

Inter-relationship between preparation methods, nickel loading, characteristics and performance in the reforming of crude ethanol over Ni/Al₂O₃ catalysts: A neural network approach

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Abstract

Artificial neural network (ANN) approach was used to design an optimum Ni/Al₂O₃ catalyst for the production of hydrogen by the catalytic reforming of crude ethanol based on determining the inter-relationships between catalyst-preparation methods, nickel loading, catalyst characteristics and catalyst performance. ANN could predict hydrogen production performance of various Ni/Al₂O₃ catalysts of various elemental compositions and methods of preparation in the production of hydrogen by the catalytic reforming of crude ethanol in terms of crude-ethanol conversion, hydrogen selectivity and hydrogen yield. Specifically on catalyst design, ANN was used to determine the optimum catalyst conditions for obtaining maximum hydrogen production performance of a Ni/Al₂O₃ catalyst for the production of hydrogen by the catalytic reforming of crude ethanol. The optimal hydrogen yield was 4.4 mol %, and the associated crude-ethanol conversion and H₂ selectivity for the optimal hydrogen yield were 79.6 and 91.4 mol%, respectively. The optimal catalyst was the one prepared by the coprecipitation method with the optimal nickel loading of 12.4 wt% and an optimal aluminum composition of 42.5 wt%. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Artificial neural network; Optimum catalyst design; Crude-ethanol reforming; Hydrogen production; Catalyst characteristics

1. Introduction

The Energy Information Administration has projected that world energy consumption will increase by 59% over the next two decades, from 1999 to 2020 (Energy Information Administration, 2001), in which the largest share is still dominated by fossil fuels (oil, natural gas and coal). Carbon dioxide (CO₂) emissions resulting from the combustion of these fossil fuels currently are estimated to account for three-fourths of human-caused CO₂ emissions worldwide (Energy Information Administration, 2001). Greenhouse gas emissions, including CO₂, should be limited, as recommended at the Kyoto Conference, Japan, in December 1997. In this regard, hydrogen (H₂) has a significant future potential as an alternative fuel that can solve the problems of CO₂ emissions as well as the emissions of other air contaminants. The demand for

hydrogen energy has increased tremendously in recent years essentially because of the recent developments in fuel cell technologies. One of the techniques to produce hydrogen is by the catalytic reforming of hydrocarbons or biomass (e.g., ethanol).

The production of hydrogen by steam reforming of pure ethanol has been widely investigated (Athanasio and Verykios, 2004; Leclerc et al., 1998; Jordi et al., 2002; Galvita et al., 2001; Das, 2003; Athanasios and Kondarides, 2002; Klouz et al., 2002) in which various catalysts such as Co/ZnO, Cu–Mn/Al₂O₃, and Ni/La₂O₃, etc., have been used. In all the cases considered, water was needed as a co-feed to the process. This would imply that there was no need to completely remove the water in the fermentation broth (i.e., crude ethanol) during ethanol-production process. Considering this concept, crude ethanol (a form of biomass) is easy to produce, is free of sulfur, has low toxicity, and is also safe to handle, transport and store. In addition, crude ethanol consists of oxygenated hydrocarbons, such as ethanol, lactic acid, glycerol, and maltose

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(Akande et al., 2005). These oxygenated hydrocarbons can be catalytically reformed completely to H_2 and CO_2 , the latter of which could be separated from H_2 by membrane technology or other technologies. This provides for CO_2 capture for eventual storage or destruction. In the case of using crude ethanol, this will result in negative CO_2 emissions.

A very important aspect for the actualization of the PEM fuel cell-powered electric vehicles that would use crude-ethanol-based H_2 is the development of a stable active catalyst for the H_2 -production process. Such a catalyst should ensure high selectivity and yield and should result in a small-sized reformer for use in a H_2 -refueling station. While there is some information on catalysts development regarding the steam reforming of pure ethanol, there is very little information in the case of the reforming of crude ethanol (Akande et al., 2005). In the literature, Al_2O_3 supported Co, Ni or Cu catalysts have been employed for pure-ethanol reforming. Also, Idem et al. (2003) indicated that Al_2O_3 -supported Ni catalysts or Cu–Mn–Al catalysts are active for crude-ethanol reforming. Ni is reported by Luengo et al. (1992) to ensure C–C bond breakage in ethanol or other oxygenated hydrocarbons while Al_2O_3 ensures good thermal stability. However, even though Ni/ Al_2O_3 catalysts appear to be active catalysts, the inter-relationships between preparation method, nickel loading, characteristics and performance of these catalysts in the reforming of crude ethanol for hydrogen production have not been established. In our previous work (Akande et al., 2005), we attempted to experimentally evaluate these relations with a view to determining the optimum conditions of catalysts for maximum performance. As is well known, experimental determination of optimum conditions for a catalyst is time consuming. Besides, it cannot be ensured that these optimum catalyst conditions will be reached. What is required is a method that will ensure that all the attributes of the catalysts can be taken into account in determining the optimum catalyst. ANN can be a very powerful tool (Jang et al., 1997) for applications in process engineering. Also, the application of ANN in applied catalysis and in chemical engineering has been reported in the literature (Bulsari, 1995; Mackay, 2002). Hou et al. (1997) applied ANN for design of a VSbWSn (P, K, Cr, Mo)/SIAL catalyst for the synthesis of acrylonitrile via propane. Also, Omata et al. (2005) designed a stable Co–MgO catalyst for dry reforming of methane by the aid of ANN technique. Furthermore, it has been shown (<http://atom.ecn.purdue.edu/~jmcweb/materials/catalyst.html>) that ANN is an advanced technique that can be used for the development of a catalyst. In this context, an ANN approach, which does not necessarily need to be programmed to follow a specific set of instructions but instead could be used as an adaptive learning algorithm to find a pattern if a set of examples is given, would provide a very useful tool for optimization. This characteristic of an ANN (Lyster; http://www.nrel.gov/hydrogen/proj_production_

[delivery.html](#); Demuth and Beale) makes it very useful for dealing not only with problems that are extremely complex to implement but also for problems whose solution has not been explicitly formulated, such as in Ni/ Al_2O_3 catalyst development for crude-ethanol reforming. The use of ANN approach to determine these inter-relationships for Ni/ Al_2O_3 catalysts in the catalytic reforming of crude ethanol to produce hydrogen is presented and discussed in this paper.

