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Prediction of Methanol Production in a Carbon Dioxide Hydrogenation Plant Using Neural Networks

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Abstract: The objective of this research was to design a neural network (ANN) to predict the methanol flux at the outlet of a carbon dioxide dehydrogenation plant. For the development of the ANN, a database was generated, in the open-source simulation software "DWSIM", from the validation of a process described in the literature. The sample consists of 133 data pairs with four inputs: reactor pressure and temperature, mass flow of carbon dioxide and hydrogen, and one output: flow of methanol. The ANN was designed using 12 neurons in the hidden layer and it was trained with the Levenberg–Marquardt algorithm. In the training, validation and testing phase, a global mean square (RMSE) value of 0.0085 and a global regression coefficient R of 0.9442 were obtained. The network was validated through an analysis of variance (ANOVA), where the *p*-value for all cases was greater than 0.05, which indicates that there are no significant differences between the observations and those predicted by the ANN. Therefore, the designed ANN can be used to predict the methanol flow at the exit of a dehydrogenation plant and later for the optimization of the system.

Keywords: simulation; DWSIM; hydrogenation of carbon dioxide; ANN

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1. Introduction

Carbon dioxide (CO_2) is a compound that belongs to the so-called greenhouse gases. In recent years emissions of CO_2 have increased into the atmosphere, causing an increase in the greenhouse effect, constituting one of the main causes of global warming; this has also led to the acidification and increase of the sea levels to some extent [1,2].

In order to mitigate CO_2 emissions, three methods have been proposed: capturing and storing CO_2 underground, biological treatment with algae, and chemical [3] conversion. The catalytic hydrogenation of CO_2 is the most promising process of chemical conversion. This process allows products such as alcohols, formic acid, and formaldehyde to be obtained; it is also possible to obtain light hydrocarbons such as methane depending on the type of the catalyst used [4,5]. Methanol is the chemical that shows higher performance both in the energy field (25.5 Kcal/H_2) and at the hydrogen use level (H_2) (67%) [6]. Moreover, methanol can be used both as a fuel for energy obtainment and as an intermediate means for the production of other more valuable chemicals such as dimethyl ether (used in aerosols) or formaldehyde (used in the manufacture of plastics) [7].

The reaction between H_2 and CO_2 is thermodynamically favorable. However, there are limitations related to the reaction kinetics since the activation energy is high. As a consequence, the hydrogenation speed decreases significantly, creating the need for a catalyst [4]. Copper-based catalysts, especially $Cu/ZnO/Al_2O_3$, due to their high activity, have been

widely used for the hydrogenation of CO_2. The main drawback of $Cu/ZnO/Al_2O_3$ is that they are deactivated in the competitive reverse water gas displacement reaction that occurs at the same time as the methanol production reaction [8]. In order to solve the problem of catalytic deactivation, numerous studies have been carried out in which the performance of supported catalysts based on transition metals such as Ni, Pd, and Ce is evaluated. These catalysts are commonly used in the hydrogenation process of the synthesis gas. Despite presenting favorable results at a lab scale, they have not been industrially tested. Furthermore, only studies related to characterization, process thermodynamics, and kinetic descriptions have been carried out [4,5,8–12].

This article discusses the use of an ANN tool to predict the catalytic process. Therefore, the state of the art includes both concepts. First, the use of catalyst followed by the limited application of ANN in processes in which different catalysts are involved.

The ANN method has been selected in this research because it can build from historical data, experimental and/or simulations and does not require exact relationships between the dependent and independent variables. Furthermore, ANN has been widely used in various industrial chemical processes [13] because they have the ability to correlate input and output variables of non-linear multivariate phenomena and have been successfully applied in the prediction of complex, realistic and synthetic processes in areas where no analytical or semi-experimental correlation is available [14].

