New Supported Catalytic Binary System for the Green and Sustainable Production of Cyanogen Fumigant Optimization Using Artificial Neural Network

Karel Zelinka1,2, Jan Simbera1,2, Richard Sevcik1, Josef Havel3 and Pavel Pazdera1

1. Centre for Syntheses at Sustainable Conditions and Their Management, Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic
2. Lucební zavody Draslovka a. s. Kolin, Czech Republic
3. Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic

Corresponding author: Pavel Pazdera (pazdera@chemi.muni.cz)

Abstract: We report a new binary Cu(n)/Fe(m) supported catalytic system for a green and sustainable oxidation of hydrogen cyanide to cyanogen by hydrogen peroxide action. The binary catalytic system Cu(n)/Fe(m), wherein n has the value of I or II, m is II or III, is supported on an acidic cation-exchanger resin. Oxidation process was carried out in a mixture of methanol-water as a solvent. We found that only two undesirable by-products, carbon dioxide and elementary nitrogen are formed during an oxidation of hydrogen cyanide. Furthermore, we observed that the relative content of the target cyanogen and undesirably CO₂ depends on all input parameters, i.e., on a character and amount of an applied resin, quantity of both metal ions Fe and Cu supported on catalyst, presence and character of a potential ligand (acetyl acetone or 2,2’-bipyridyl for the stabilization of possible metal oxidation states), input rates of both reagents, and reaction temperature, respectively. Relationship among input and output parameters was studied by using artificial neural networks (ANNs) and the model for the characterization of relationship within the synthetic process was found, described and used for the optimization. Predicted optimal synthetic input data were successfully verified in experiments. It was found that weakly acidic polyacrylate cation exchanger applied without presence of potential ligands is the most convenient resin for the supported catalytic system. Cyanogen is recently introduced for the protection of agricultural products as a “greener” fumigant to replace existing environmentally dangerous fumigants such as methyl bromide or sulfuryl difluoride.

Key words: Solid support catalysis, cation-exchanger resin, fumigants, cyanogens, artificial neural networks.

1. Introduction

Cyanogen (CN)₂ [1], chemically ethane dinitrile, also known as dicyane, oxalyl cyanide or oxalyl nitrile, is a chemical compound with a very small difference between boiling point(-21 °C) and melting point (-28 °C), possessing the second highest known combustion temperature 4,640 °C [2], for which it is used as a welding medium, and it has recently acquired a very wide range of application. For instance, it is used in organic synthesis for production of intermediates for pharmaceutical and agrochemical industry. It is applied as a rocket fuel, and in highly pure condition for the preparation of cyanogen polymers (paracyanogens) [3] used in nanotechnologies for polymer semiconductor layers. And finally, the last time hydrogen cyanide begins to be very interesting and important chemical compound because of its use as a fumigant.

Fumigants [4] are gaseous pesticides, e.g. methyl bromide, formaldehyde, ozone or sulfuryl fluoride, or vapors from liquid pesticides such as
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1,3-dichloropropene, chloropicrin, hydrogen cyanide, and methyl isocyanate. Fumigant gases can be also formed in situ from solid pre-fumigants by hydrolytic or similar processes [5], e.g. a pellet or tablet type of fumigants such as aluminum phosphide (Fumitoxin) for phosphone and diphosphate, sodium methylaminomethanedithioate (Metham Sodium) as well as 3,5-dimethyl-1,3,5-thiadiazinane-2-thione (Basamide) for methyl isothiocyanate.

Fumigation is applicable process for pest control executed by filling up a controlled area with gas, i.e. structural fumigation of buildings including green-houses or surface fumigation of soil, grain, and production, and is also used during processing of goods to be imported or exported to prevent transfer of exotic organisms. This method also affects the structure itself including pests that inhabit the physical structure, such as woodborers and drywood termites, etc. It stands to reason that vast majority of fumigants is toxic for humans as well.

The agricultural industry has relied heavily on the use of methyl bromide in a wide variety of application ranging from soil to structural fumigation for more than 50 years until its production and use as fumigant was restricted by the “Montreal Protocol on Substances that Deplete the Ozone Layer” (1987) due to its negative role in ozone depletion [6].