2. Application of artificial neural networks in catalyst design

2.1. Artificial neural networks learning process

As illustrated in the literature http://www.doc.ic.ac.uk/~nd/surprise_96/journal/vol4/cs11/report.html, ANNs are a type of artificial-intelligence technology, which offers a very strong learning ability, especially for problems with unknown inter-relations or very complicated relations between input dataset and output dataset. The learning process can be categorized into supervised learning and unsupervised learning. These are basically the two ways for training of the ANNs (Jang et al., 1997).

According to Anderson and McNeill (1992), supervised learning is the most popular method to train the ANN. Training data (including input data and desired output data) are fed into the neural networks and the target (or error function), respectively. Then, the neural networks with a random weight matrix give an output to the error function to compare with the desired output data. If the error between the output data from the neural networks and the desired output data is out of the proposed accuracy range, the training algorithm will adjust the weights to the neural networks. Then, the same data are processed as performed in the previous case until the error is minimized to the proposed accuracy range by the training algorithm. Finally, the training process is finished with fixed weights.

On the other hand, in the case of unsupervised learning, the neural networks are trained to govern themselves without any external supervision. Consequently, there are no desired output data to modify the interconnection weights of the trained neural networks. This means that the neural networks with unsupervised learning have no reference. This makes the important feature of unsupervised learning to be based on self-organization <http://www.statsoft.com/textbook/stneunet.html>.

A decision as to whether to use supervised learning or unsupervised learning may not be straightforward. For situations where the environmental conditions are well known (i.e., the input data and desired output data for the neural networks are well known) the supervised learning for the neural networks training is more helpful than the unsupervised learning (http://www.cs.brandeis.edu/~cs113/classprojects/~jlittman/cs113/Web_Project_231_Unsupervised_Learning.html). However, for situations where the desired output data are less known or unknown, then the supervised learning is not appropriate. In this case,

the unsupervised learning is more useful than supervised learning (http://www.cs.brandeis.edu/~cs113/classprojects/~jlittman/cs113/Web_Project__231__Unsupervised_Learning.html). In our case, we used the supervised-learning approach.

2.2. Multilayer feed-forward artificial neural networks configuration

Feed-forward multiple-layers neural networks configuration was used for this work for the reason that it is the most popular type which is widely in use. The feed forward neural networks consist of input layer, hidden layers and output layer. Each layer has a large number of neurons. As is well known, the more complicated the configuration of the neural networks is, the more powerful are the functions of the neural networks. In addition, non-linear functional relationships are the most basic characteristics in ANNs. This feature makes ANN especially powerful tools in data processing with unknown relations.

In executing the network, the input data are fed into the input layer, and then the results from the input layer become the input data to the hidden layers, summed by the weights plus the bias for the hidden layers. The outputs from the hidden layers then become the inputs for the output layers. These undergo similar data processing as in the hidden layers. The final outputs for the entire feed-forward neural networks are produced. During the data processing from the inputs to the outputs of the entire neural networks, each neuron plays a very important role. For example, for any neuron, the output from the neuron is the sum of the total weighted inputs plus a bias, which is expressed in the following equation (Kroese and van der Smagt, 1996):

$$a = f(w_{1,1}p_1 + w_{1,2}p_2 + \dots + w_{1,RpR} + b),$$

where w is the weight for each input data for the neuron.

2.3. Neural networks training with Levenberg–Marquardt algorithm (Trainlm) (adapted from <http://atom.ecn.purdue.edu/~jmcweb/materials/catalyst.html>)

In this paper, the Levenberg–Marquardt algorithm is used for the training of the ANNs without calculating the Hessian matrix. For neural networks training performance function of the form of the sum of squares, the Hessian matrix can be expressed as in the following equation:

$$H = J^T J.$$

Then the Levenberg–Marquardt algorithm has the following forms

$$x_{k+1} = x_k - [J^T J + \mu I]^{-1} J^T \mathbf{e},$$

where J is the Jacobian matrix that contains the first derivatives of the network errors with respect to the weights and biases, and \mathbf{e} is a vector of network errors.

3. Experimental

3.1. Synthesis of catalysts

Three methods of catalyst synthesis: coprecipitation (CP), precipitation (PT) and impregnation (IM) were investigated. The preparation procedures used for these synthesis methods are described in detail elsewhere (Akande et al., 2005). The designations and elemental compositions of the calcined catalysts are given in Table 1. In the table, CP, PT and IM indicate coprecipitation, precipitation and impregnation synthesis methods, respectively. The numbers under DATA-1 in the designations in Table 1 represent the loadings while the symbols represent the synthesis method. For example, CP10 indicates a catalyst with 10% Ni loading prepared by CP synthesis method.