The Methanol Production Process from CO_2 Hydrogenation

Figure 1 illustrates the process of producing methanol from the hydrogenation of CO_2 adapted from [15]. The entrance to the hydrogenation plant consists of a stream of CO_2 and another of hydrogen, 88,000 kg/h and 12,100 kg/h, respectively. The stream of carbon dioxide is compressed to 78 bars in a series of compressors with an isentropic efficiency of 70.3%, in each of these, the stream outlet pressure was specified, while the H_2 stream is compressed in only one step up to 78 bar. In Tables 1 and 2, the conditions to which the currents enter are detailed.

Table 1. Input flow's conditions (CO_2) [15].

Parameter	Value	Unit
Temperature	25	°C
Pressure	1	bar
Mass flow	88,000	kg/h
Molar flow	1999.57	kmol/h
Volumetric flow	48,667.4	m^3/h

Table 2. Input flow's conditions (H_2) [15].

Parameter	Value	Unit
Temperature	25	°C
Pressure	30	bar
Mass flow	12,100	kg/h
Molar flow	6002.34	kmol/h
Volumetric flow	5038.15	m^3/h

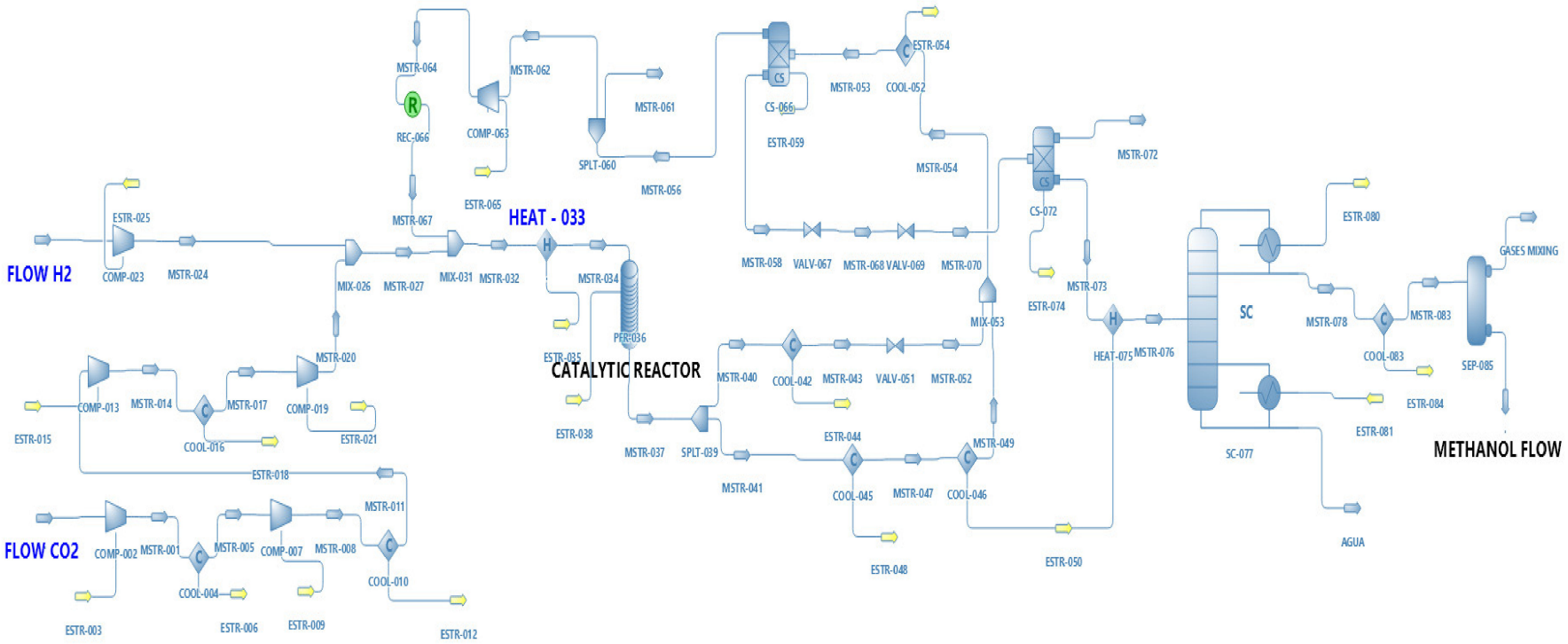

Figure 1. Flowsheet methanol production.