In view of the wide application spectrum of cyanogen, a wide range of methods for its preparation, or production, was previously described and patented. A review article [11] presents a number of methods of its preparation with references to primary literature. Industrially significant methods based on hydrogen cyanide and its oxidation by air or oxygen on rare metal catalysts such as Pt, Ir, Rh or their alloys, are described in numerous patents [12-23]. A very significant disadvantage of mentioned procedures is a possibility of hazard on the ground of a formation of high explosive mixtures containing hydrogen cyanide, cyanogen and oxygen in a broad interval of their concentrations (5-40 vol.%).

Different method with minimal risk is based on the reaction of cupric cations with cyanide anions to form unstable cupric cyanide which decomposes immediately through the disproportionation reaction to form cyanogen and cuprous cyanide according to Eq. 3.

\[ 2Cu^{2+} + 4CN^- \rightarrow [2Cu(CN)_2] \rightarrow (CN)_2 + 2CuCN \] (3)

Stoichiometric process realized in this way would not be really applicable in industrial scale. On the other hand, the insoluble cuprous complex can be recovered into soluble cupric cations by ferric cations, for example. The resulting ferrous cations can then be reoxidized back to ferric (by air, oxygen, and preferably by hydrogen peroxide)—Scheme 1. The whole procedure can be thereafter carried out as catalytic and the process can be described by Eq. 4.
The US patent [24] cites a homogeneous catalytic semi-continual system containing iron(III) bromide and copper(II) bromide dissolved in the mixture of water and sulfolane (tetramethylene sulfone). The procedure referred in the patent [24] states that the liquid hydrogen cyanide 1 and 35% hydrogen peroxide 7 are concurrently dosed in the molar ratio of 2:1 into a cooled through-flow reactor, the temperature of the highly exothermic reaction is maintained at about 35 °C and the pressure is 3.04 kPa. After the completion of reaction, the products are removed out from the reactor for purpose of purification using fractional distillation. The yield of the raw 2 is stated to be 97.6%. The product contains 98.1% of cyanogen 2, 0.2% of oxygen, and 1.7% of nitrogen. The iron and copper salts were used in the reaction mixture in the concentrations from 10% to 20% by weight in the equimolar ratio. The concentration of sulfolane in the reaction mixture is given from 0 % to 80% by volume. In agreement with the described patent solution, the sulfolane acts as a stabilizer for the salts of iron and copper in the bromide form to suppress their undesirable side reactions, such as the formation of an insoluble mixture of oxides of both metals, elimination of elementary metals, formation of halo-cyanogen, and hydrolysis of cyanogen (i.e. oxalic diamide) according to Eq. 5.

\[
(CN)_2 + 2H_2O \rightarrow (CONH)_2
\]  

when using the metal bromides, in comparison with chlorides, sulfates and nitrates, these provided the highest conversion of 1 and the better yield of 2. The disadvantages of the mentioned procedure [24] are the use of at present relatively expensive metal bromides, their corrosiveness in the technological equipment, toxicity including environmental toxicity, and further the fact that the long-term stability of the system is relatively low. Another disadvantage is the necessity of cooling the reactor because of the high exothermicity of the process. A significant disadvantage of this solution is the fact that the addition of 35% hydrogen peroxide increases the volume of the aqueous reaction mixture hence it reduces the concentration of both salts and of sulfolane, which leads to reduction of the efficiency of the process and to reduction of system stability. It is then necessary to discontinue the process to remove water by distillation, which further increases the operating costs.

Whereas US patent [24] suffers from the great above mentioned disadvantages connected with realization of homogeneous catalytic redox process, the aim of this work was to elaborate new and optimized procedure for synthesis of cyanogen based on the application of binary hybrid catalysts supported on cation-exchanger resins. For optimization of complex synthetic process a method of artificial intelligence, namely Artificial Neural Networks (ANNs), to apply. Finally, this process should be as simple to manage as possible, semi-continual, low-cost, safer, chemically greener and cleaner, and more sustainable, respectively.

Cation-exchanger resins used currently in the chemical industry are based on co-polymers of acrylic acid and divinylbenzene, i.e. weakly acidic resins, or on sulfonated co-polymers of styrene and divinylbenzene—strongly acidic resins. Both sorts of acidic resins can be used in macroporous or gel form, namely, according to the degree of crosslinking via divinylbenzene.

