted into the reactor simulator in order to calculate the rate of the reactions (formaldehyde formation, formaldehyde oxidation to carbon dioxide and gas-phase formaldehyde decomposition to carbon monoxide). The ANN training was performed through an association of genetic algorithm and classic back-propagation.

The hybrid reactor simulator, constructed with deterministic fixed-bed model and a trained ANN, proved the ability to correctly predict conversion and selectivity for desired formaldehyde process conditions. The methods presented here were tested with two case-examples: experimental work from literature and actual industrial data. The later one comprised a large set of data rows, containing noisy plant measured data. Good results were achieved for the two studied cases, providing estimates much closer to the experimental values for conversion and selectivity, compared to previously available models.

The system is a powerful tool for operators and engineers in foreseeing abnormal situations, anticipating corrective actions, defining best operational policies to reduce costs, improve throughput and minimize carbon emissions.

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