The feed streams are mixed with the recycling stream and then are heated to 210 °C for being fed to the reactor; in this a 30% conversion of CO_2 to methanol is obtained. The kinetic model used was developed by Bussche and Froment [16] with mathematical artifices developed in [15]. The kinetic model considers that the carbon source to produce CH_3OH comes from CO_2. The reactions that occur inside the reactor are shown in Equations (1) and (2), and the kinetic models are described by Equations (3)–(5), Table 3 summarizes the kinetic parameters employed:

Table 3. Values of reordered kinetic parameters [15].

Constant	Parameter	Value
k_1	A_1 B_1	−29.87 4811.2
k_2	A_2 B_2	8.147 0
k_3	A_3 B_3	−6.452 2068.4
k_4	A_4 B_4	−34.95 14,928.9
k_5	A_5 B_5	4.804 −11,797.5
k_6	A_6 B_6	17.55 −2249.8
k_7	A_7 B_7	0.131 −7023.5

- Methanol production reaction:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{1}$$

- Reverse water gas shift reaction:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{2}$$

- Reaction kinetics of methanol production:

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 \cdot \frac{P_{H_2O} \cdot P_{CH_3OH}}{P_{H_2}^2}}{\left(1 + k_2 \cdot \frac{P_{H_2O}}{P_{H_2}} + k_3 \cdot P_{H_2}^{0.5} + k_4 \cdot P_{H_2O}\right)^3} \tag{3}$$

- Reaction kinetics reverse water gas shift:

$$r_{rws} = \frac{k_5 P_{CO_2} - k_7 \cdot \frac{P_{H_2O} \cdot P_{CO_2}}{P_{H_2}}}{1 + k_2 \cdot \frac{P_{H_2O}}{P_{H_2}} + k_3 \cdot P_{H_2}^{0.5} + k_4 \cdot P_{H_2O}} \tag{4}$$

- Kinetics constants:

$$ln\ k_i = A_i + \frac{Bi}{T} \tag{5}$$

where, k_i, A_i and B_i are the kinetic model constants.

The effluent of the reactor is divided into two streams; one is used to preheat the feed to the distillation tower. Subsequently, the streams are mixed and condensed to separate the unconverted gases of the product stream. The unconverted gases are recirculated to the reactor while the water-methanol mixture expands to 1.2 bar where the unconverted remaining gases are removed. Finally, this stream enters the distillation tower, from which

methanol is obtained as a head product with 99% purity; this is cooled to 40 °C where it separates from waste gas still contained in the phase separator.

2. State of the Art

In this section, a state of the art assessment is carried out focused on the two main concepts related in this study; the hydrogenation process and the use of ANN as a prediction method tool for catalytic process.

2.1. Catalysts and Simulation of the Hydrogenation Process

Despite the deactivation suffered by copper-based catalysts, they continue to be the object of study to improve their catalytic properties. Fang et al. [1,17] prepared copper-based catalysts with hydrotalcite. The catalysts prepared from $Cu/ZnO/ZrO_2$ and $Cu/ZnO/Al_2O_3$ contained 56.6% and 40% respectively of hydrotalcite in their structure. As a result of the addition of hydrotalcite, the catalysts had a greater dispersion of copper atoms on its surface. After performing several tests at different conditions, comparing the performance of the catalyst with and without hydrotalcite, it was determined that the later shows higher yields and selectivity than the base catalysts (selectivity of 84% for the $Cu/ZnO/ZrO_2$ catalyst and 73.4% for $Cu/ZnO/Al_2O_3$).