Industrial cation-exchanger resins, strong acidic namely, are used as solid support for immobilization of metal ions or complexes such as catalysts for

\[
2HCN + H_2O_2 \rightarrow (CN)_2 + 2H_2O
\]
synthetic application, effectively [25]. Ethanolamine complexes of Co(II), Cu(II), Ni(II), Fe(III), Fe(II) and Mn(II) supported on strong acidic resin were used for a chemiluminiscence of luminol in the presence of hydrogen peroxide for analytical application [26].

Cu(II) catalyst supported on industrial weak-acidic cation-exchanger resin was applied for oxidation of cumene to cumene hydroperoxide by action of oxygen [27]. Cu(II) catalyst in the form of aqua or ammine complex supported on weak-acidic polyacrylate cation-exchanger was used for oxidative transformation of 1-(2-methoxycarbonylhydrazino) cycloalkane carbonitrile to cycloalkane carbonitrile by action of hydrogen peroxide or oxygen in methanol realized as one-pot process [28].

Artificial Neural Networks (ANNs) belong to the so-called Artificial Intelligence family of methods, which were inspired by neurobiology and by the architecture of the human brain [29-31], and are used for elucidation of complex processes including biological, chemical, engineering and environmental processes, etc. [32-36].

The use of ANN is advantageous when industrial processes are including even non-linear and/or complex kinetics which not necessarily should be known and/or determined [37]. Further, ANN model enables to predict the behavior of the system under the conditions which have not been applied to any experiment so far, to select the perspective conditions and perform other limited number of experiments. Approaches as modeling or prediction experiments represent an algorithm to optimize complex technological processes with lower expenses [38-40]. The paper [41] is an example of ANN optimization in biotechnology.

Generally, ANNs can be used to model data even in case when the relations or functions are not known.

The attractiveness of ANNs comes from their capability to “learn” and/or model very complex systems. The ANN is a computational model formed from a certain number of single units, artificial neurons, or nodes, connected with each other. To each connection some coefficients (weights), $w_{ij}$, are assigned. Many different neural network architectures can be used. One of the most common is the feed forward neural network of multilayer perceptions. The network is conventionally constructed with three or more layers, that is, Input, Output, and one or more Hidden layers, Fig. 1.

Each layer has different numbers of nodes. The input layer receives the information about the system (the nodes of this layer are simple distributive nodes, which do not alter the input values at all). The hidden layer processes the information initiated at the input, while the output layer is the observable response or behavior. The inputs, input$_i$, multiplied by connection weights $w_{ij}$ are first summed and then passed through a transfer function to produce the output, output$_i$. The determination of the appropriate number of hidden layers and number of hidden nodes in each layer is one of the most critical tasks in ANN designs. Unlike the input and output layers, one starts with no prior knowledge of the number and size of hidden layers.

The use of ANN consists of three steps: “Training”, “Verification” and “Prediction”. The “Training” consists first of creating the database, selecting input and output data for the network and finding the model (training phase). In the training phase, when actual data are used, the optimum structure, weight coefficients and biases of the network are to be determined. Training is considered complete when the
neural networks achieve the desired statistical accuracy; when they produce the required outputs for a given sequence of inputs. A good criterion to find the correct network structure and therefore to stop the learning process is to minimize the root mean square (RMS) error calculated as follows Eq. 6:

$$RMS = \sqrt{\frac{\sum_{j=1}^{M} \sum_{i=1}^{N} (y_{ij} - \text{out}_{ij})^2}{M \times N}}$$

where $y_{ij}$ is the element of the matrix $(N \times M)$ for the training set or test set, and $\text{out}_{ij}$ is the element of the output matrix $(N \times M)$ of the neural network, where $N$ is the number of variables in the pattern, and $M$ is the number of samples. RMS gives a single number, which summarizes the overall error.

After a supervised network performs well on training data it is important to check its performance with data that has not been used in training. This process is called “verification”. This testing is critical to insure that the network has not simply memorized the training set but has learned the general patterns involved in application. At this stage, other input data is submitted to the network in order to evaluate if it can predict the outputs. The predicted value is compared to the experimental one to see how accurately the network is performing. If the system does not give reasonable outputs for this test set, the training period is not over or the network is able to model data only but cannot predict them.