Table 1
Original experimental data used for linear interpolation

| Catalyst name | Data-1 | | | Data-2 | | | | Data-3 | | |
|---------------|--------|----------|----------|-------------------------|---------|---------|---------|----------|-------------------------|-------------------------|
| | PM | Ni (wt%) | Al (wt%) | BSA (m ² /g) | PS (nm) | PV (nm) | CS (nm) | C (mol%) | H ₂ S (mol%) | H ₂ Y (mol%) |
| CP10 | 1 | 10 | 47.63 | 83 | 12.6 | 0.26 | 26.5 | 32 | 91 | 2.12 |
| CP15 | 1 | 15 | 44.98 | 77 | 14.5 | 0.29 | 29.8 | 79 | 90 | 4.33 |
| CP20 | 1 | 20 | 42.34 | 69 | 12.8 | 0.22 | 38.5 | 54 | 89.6 | 2.9 |
| CP25 | 1 | 25 | 39.69 | 65 | 12 | 0.19 | 47.2* | 59 | 87 | 3.1 |
| PT10 | 2 | 10 | 47.63 | 177 | 5.4 | 0.23 | 21.5 | 44 | 87 | 2.32 |
| PT15 | 2 | 15 | 44.98 | 165 | 5.6 | 0.22 | 20.8 | 85 | 82 | 4.24 |
| PT20 | 2 | 20 | 42.34 | 155 | 5.4 | 0.12 | 39.6 | 83 | 82 | 4.18 |
| IM10 | 3 | 10 | 47.63 | 168 | 4.3 | 0.18 | 15.3 | 44 | 85 | 2.28 |
| IM15 | 3 | 15 | 44.98 | 158 | 4.6 | 0.18 | 105.8 | 47 | 88 | 2.52 |
| IM20 | 3 | 20 | 42.34 | 156 | 4.5 | 0.17 | 160.2 | 47 | 86 | 2.45 |

Note: '1' stands for the calcination method-CP; '2' stands for the calcination method-PT; '3' stands for the calcination method-IM; PM, preparation method; BSA, BET surface area; PS, pore size; PV, pore volume; CS, crystallite size; C, ethanol conversion; H₂S, H₂ selectivity; H₂Y, H₂ yield.

*This value is estimated by ANN.

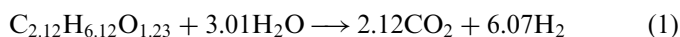
3.2. Catalyst characterization

The dried, calcined and reduced catalysts were characterized for BET surface area, pore size and distribution, and pore volume. The other characterization techniques to which these catalysts were subjected were: temperature-programmed reduction studies using H_2 (TPR- H_2) to determine reducibility, thermogravimetric analysis (TGA) for determining the optimum calcination temperature, powder X-ray diffraction (XRD) analysis for identifying the crystalline phases in the catalysts, X-ray line broadening for determining the Ni crystallite sizes, and temperature-programmed oxidation (TPO) to evaluate coke formation on the catalysts. Details concerning the characterization procedures and the equipments used for all the techniques mentioned are given elsewhere (Akande et al., 2005).

3.3. Catalytic activity tests

3.3.1. Feed material

The feed for this process was crude ethanol (i.e., fermentation broth) and was obtained from Pound Maker Adventures, Lanigan, Saskatchewan, Canada. This was used as received except for the removal of particulate matter by filtration. However, for the purpose of evaluating the performance of the catalysts, crude ethanol was defined as the combination of all the oxygenated hydrocarbon components present in fermentation broth; namely, ethanol, lactic acid, glycerol and maltose. We performed an analysis in our laboratory to both identify and quantify these components of fermentation broth using a high-performance liquid chromatograph (HPLC; model Agilent 1100 series, Agilent Technologies, Wilmington, DE, USA). The HPLC was equipped with a 250×4.1 mm HC-75 column and a refractive index detector, while 0.05 M succinic acid was used as the mobile phase. Based on this analysis, the overall molecular formula of crude ethanol based on the weighted average of these components could be given as $C_{2.12}H_{6.12}O_{1.23}$. Also, based on this composition, the general equation representing the reforming of crude ethanol can be represented as in Eq. (1).



3.3.2. Activity tests

The reactor used to obtain experimental data was BTRS (model number 02250192-1, Autoclave Engineers, Erie, PA, USA). It was made of a stainless-steel tube of 8.0 mm internal diameter (D) placed in an electric furnace. Crude ethanol was delivered to the reactor chamber by means of a HPLC pump regulated at the desired flow rates. The reaction temperature was measured with a sliding thermocouple placed inside the bed. The error on temperature measurement was within $\pm 1^\circ C$.

A typical run for the reforming of crude ethanol was performed as follows. Approximately 1 g of the catalyst was mixed with 2 g of Pyrex glass (i.e., inert material) of the

same average particle size and then loaded into the reactor. The feed consisting of crude ethanol (comprising of ethanol plus other organics and water) was then pumped at the desired flow rate (i.e., space velocity) to the vaporizer maintained at $250^\circ C$ before entering the reactor. Prior to reaction the catalyst was reduced in situ by treatment with 5% H_2 in N_2 gas (PRAXAIR, Regina, SK, Canada) flowing at 100 ml/min for 2 h. The reactions were carried out at atmospheric pressure and reaction temperature of $400^\circ C$. The product mixture during reaction was passed through a condenser and gas-liquid separator to separate the gaseous and liquid products for analysis.

3.3.3. Analysis of liquid and gaseous products

The liquid product was analyzed using the same HPLC described earlier. This liquid product was also analyzed with GC-MS in order to identify the components for subsequent HPLC analysis. GC-MS analysis was performed using GC-MS model HP 6890/5073 (Hewlett-Packard Quebec, Canada). A HP-Innowax column (length = 30 m, internal diameter = $250 \mu m$, thickness = $0.25 \mu m$) packed with cross-linked-poly-ethylene glycol was used in the GC for the separation of components. The composition of the output gas stream was analyzed on-line by gas chromatography (Model HP 6890) using molecular sieve and Haysep columns, a thermal conductivity detector (TCD) and helium as carrier gas. The schematic diagram of the experimental set-up used for the reforming reaction is shown in Fig. 1.