Furthermore, it was observed that the conditions under which the absorbent enhanced catalyst operates are lower than those under which the base catalyst operates. These observations are due to the fact that hydrotalcite improves the capacity of the catalyst to absorb CO_2.

Sadeghinia et al. [18] prepared samples of commercial catalysts $Cu/ZnO/Al_2O_3$, to which different proportions of In_2O_3 were added. Then tests were conducted to measure the catalytic activity using as feed a stream containing H_2, CO, and CO_2 and another containing only H_2 and CO_2. These studies showed that, in the first stream, the use of In_2O_3 causes a drop in the production of methanol. This is because the improved catalyst has more capacity to absorb CO_2, favoring only the hydrogenation of CO_2.

Due to the high costs associated with the construction of pilot plants, studies were carried out to evaluate the performance of the hydrogenation process at an industrial level; they have been conducted by employing commercial software such as ASPEN PLUS [19].

Perez-Fortes et al. [20] developed the simulation of a CO_2 capture and use plant. The plant was simulated in the CHEMCAD software [21] in order to obtain the flow value of energy and matter. Based on the results, they developed an economic analysis, obtaining that the plant can produce 440 kTn/year of methanol. This study concluded that the operation of the plant is not economically viable. Kiss et al. [22] proposed the use of a stripping column to process a stream of wet hydrogen. This stream flows countercurrent together with the effluent leaving the reactor. The use of the stripping column allows a more efficient separation of unconverted gases present in the product stream from the methanol-water mixture. This scheme allows the reduction of the amount of water present at the inlet of the reactor, causing a drop in the flow of methanol produced. In turn, it allows the recirculation of a greater quantity of unconverted CO and CO_2. As a result, this scheme consumes 550 kW/Tn of methanol produced and 0.48–1.16 Tn of steam for each ton of methanol produced. As the studies [20,22] show in the proposed industrial schemes, the energy consumption associated with methanol production is considerably high. To solve this problem, Szima et al. [23] propose the use of a gas turbine and a simple Rankine cycle that operates at low pressure to compensate for the energy requirements of the plant. The plant was simulated in [21]. The supply to this plant was hydrogen that comes from a water electrolysis process, while the CO_2 was captured from a coal plant. The results of the simulation showed that it is not economically profitable for its construction. Through a sensitivity analysis, they determined that the plant would be economically viable if the sales price of methanol was doubled or the costs of electricity decreased by half.

Do and Kim [24], to solve the energy problem, conducted a simulation in [19]. In this process, the energy required for hydrogen obtainment from the water decomposition was

obtained from solar collectors, while the CO_2 is reduced to carbon monoxide using solar energy. The primary CO_2 reduction yielded methanol using the traditional process. This technology proved to have a high energy efficiency of 15.5%. Moreover, it managed to establish a competitive selling price of methanol.

Van Dal and Bouallou [15] carried out a simulation in [19], where the hydrogenation plant is fed with CO_2 captured from a thermoelectric plant. The hydrogen necessary to produce methanol was obtained from the electrolysis of water. The results determined that to produce one ton of methanol, 1.6 tons of CO_2 can be removed.

On the other hand, the studies carried out to analyze the feasibility of implementing an ethanol production process from CO_2 and improving the capabilities of the catalyst involved present great limitations. There are models that describe the behavior of a system in a realistic way. However, they lead to the establishment of robust differential equations that involve complex calculations and increase computational time. This procedure is impractical for sensitivity and optimization studies [2]. Studies related to kinetic models and characterizations of new catalysts are limited by DTF (density functional theory) calculations that make idealized assumptions [15].

2.2. Artificial Neural Networks (ANN) as a Prediction Tool in Catalysis Processes

Artificial neural networks (ANN) are predictive tools able to learn directly from a process and give short response times; this allows the modeling of systems in a more complex and realistic manner [25,26].