In this paper, the ANN was used for a characterization of relationship among input parameters, i.e. a character and amount of applied resin, quantity and ratio of Fe/Cu in a catalytic system, a presence and character of a potential ligand, input rates of HCN and hydrogen peroxide, respectively, and output values, i.e. relative contents of the target cyanogen and undesirable CO₂ in a gaseous mixture on output of reactor, for thirty effected experiments.

2. Materials and Methods

2.1 Materials

Hydrogen cyanide 1 and cyanogen 2 were obtained from Lučebnízavody Draslovka a. s. Kolín, Czech Republic, as liquefied gases with purity of 99.6% and 99.8%, respectively. Carbon dioxide with min. purity of 99.9% (Linde, Czech Republic) was used as standard. Hydrogen peroxide 7, for analysis, 35 wt.% solution in water, stabilized (Acros Organics, Belgium) was used for experiments after concentration verification (iodometric titration) diluted to 30 wt.% solution in water.

Organic resins $K_i$ (Purolite® Worldwide): $K_1$ Purolite C 104, weakly acidic polyacrylate cation exchanger resin of macroporous type in non-ionized H⁺ form, with the minimum capacity of 4.5 mol·L⁻¹ and powder density of 750 g·L⁻¹; $K_2$ Purolite C 150, strongly acidic sulfonated poly(styrene-divinylbenzene) cation exchanger of macroporous type in ionized Na⁺ form, with the minimum capacity of 1.8 mol·L⁻¹ and with the powder density 780 g·L⁻¹; $K_3$ Purolite C 100 × 10, strongly acidic sulfonated poly(styrene-divinylbenzene) cation exchanger of a gel type in ionized Na⁺ form, with the minimum capacity of 2.2 mol·L⁻¹ and with powder density of 840 g·L⁻¹.

Iron(III) chloride hexahydrate, 98%, pure; copper(II) chloride dihydrate, 98%, pure; and methanol, 99.8+%, ACS reagent (all from Acros Organics, Belgium) were applied.

2,2'-Bipyridyl, ≥98.0%, pure; and acetyl acetone, ≥99.3%, pure (both from Sigma-Aldrich, Worldwide) were used.

The supported hybrid Cu(II)/Fe(III) catalysts used below were purchased from Tau-Chem Ltd. (Slovakia), see http://www.tau-chem.sk/.

2.2 Methods

Gas chromatography was acquired on Shimadzu GC-17A instrument, using Agilent’s 7697A Headspace Sampler for sample preparation.

The ANN calculations were made using Trajan 4.0 software package [42]. Usually the default settings of
Trajan software were used but for the final network adjustment the Jog Weights procedure was applied, which adds a small random quantity to each weight to help the training algorithm to go out of a local minimum. For comparison purposes a non-hierarchical one-way-ANOVA as well as three discriminant techniques was used—linear discriminant analysis, quadratic discriminant analysis and the K-th nearest neighbor [43].

They should bring light on the classification process from a different point of view.

2.3 Chemistry

2.3.1 Preparation of Supported Hybrid Cu(II)/Fe(III) Catalyst

Resin $K_i$ in ionized Na$^+$ form, mass interval of resin $M = 70-80$ g for individual experiments, was stirred at room temperature in 300 mL of water for 15 min. Copper(II) chloride dihydrate (mass interval $n = 15-25$ g for individual experiments) and next iron(III) chloride hexahydrate (mass interval $m = 7-25$ g) were added portion-wise within 30 min and the mixture was then stirred for next 30 min. After, an appropriate ligand $L_i$ ($L_0$ without ligand; $L_1$ = acetyl acetone, molar interval $o = 10-25$ mmol; $L_2$ = 2,2'-bipyridyl, molar interval $o = 10-25$ mmol) was added into the solution and the mixture was stirred for further 1 h. Then the aqueous phase was removed and the solid phase was washed twice by 150 mL of water and subsequently twice by 150 mL of methanol. The supported catalyst was used after suction into the following reaction.