3.3.4. Evaluation of hydrogen-production performance

The catalysts were evaluated for their performance in the reforming of crude ethanol. The evaluation criteria used

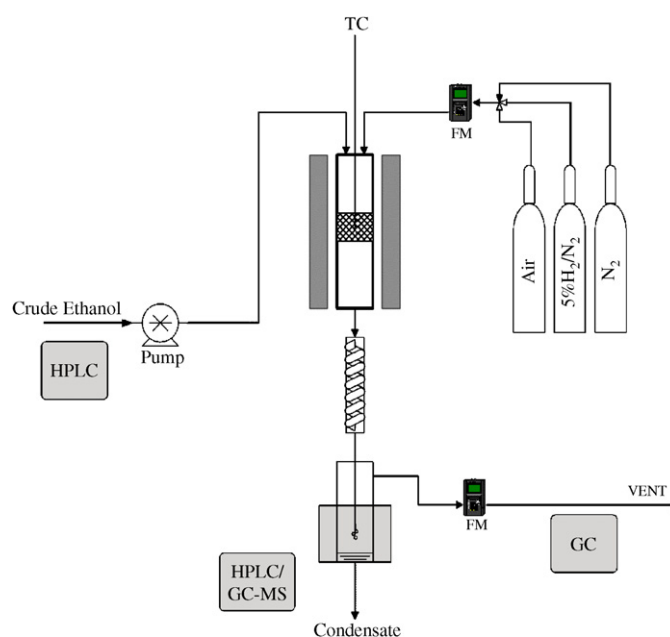


Fig. 1. Schematic diagram of the experimental rig for the production of hydrogen by the catalytic reforming of crude ethanol.

were crude-ethanol conversion, H₂ selectivity and H₂ yield. Crude-ethanol conversion was defined according to Eq. (2) while H₂ yield and selectivity were defined according to Eqs. (3) and (4), respectively.

Crude conversion (X)

$$= \frac{\text{gmol (organics) in} - \text{gmol (organics) out}}{\text{gmol (organics) in}}, \quad (2)$$

where organics = ethanol + lactic acid + glycerol + maltose,

$$\text{Hydrogen yield (} Y \text{)} = \frac{\text{gmol (H}_2\text{) out}}{6.07 \times \text{gmol (organics) in}}, \quad (3)$$

Hydrogen selectivity (S)

$$= \frac{\text{gmol (H}_2\text{) out}}{6.07 \times \text{gmol (organics) in} \times \text{Conversion}(X)}. \quad (4)$$

3.4. Linear-interpolation methods

For catalyst development, the analysis or optimization of parameters may not always be possible because of the availability of only limited experimental data. At the same time, it may not be necessary to make unlimited laboratory experiments to obtain sufficient data since this could be expensive and time consuming. For this type of situation, interpolation plays an important role in solving the problem. Even though interpolation has many different methods, we focused mainly on linear-interpolation method. Linear interpolation has the ability to predict an unknown value (position, shape, population, etc.) if any two particular values are known and is based on the assumptions (<http://www.cs.brown.edu/stc/outrea/greenhouse/nursery/interpolation/itworks.html>) that (a) two particular values are known, (b) the process is changing at a constant rate, and (c) there is the desire to find an unknown data point.

For our situation, the catalyst calcination temperature and catalyst reduction temperature are set-up to be constants. Thus, pore volume, pore size, BET surface area, and crystallite size of the catalysts, which form part of the characteristics of the calcined Ni/Al₂O₃ catalysts, were the focus of the outputs section based on linear interpolation. On the other hand, Ni loading, Al loading and the catalyst synthesis method formed the corresponding inputs section. Some of the input values were derived from linear interpolation.

With regard to the hydrogen production or the reaction operation process, the reaction temperature and the crude ethanol weight hourly space velocity (WHSV) were also set-up to be constants. In this case, only the Ni loading, Al loading and the catalyst-preparation method formed the input section some of the values of which were derived using linear interpolation. On the other hand, the crude-ethanol conversion, hydrogen selectivity and hydrogen yield formed the output section with some of the values derived using linear interpolation. DATA-1, DATA-2 and

DATA-3 in Table 1 are the original experimental data. As indicated earlier, these data are not enough to feed to the neural networks in order to learn the functions between DATA groups. Therefore, it became necessary to obtain sufficient data based on the original data table. It is well known that the relationship between catalyst performance (dependent variable) and the characteristics (independent variable) cannot be theoretically determined between points. Thus, data for additional points were derived from two approaches: (i) by linear interpolation and (ii) by drawing a line of best fit through the experimental data sets. The deviation between the two sets of addition data was less than 4%. The experimental error was also less than 4%. Consequently, linear interpolation was used to generate additional data. The small deviation/error, guarantees the accuracy of the values of the data generated, within limits of the experimental error. As such, this did not change the trends obtained in our experimental results.

4. Results and discussion

4.1. Neural networks application for the characteristics of the Ni/Al₂O₃ catalysts

4.1.1. Neural networks one (NN-1)

It was shown earlier that for our calcined Ni/Al₂O₃ catalysts for which the optimum temperatures for calcination and reduction have already been established, respectively, by TGA and TPR-H₂, there are four catalyst characteristics that were measured and thus could be considered. These are BET surface area, pore volume, pore size and nickel crystallite size. Thus, in our case, the calcination and the reduction temperatures were set-up to be constants. As such, effort was focused only on the other four physical properties (BET surface area, pore volume, pore size, nickel crystallite size).

It can be seen from Fig. 2 that for the given calcination temperature, when the preparation method, nickel loading and aluminum loading are known, the characteristics of the calcined catalysts can be determined. The characteristics of the calcined catalysts are therefore a function of the preparation method, nickel loading and aluminum loading. NN-1 for this relation is described in Fig. 3a, the preparation methods (CP, PT, IM), Ni loading and Al loading are the inputs while the BET surface area, pore volume, pore size and crystallite size are the outputs of NN-1. The details of the configuration are given in Table 2.