ANNs are a computational model that can handle multiple complex problems of the real world. The versatility of the ANN is due to the ability of information processing, high parallelism, fault tolerance, nonlinearity, noise, and tolerance generalization capabilities [27]. ANNs in their structure are made up of several layers of neurons that connect to each other to share information and are distributed in input, hidden and output layers; each neuron has an activation function that allows information to be reconstructed or predicted [28]. Nowadays, ANNs are among the most used tools in different areas of engineering and science to create complex and nonlinear models and to describe the natural behavior of the system. They constitute a good way to find issues of malfunctions inside a system. They have been used for years in different areas of engineering, science, and business to deal with highly complex and non-linear data sets [29–31].

There are several relevant studies in the area of catalysis, and in most cases, the main objectives are: setting the experimental conditions and/or properties of the catalyst system as inputs and the catalytic activities as outputs of the model. In addition, research suggests that automatic learning can be a good option to reduce the computational cost of the catalysis study and promote the discovery of new catalysts. However, ANN in the field of catalysis is not well studied since the acquisition of a database for training models is costly and, at the same time, should take into account too many input variables for creating the model [32].

Kito et al. [33] developed an ANN to estimate the acid strength of mixed oxides, catalytic performance, and selectivities to various products in the oxidative dehydrogenation of ethylbenzene in a series of promoted catalysts SnO_2. The results from the study indicated that the ANN has a large capacity of interpolation, extrapolation, prediction of the catalytic performance of multiple components.

Liu et al. [34] trained a neural network with the ability to predict the catalytic activity as well as the selectivity of various catalysts used for CO_2 hydrogenation. The objective was for the network to select the appropriate catalyst based on the products to be obtained. The result of the work indicates that ANN can satisfactorily predict the activity and selectivity of each catalyst. However, it is not possible to satisfactorily select the right catalyst for each experiment because of the limited data used for training.

Zahedi et al. [2] designed an ANN in conjunction with a mathematical model to study the behavior of an industrial packed bed reactor. The ANN is responsible for the prediction of the reaction kinetics, while the mathematical model is used to determine temperature

and pressure data at the outlet of the reactor. Two types of neural networks were trained, a perceptron-type network and a radial-based one. The radial base network obtained a lower root mean square error (RMSE) value, indicating it as the most suitable for predicting the data. The results showed that there is a great agreement with the real values of the reactor studied.

Sun et al. [35] designed an ANN with the ability to predict the selectivity of a catalyst in a microchannel reactor. The neural network used was of the perceptron type with two hidden layers and was trained with real data taken from a reactor. The ANN determined the optimal operating conditions of the reactor.

Borisut and Nuchitprasittichai [13] developed an artificial neural network to analyze the minimum cost of methanol production with three different configurations (I: once-through reactor methanol production; configuration II: methanol production with recycling and configuration III: two reactors in series), the configurations were analyzed with APSEN HYSYS. However, this study proposes and design an ANN from the platform of open-source chemical processes "DWSIM" using a new configuration proposed by Van Dal and Bouallou [15]. In contrast to [13], this simulation of the methanol production process is more realistic since it does not consider a perfect separation between liquid and gas in the flash tank and, therefore, considers a fraction of gases in the column feed and moreover contemplates a adiabatic reactor packed with a fixed bed of $Cu/ZnO/Al_2O_3$ commercial catalyst. The ANN can be scaled to real processes in industry, using historical data as input and output neurons. In this sense, the ANN would replace the simulation process, which on several occasions is tedious and expensive.

3. Materials and Methods

The first part of this study deals with simulating the process of Figure 2, taking into account the operating conditions of the process. The next step is to validate the results and proceed with the design of an artificial neural network considering the inputs and outputs determined for the prediction of the process and the restrictions imposed by the simulation. Subsequently, training and validation of ANN using graphical and statistical analysis to evaluate the predictive ability of the neural network are performed. Figure 2 illustrates the flowchart of the methodology.