2.3.2 Preparation of Cyanogen by Hydrogen Peroxide Oxidation of HCN on Supported Hybrid Cu(II)/Fe(III) Catalyst

In a three-necked round-bottom 5 L flask equipped with stirrer and a Graham condenser (length 50 cm) with a cooling medium (temperature approximately 5-10 °C) and with an outlet to cryoscopic distillation apparatus, the above described hybrid catalyst Cu(II)/Fe(III), doped with ligand, eventually, was added to 500 mL of methanol.

Liquid hydrogen cyanide (b. p. 25-26 °C/1,013 hPa) was added to the reaction mixture with the rate of 3.5 g/min (130 mmol·min$^{-1}$) for the period of 3 minutes. Subsequently, the rate of a hydrogen cyanide dosage was modified to value $v$, which was adjusted in range 100-260 mmol·min$^{-1}$ for individual experiments and 30% hydrogen peroxide started to be added dropwise at the same time with the addition rate $u$ ranging between 200-260 mmol·min$^{-1}$ for individual experiments. The entire process was maintained at the temperature of $t$ in interval 20-50 °C for the period of 2 hours. The gaseous products, i.e. the cyanogen and carbon dioxide and hereafter the unreacted hydrogen cyanide with airy and generated nitrogen, and trace of methanol vapors, were continuously conveyed through the condenser to the apparatus for cryoscopic fractional distillation. Cyanogen was purified and adjusted, unconverted hydrogen cyanide was recycled backwards into the process, as well as methanol. The composition of gaseous phase in its total volume arisen for the period of two hours measured directly at the output from the reaction vessel (first analysis position-Fig. 2) into a condenser (as monitored by the gas chromatography using the integral peak intensity) was: ca. 1-33 rel.% of carbon dioxide (and the half-amount of nitrogen, see Eq. 6 below), ca. 26-65 rel.% cyanogen, ca. 10-35 rel.% of unreacted hydrogen cyanide and the remaining part to 100 rel.% of methanol (methanol maximum ca. 10 rel.%), and the total volume of formed gases was around 350-820 L (at the temperature about 8 °C and pressure 2 kPa). “Dead volume”, i.e. volume of vessel before the start of hydrogen cyanide and hydrogen peroxide addition was 4.4 L and 4.7 L including condenser volume, respectively. Both of the presented volumes are negligible compared with volume of formed gases.

After two hours of oxidation process, the addition of reactants and the stirring of the reaction mixture were stopped, the reaction vessel was replaced with a
new one containing methanol and catalyst in a required amount and the entire process was repeated. The catalyst was separated by decantation and used again in the process, methanol was distilled from the water mixture and recycled backwards into the process, and water was processed in the wastewater sewage plant.

3. Results and Discussion

The results obtained after realization of preliminary experiments, are described in the part 2.3. As indicated above chemistry experiments the mixture of all gases outgoing directly from the reaction vessel (the first analysis position, Fig. 2) contained the required cyanogen, unwanted carbon dioxide and nitrogen, unreacted hydrogen cyanide and vapors of methanol.

On the other hand, analysis of methanol-water mixture after the end of reaction certified absence of cyanogen hydrolytic products such as oxalic diamide in the contrast to observations obtained from homogeneous process according to US patent [24] above. The analytical tests for the presence of iron and copper compounds in the methanol-water mixture after the reaction processes proved no traces of these metal ions. In consequence of these very important findings a waste management of wastewater was simplified. The solid supported catalyst was tested for reusing. It was found that all of three types of catalyst can be used ca. ten-fifteen times with the same good result as at the beginning, however, further reusing of recycled catalyst provided worse results. The knotty problem, whether formation of carbon dioxide and nitrogen is based on oxidation of cyanogen according to Eq. 2 or on oxidation of hydrogen cyanide, Eq. 6 below, was solved experimentally.

Cyanogen was introduced along with hydrogen peroxide into water-methanol solution containing Cu(II)/Fe(III) supported catalytic system, but formation of carbon dioxide was not observed. It follows that the formation of carbon dioxide and nitrogen proceeds as the direct competitive oxidation of hydrogen cyanide on a catalyst, see Eq. 7.

$$2\text{HCN} + 5\text{H}_2\text{O}_2 \rightarrow 2\text{CO}_2 + \text{N}_2 + 6\text{H}_2\text{O}$$

Another experiment using supported Fe(III) only as the catalyst demonstrates a formation of carbon dioxide besides nitrogen only.