4.1.2. Neural networks two (NN-2) for the function $Y = f(X)$

Based on Fig. 2, crude-ethanol conversion, hydrogen selectivity and hydrogen yield are the main parameters that characterize hydrogen-production performance of the catalysts by the catalytic reforming of crude ethanol, and are the outputs for the NN-2. On the other hand, the catalyst-preparation method (CP, PT, IM), nickel loading, aluminum loading and reaction operation temperature as

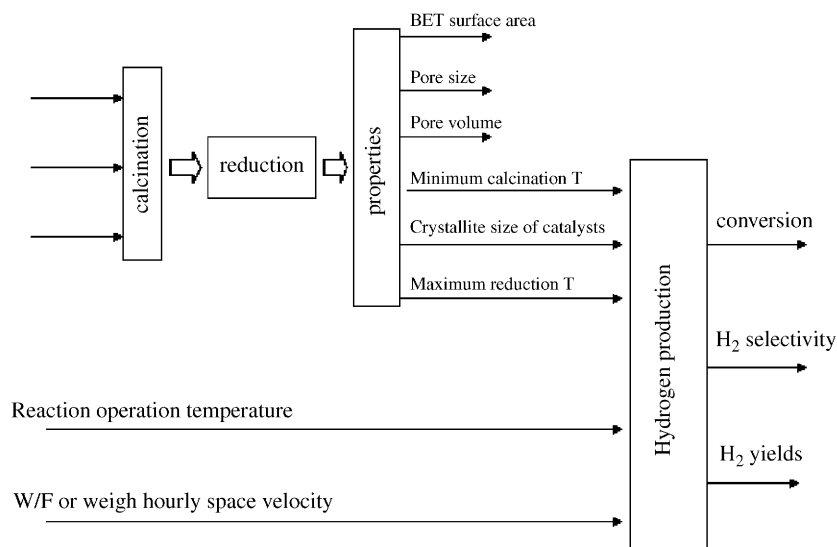
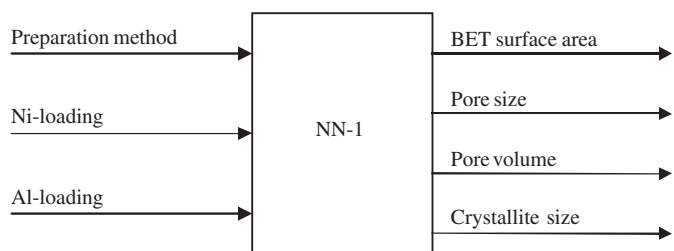
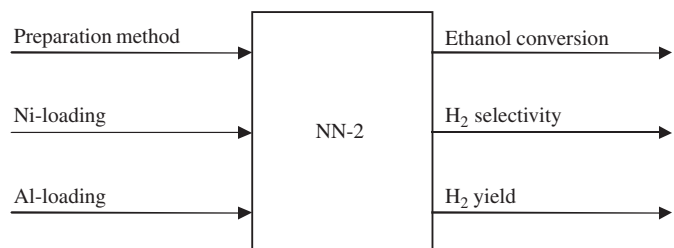


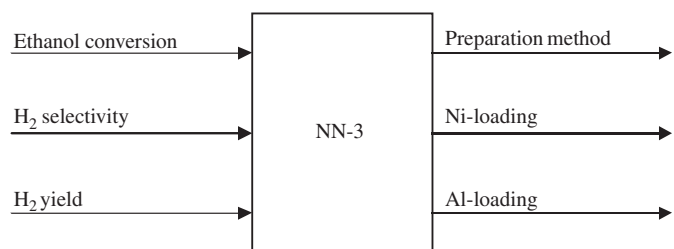
Fig. 2. Overall relationship between catalysts-preparation conditions, catalyst characteristics and catalyst hydrogen-production performance.



(a) NN-1 for catalyst synthesis process



(b) NN-2 for hydrogen production



(c) NN-3 for inverse of hydrogen production

Fig. 3. Neural networks for the catalyst properties and hydrogen production.

inputs for the NN-2. These are given in Fig. 3b. At fixed calcination and reaction temperatures as well as fixed WHSV, hydrogen production is only a function of preparation method, nickel loading and aluminum loading as the input variables. Fig. 3b thus shows that only these are the inputs of the NN-2, while the outputs of the NN-2 are crude-ethanol conversion, hydrogen selectivity and hydrogen yields. The details of the configuration for NN-2 are given in Table 2. The relationship between the input and output variables can be expressed in the formula $Y = f(X)$ where

$$X = \begin{bmatrix} \text{Preparation method (CP, PT, IM)} \\ \text{Nickel loading} \\ \text{Aluminum loading} \end{bmatrix}$$

$$Y = \begin{bmatrix} \text{Crude-ethanol conversion} \\ \text{Hydrogen selectivity} \\ \text{Hydrogen yield} \end{bmatrix}$$

4.1.3. Neural networks three (NN-3) for the inverse function $X = f^{-1}(Y)$

Normally, ANN are used to learn a function mapping $Y = f(X)$, where Y is the vector of the output and X is the vector of the input and $f(X)$ is the function to learn. In many cases in engineering and science problems, it is also desired to learn the inverse function, $X = f^{-1}(Y)$. It has been proven that ANNs do well for the forward and inverse functions.

For our situation, the function between the input and the output is unknown. If hydrogen production (crude ethanol conversion, hydrogen selectivity and hydrogen yields) is known, it may sometimes be desirable to know both the

well as the crude-ethanol WHSV are the main operating conditions and reaction conditions which could affect hydrogen production. Therefore, these conditions are the

Table 2
Implementation details for NN

| | Neural network | | |
|-------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| | NN-1 Feed-forward back propagation | NN-2 Feed-forward back propagation | NN-3 Feed-forward back propagation |
| Total number of layers ^a | 3 | 3 | 3 |
| Neurons per layer | 5–5–4 | 5–5–3 | 5–5–3 |
| Transfer function | Sigmoidal | Sigmoidal | Sigmoidal |
| Training algorithm ^b | LM Back propagation | LM Back propagation | LM Back propagation |
| Training epoches | 5 | 79 | 59 |
| Mean square error | 0.008299 | 0.006934 | 0.009965 |

^aOne input layer, one hidden layer and one output layer.