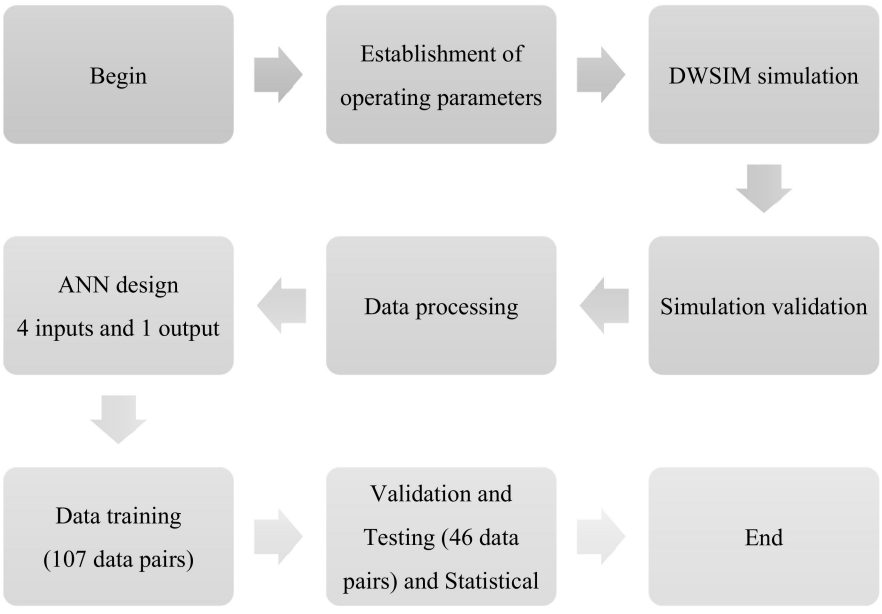

Figure 2. Methodology to devolopment the artificial neural networks (ANN).

This section describes the applied mathematical model, as well as the design model and training ANN. This section describes the applied mathematical model, as well as the design model and training ANN.

3.1. DWSIM Simulation

Different thermodynamic models were used, following the recommendations established in [22,36,37] for this type of system. For currents higher pressure 10 bar, the SRK (Soave-Redlich-Kwong) model was used. For the remaining flows, the NRTL (Non-Random Two Liquids) model was used. The model was simulated using the flash method of nested valid loops for calculating the balance between liquid and vapor phases. Table 4 shows the detailed reactor geometry configuration and the characteristics of the catalyst used for the simulation of the packed bed reactor.

Table 4. Packed bed reactor configuration.

Property	Value	Unit
Pressure drop	0.453	bar
Residence time	0.007	h
Length	10	m
Catalyst loading	1775	kg/m^3
Catalyst diameter	5.5	mm
Catalyst void fraction	0.4	
Temperature difference	62.983	C
Heat load	0	kW

3.2. Design and Training of the ANN

ANNs consist of multiple layers of neurons, and each neuron uses the output of the previous layer as input. Each neuron has a summation function that calculates the weighted sum of the inputs and a sigmoid activation function (Equation (6)) that transforms the weighted sum in values of different magnitudes between 0–1.

$$f(x) = \frac{1}{1 - e^{-x}} \tag{6}$$

The design of the ANN (Figure 3) is based on four input parameters and one output parameter. There are studies, such as the one carried out by Wang et al. [38], where an analysis based on the mean value of impact is used to determine the input parameters to RNA. However, there is sufficient evidence [6,14,39–42] that determines that the pressure and temperature in the reactor are the parameters that most influence the production of methanol compared to other factors such as the type of catalyst and operating conditions of the other equipment involved in the process. In this sense, the input parameters are the outlet pressure and outlet temperature of the exchanger (HEAT–033) and the mass flow of CO_2 and H_2 (the increase in the inlet pressure of the reactor and the decrease in the inlet temperature can lead to increased methanol production). The output parameter corresponding to the mass flow rate of methanol at the outlet of the hydrogenation plant.