The obtained experimental observations hereafter show that the competitive oxidation of hydrogen cyanide, which declines the yield of target cyanogen during all process and devalues the starting hydrogen cyanide, could be dependent on all input factors. On the base of preliminary experimental results we realized next experiments. However, the output from the condenser was the place for point of a gas automatic sampling now (the second analysis position, Fig. 2). We supposed the condenser to be able to minimize a presence of unreacted hydrogen cyanide and vapors of methanol. Their presence within output gaseous mixture is, on one hand, dependent on a rate of carbon dioxide and nitrogen formation, reaction temperature, and, on the other hand, is not important for production process of cyanogen on the ground of their easy recycling.
The output data from these experiments was in range \( W = 30.0 - 98.0 \) rel.% for cyanogen, \( Z = 1.0 - 46.5 \) rel.% for carbon dioxide. Amount of applied support resins were set up so that the resin capacity achieved \( 2/3 \) of maximum value because of to suppress the release of both used metals from support resin, namely in the course of their oxidation stay changes. The mentioned proceeding proved to be successful as it is presented above.

In order to understand relations between input and output parameters, following queries were put and answers were sought on the ground of further experiments, at first:

Has a type of resin an effect on a composition of output gases, reaction selectivity (it is defined above)? The obtained data of realized experiments implies that the resin \( K_1 \) (Purolite C 100 \( \times \) 10) gave the best results whereas resin \( K_2 \) (Purolite C 150) showed the worst output data. The resin \( K_1 \) (Purolite C 104) gave results between them in the presence of ligand. However, in absence of ligand the resin \( K_1 \) provided the very best results in some cases.

What is the relationship between kind of resin and ligand? The found results on output imply that the relationship among resin \( K_1 \) and both of the used ligands is not significant than in case of resin \( K_2 \) and \( K_3 \), an action of ligand \( L_1 \) (acetyl acetone) is slightly higher than that of ligand \( L_2 \) (2,2'-bipyridyl).

What is an optimal proportion between amount of \( \text{Cu(II)} \) and \( \text{Fe(III)} \) in supported catalytic system? The obtained results imply optimal ratio \( \text{Cu(II)}:\text{Fe(III)} = 2:1 \). Higher contain of \( \text{Fe(III)} \) evokes higher formation of carbon dioxide, probably.

What is an optimal proportion of input rates of both reagents? The experimental results imply that optimal ratio hydrogen cyanide:hydrogen peroxide is 1:1, however, on the other hand, the excess of peroxide has not expressive influence on a selectivity of process.

Is lower or higher process temperature optimal for obtaining good results? The experimental output data implies that higher temperatures of the process (50 °C, 60 °C) provide better results than lower temperatures.

The queries and answers presented above evoke series of further queries with potential answers, but orientation in the problem of relationships between inputs and outputs remains vague.

In order to solve more complex relationship between input parameters values on the one hand, and values of several outputs on the other hand, for this study and optimization of input parameters we used the artificial neural networks tools to reduce the time and cost of obtaining further experimentally determined data sets.

The obtained experimental data, their architecture is for concept presented in the Table 1, were used as the training set for the “network learning”. Thirty experiments with three kinds of cation-exchanger resin and eight process condition sets presented above and relative content of cyanogen and \( \text{CO}_2 \) in gases directly outgoing from the condenser were finally accepted as variables.

During the training step numerous networks with different architectures were examined. The network selection was based on the appropriate selection of: (1) the number of hidden layers in multilayer perceptrons, (2) the number of hidden neurons in the network. The key decision on the number of hidden layers was made by Trajan’s Intelligent Problem Solver. By the Solver a variety of algorithms for different network types have been automatically tested and the best alternatives were determined. The Solver was applied separately for each of the three classification problems and it was found that in all cases the best network type is the three-layer multilayer perceptron (3-MLP), \textit{i.e.} that with just one hidden layer.