^bLM, Levenberg–Marquardt training algorithm.

catalyst conditions and the reaction operating conditions that will yield the known hydrogen production. This scenario is given in the NN-3 as described in Fig. 3c. The details of the configuration for NN-3 are also given in Table 2.

4.2. Hydrogen production with neural networks

4.2.1. Using the neural networks to obtain optimal operation and catalyst conditions for maximum crude-ethanol conversion, hydrogen selectivity or hydrogen yield

For this case study, the reduction temperature, T1, was 600 °C, the reaction temperature was 400 °C, and the WHSV was 1.68 h⁻¹. Then, NN-2 was used for the purpose of making the preparation method, and Ni and Al loading optimal in order to obtain the maximum hydrogen production. The hydrogen production itself depended on whether hydrogen yield, hydrogen selectivity or crude-ethanol conversion was the main target. In our case, hydrogen yield was the main target.

The optimization procedure is as described in Fig. 4. It involves the setting up of the delta units for Ni and Al loadings, respectively. Initially we fix CP, and let Al loading to equal maximum Al loading and Ni loading to equal minimum Ni loading. Then, this is followed with the Ni loading plus one delta unit, via NN-2, getting temporary maximum hydrogen yield and the corresponding Ni loading, until Ni loading is equal to maximum Ni loading. Further, this is followed by using Al loading minus one delta unit, using similar procedure as shown earlier until Al loading becomes the minimum Al loading, getting temporary maximum hydrogen yield and the corresponding Ni loading and Al loading. These procedures are repeated for PT and IM preparation methods.

After processing and optimization, the results for hydrogen yield and the corresponding catalyst-preparation conditions are described in Fig. 5. The optimal hydrogen yield was 4.4 mol%, and the associated crude-ethanol conversion and H₂ selectivity for the optimal hydrogen yield were 79.6 and 91.4 mol%, respectively. The optimal

catalyst-preparation method was the CP method, the optimal nickel loading was 12.35 wt% and the optimal aluminum loading was 42.49 wt %.

4.2.2. Verification with ANN

In order to verify the prediction accuracy of the ANN, a series of experimental data were obtained and then compared with those predicted by ANN. The results are given in Table 3. The table shows, for example, that for catalyst CP11.5 (i.e., catalyst with 11.5% Ni and prepared by the CP method), the actual experimental values for crude-ethanol conversion, hydrogen selectivity and hydrogen yield were 40, 89 and 2.16 mol%, respectively. On the other hand, the corresponding predicted values by ANN were 45.85, 90.71 and 2.77, respectively. For the CP catalysts, the AAD% for crude-ethanol conversion, hydrogen selectivity and hydrogen yield were 17.9, 4.6 and 13.8, respectively. These are reasonable for this type of process. For the PT catalysts, the corresponding AAD% were 24.8, 5.4 and 10.5, respectively, while for the IM catalysts, the corresponding AAD% were 3.4, 2.5 and 2.6, respectively. The parity charts for these comparisons are displayed in Fig. 6 for crude-ethanol conversion, hydrogen selectivity and hydrogen yield, respectively. These show good predictive abilities. The better prediction ability for the IM catalyst could be attributed to the better control of the elemental compositions of the catalysts to their nominal values when the catalysts are prepared by the IM method as opposed to those by other methods of preparation (namely, CP and PT catalysts).

5. Conclusions

Artificial neural network (ANN) has been used to design an optimum Ni/Al₂O₃ for the production of hydrogen by the catalytic reforming of crude ethanol. ANN could predict hydrogen production performance of various Ni/Al₂O₃ catalysts of various elemental compositions and methods of preparation in the production of hydrogen by the catalytic reforming of crude-ethanol in terms of crude