Taking into account the recommendations established by Chen et al. [43] from the total set of data generated, 70% of the data are selected for the design and training of the ANN (107 data pairs), while 30% of the data are used to perform a validation (23 data pairs) and testing (23 data pairs) to evaluate its level of learning. Figures 4 and 5 show the distribution of the inputs and outputs used in the training, validation, and testing process of the ANN. A correlation analysis between the input variables used in the model has been carried out using SPSS 22.0. As shown in Table 5, all the analyzed data pairs do not present a significant correlation (p-value > 0.05).

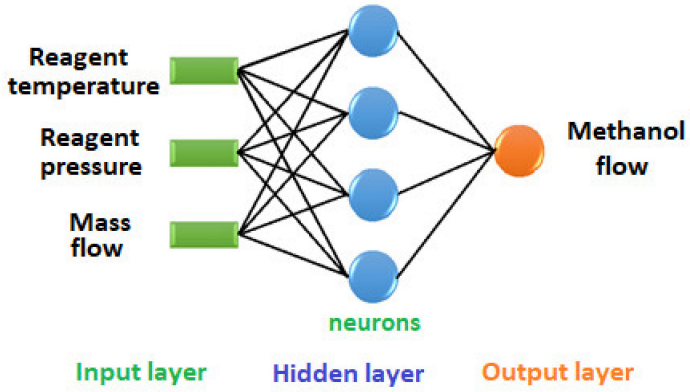

Figure 3. The ANN designed.

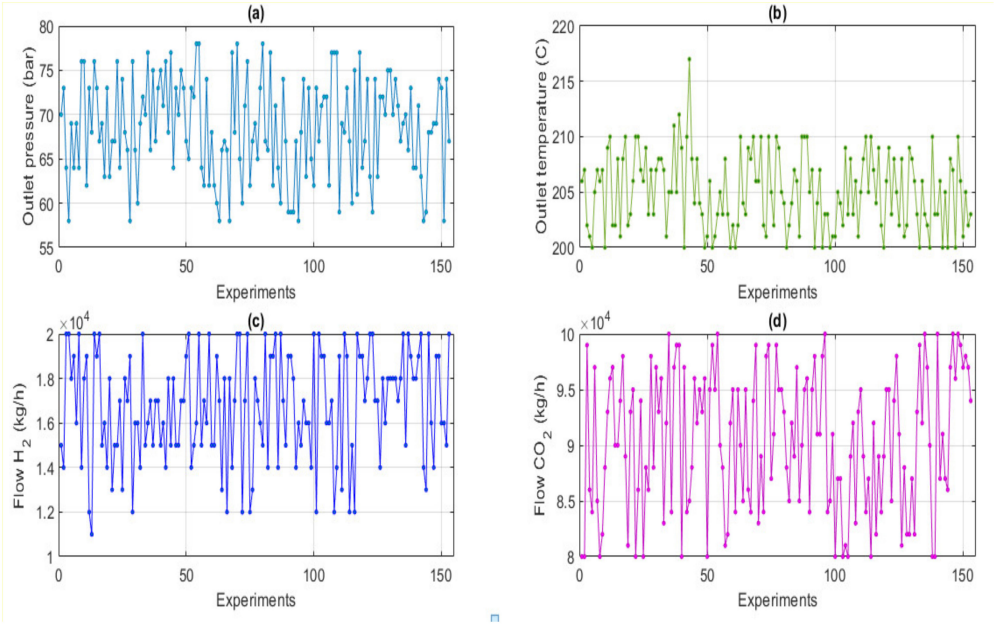

Figure 4. Input values employed to training, validation and testing the ANN. (**a**) Outlet pressure (bar); (**b**) outlet temperature (°C); (**c**) flow H_2 (kg/h); (**d**) flow CO_2 (kg/h).