The number of nodes in the hidden layer, \( N_h \), was found by examining several types of the 3-MLP with regard to the corresponding final root mean squared (RMS) error. The optimal number of hidden units was found according to the break in the RMS vs.\( N_h \) dependence (Fig. 3).
Table 1  Partial set of input data, $K_i$ is kind of resin, $M$ its amount (g), $n$, $m$ is amount of used Cu, Fe salts (g), $L_i$ is kind of a prospective ligand, $o$ its amount (mmol), $V$, $U$ rate of hydrogen cyanide and hydrogen peroxide addition (mmol·min$^{-1}$), reaction temperature $t$ (°C) and output data, $W$ relative contain of cyanogen (rel. %), and $Z$ relative contain of CO$_2$ (rel. %) in gases directly outgoing from the condenser, for ANN calculations (network learning). Remark: The complete data set is available on request.

<table>
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<th>Entry</th>
<th>$K_i$</th>
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The value equal to 3 or 4 is to be used as optimal value of the number of nodes in the hidden layer, in the next work number of nodes in the hidden layer equal to 4 was used.

ANN calculations, i.e. the optimum structure, weight coefficients and identified biases of the network model (Fig. 4) show that used training database is suitable for the description of interrelationship among the input values and output ones.

Thus, the optimal model can be described as three-layer ANN architecture with 9 input parameters, 4 hidden nodes and 2 output parameters.

Fig. 5 demonstrates very good correlation between experimental and ANN calculated values for $W$, rel.% (CN)$_2$, correlation between experimental and ANN calculated values for $Z$,rel. % CO$_2$,is very good as well.

4. Conclusions

For an industrial use we found and optimized the new on cation-exchanger resins supported Fe/Cu binary catalytic system for the production of cyanogen based on oxidation of liquid hydrogen cyanide by action of hydrogen peroxide in the water-methanol
mixture and conditions for its effective application were examined as well.

The experimental output data obtained from the set of input reaction conditions were applied to construct a representative ANN model of the process, which successfully modeled the system. The models of optimal input/output parameters were designed and successfully verified in experiments.

We also observed that the long-term stability of the supported binary catalytic system is very good. Next advantage of the solution is the substitution of a homogenous catalyst with a resin supported catalytic system. Water with the addition of sulfolane used in the state-of-the-art process as the solvent was replaced by methanol. The reaction using the supported heterogeneous catalyst is slower and it does not need cooling; the optimum temperature mode is about 50 °C. Methanol is separated from the reaction solution after the reactor shutdown by distillation; the advantage is that it does not form azeotropic mixture with water, and further the fact that its boiling point is approximately two thirds of the boiling point of water, which is energetically advantageous. The catalyst is significantly more stable in methanol or in its mixture with water than in water itself. The bidentate ligands present help to stabilize Fe(II) and Cu(I) against the reduction to elementary metals during the process, which deteriorates the catalytic system, and it suppresses the possible hydrolytic oxidation of ethane dinitrile to carbon dioxide, which decreases the selectivity of the process. The process according to the present solution does not have to use the expensive and toxic copper and iron bromides. More available and cheaper salts of copper and iron than bromides can be used for preparation of the catalyst. Cation exchanger is an industrial resin used for treatment of water, it is easily available and cheap, and it forms a highly stable complex with the copper and iron cations. Further advantages of the solution according to the present one are easier maintenance of the reaction mixture during and after the process, especially elimination of waste solvent from the heterogeneous system of catalyst, absence of metal ions from the catalyst in the waste solvent, and lower energy demands on the liquid mixture processing; see the above-mentioned advantages of methanol versus water. The reaction medium has minimum corrosive effects on the technological equipment, in particular because water is not contaminated with copper and iron ions. The system according to the invention shows a higher efficiency than the known systems used in the industry, which leads to lower consumption of the hydrogen peroxide used. Further, there is no more need for cooling the reaction mixture allowing an easier control of the entire process, with the possibility of regulation and automation of the process in the reactor, which on the contrary runs under a slightly increased temperature, which brings further decrease of operating and production costs. The catalytic system, by the means of its concept and the method of cyanogen production according to the present invention, meets the criteria of “green chemistry” and “sustainable chemistry”.

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