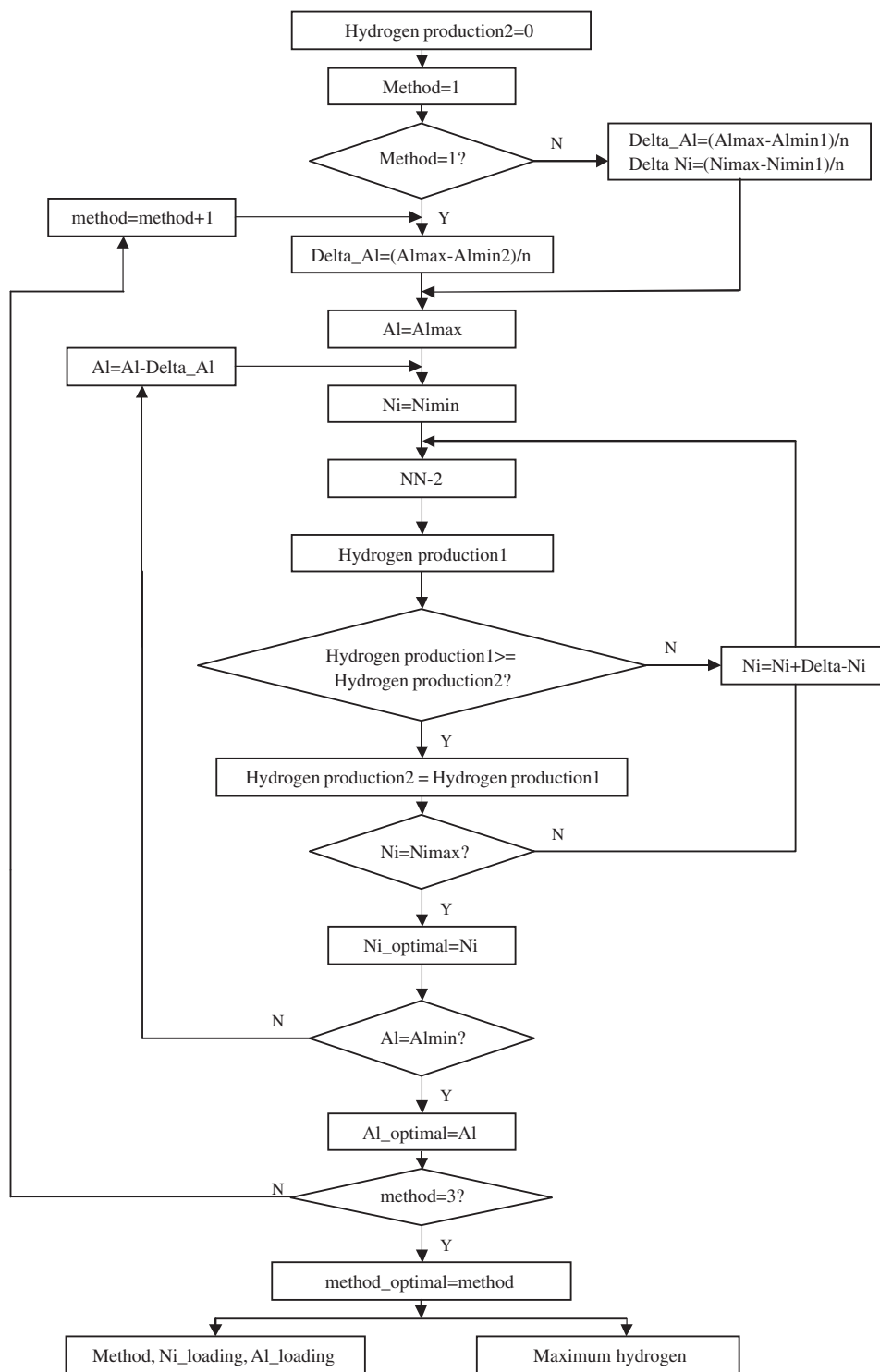


Fig. 4. Optimization procedure.

ethanol conversion, hydrogen selectivity and hydrogen yield. Specifically on catalyst design, ANN was used to determine the optimum catalyst conditions for obtaining maximum hydrogen-production performance of a Ni/Al₂O₃ catalyst for the production of hydrogen by the catalytic reforming of crude ethanol. The optimal hydro-

gen yield was 4.4 mol%, and the associated crude-ethanol conversion and H₂ selectivity for the optimal hydrogen yield were 79.6 and 91.4 mol%, respectively. The optimal catalyst was the one prepared by the CP method with the optimal nickel loading of 12.4 wt% and an optimal aluminum composition of 42.5 wt%.

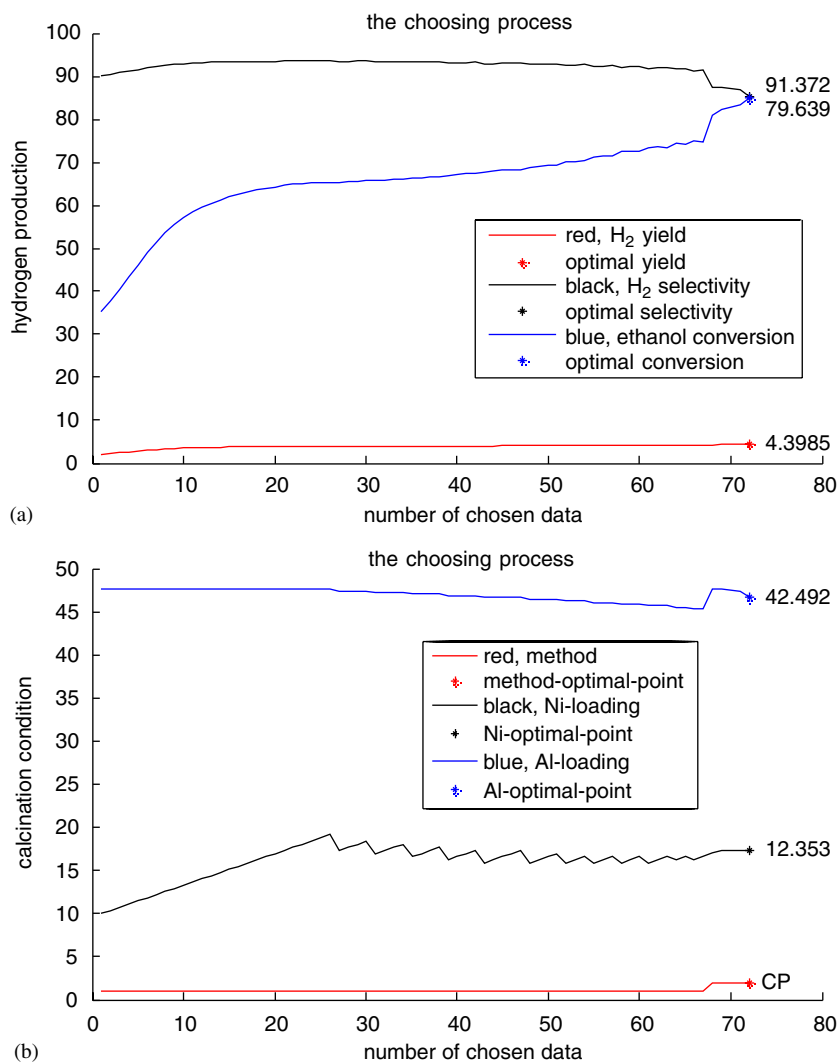


Fig. 5. Optimization results. (a) Hydrogen production (b) catalyst preparation conditions.

Table 3
The prediction values and the actual values corresponding to the catalysts

| Catalysts | Composition | | | Actual values | | | Predicted values | | |
|-----------|-------------|----------|---------|---------------|-----------------|-----------------|------------------|-----------------|-----------------|
| | Ni (wt%) | Al (wt%) | O (wt%) | X | SH ₂ | YH ₂ | X | SH ₂ | YH ₂ |
| CP11.5 | 11.5 | 46.85 | 41.65 | 40 | 89 | 2.16 | 45.853 | 90.709 | 2.7715 |
| CP13.5 | 13.5 | 45.79 | 40.71 | 65 | 90 | 3.55 | 64.638 | 90.315 | 3.6546 |
| CP16.5 | 16.5 | 44.21 | 39.29 | 62 | 88 | 3.31 | 71.582 | 89.88 | 3.9057 |
| CP18.5 | 18.5 | 43.15 | 38.35 | 57 | 91 | 3.15 | 61.622 | 89.722 | 3.336 |
| PT11.5 | 11.5 | 46.85 | 41.65 | 45 | 87 | 2.38 | 56.431 | 85.499 | 2.9019 |
| PT13.5 | 13.5 | 45.79 | 40.71 | 60 | 86 | 3.13 | 72.935 | 83.482 | 3.675 |
| PT16.5 | 16.5 | 44.21 | 39.29 | 81 | 84 | 4.13 | 84.446 | 81.992 | 4.2238 |
| PT18.5 | 18.5 | 43.15 | 38.35 | 83 | 83 | 4.18 | 83.633 | 81.996 | 4.1993 |
| IM11.5 | 11.5 | 46.85 | 41.65 | 43 | 86 | 2.24 | 44.916 | 85.887 | 2.3524 |
| IM13.5 | 13.5 | 45.79 | 40.71 | 45 | 86 | 2.35 | 46.147 | 87.075 | 2.4496 |
| IM16.5 | 16.5 | 44.21 | 39.29 | 47 | 88 | 2.51 | 47.001 | 87.371 | 2.4979 |
| IM18.5 | 18.5 | 43.15 | 38.35 | 47 | 86 | 2.45 | 46.998 | 86.574 | 2.4700 |

X, crude ethanol conversion; SH₂, hydrogen selectivity; YH₂, hydrogen yield.

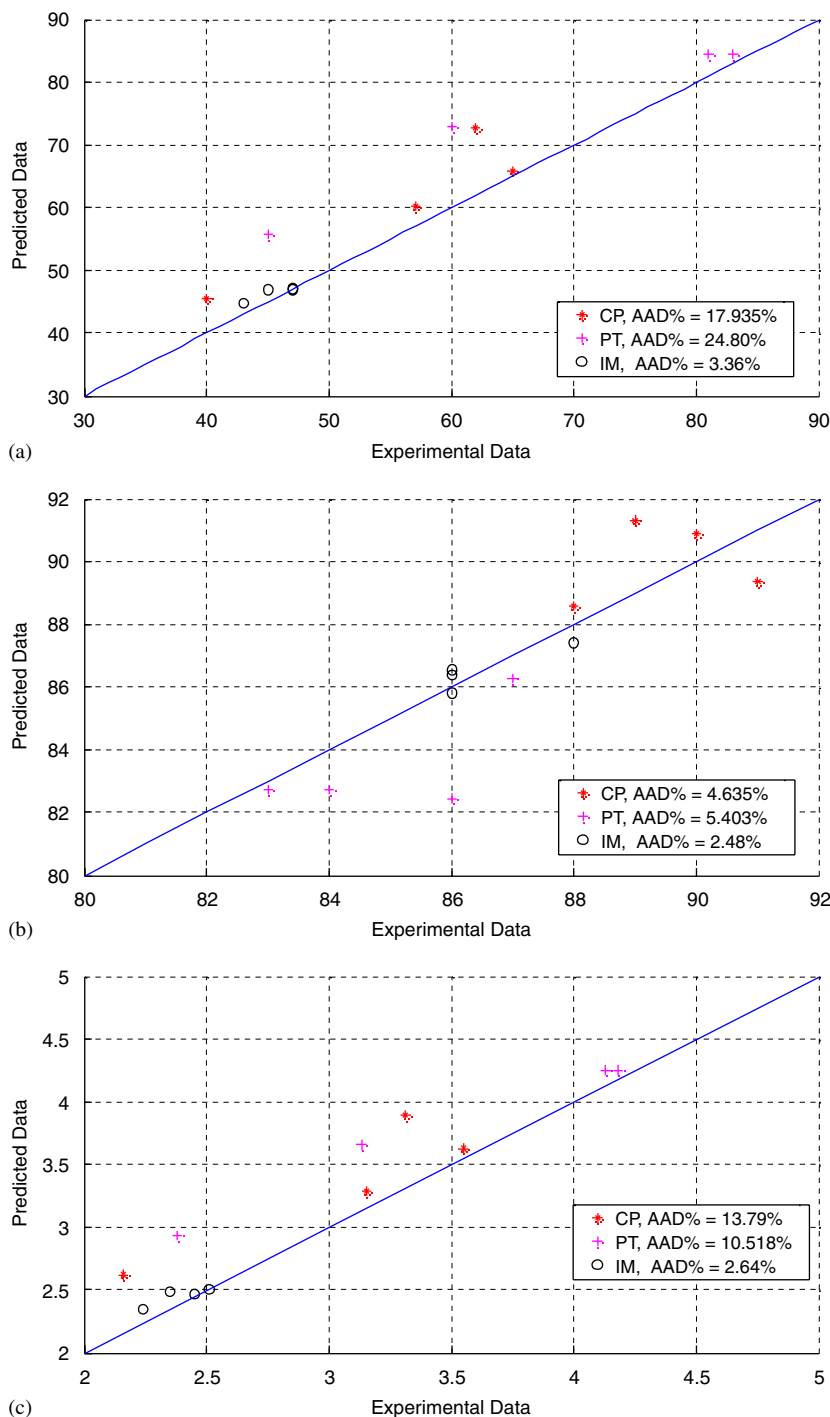


Fig. 6. Parity charts: (a) ethanol conversion, (b) hydrogen selectivity, and (c) hydrogen yield.

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