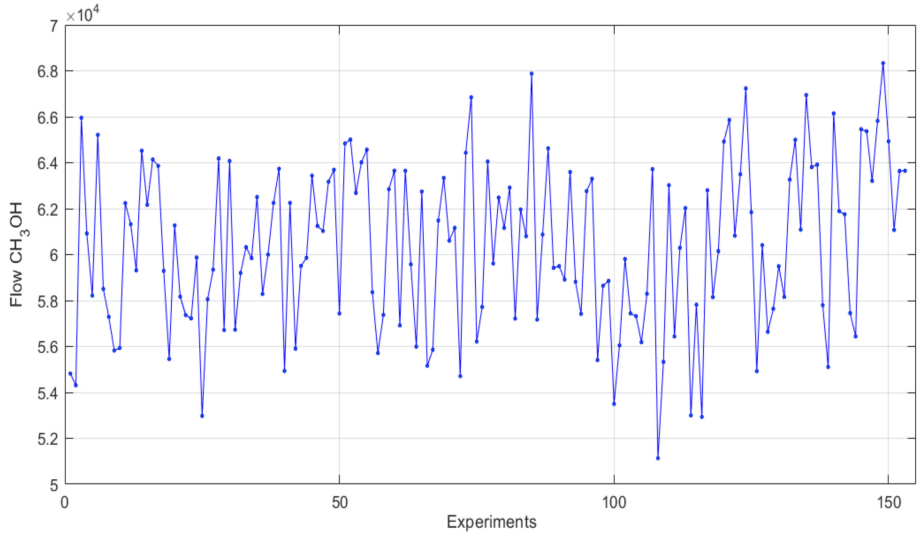

Figure 5. Outlet values (flow CH_3OH) employed to training, validation and testing the ANN.

Table 5. A correlation analysis between the input variables.

p-Value	Pressure	Temperature	Mass Flow CO_2	Mass Flow H_2
Pressure	-	0.636	0.934	0.06
Temperature	0.636	-	0.441	0.916
Mass flow CO_2	0.934	0.441	-	0.2355
Mass flow H_2	0.06	0.916	0.2355	-

The training process seeks to adjust the weights of the connections between neurons in such a way that the predictions made by the network are as accurate as possible with respect to those selected as the target. Validation is a process where the error thrown by the network is measured with respect to the objective data and is used as a measure of the performance of the network. ANN testing is equivalent to presenting data to the network that was not used for training; this involves generating new pairs of data, presenting them to the ANN without showing the desired outputs, and comparing how accurate the predictions are. It is important to note that the Levenberg–Marquardt algorithm in some cases is sensitive to the number of neurons and may suffer overtraining problems caused by the noise present in the data outputs with which the ANN trains [44,45] and when an ANN is overtrained lower its prediction capacity and will begin to "memorize" the data too often; that is, it will try to predict the exact output values, rather than the expected general trend in the data [46].

Once the simulation process of the carbon dioxide hydrogenation plant in DWSIM was validated. The specialized bibliography in the development of ANN suggests a minimum of 50 points to predict quantities determined with regression algorithms [47–49]. In this sense, 153 data pairs (4 inputs and one output) were generated to train the network. Table 6 details the variation range of the input variables selected for the study. To validate the ANN and demonstrate the reliability of the model for the prediction of methanol flow, the general performance indicators were used: RMSE, Pearson's correlation coefficient (R), and additionally a comparative statistical analysis of variance (ANOVA). Similarly, to determine the optimal ANN, a trial and error procedure was carried out until the neural network with the lowest RMSE associated with the network was found and based on the correlation coefficients obtained for the training, validation, and testing process of the network.

Table 6. ANN input's restrictions.

Parameter	Pressure	Temperature	Mass Flow (CO_2)	Mass Flow (H_2)
Details	bar	°C	kg/h	kg/h
* Range	58–78	200–210	88,000–100,000	12,100–20,000

* Less or greater than the established ranges, the simulation does not run.

4. Results and Discussion

The analysis and discussion of results include both the description and validation and topology of the ANN and the performance of the model. In this section, both are presented.

4.1. Simulation Validation

Before designing the ANN, it is essential to carry out the comparison of the simulation developed in DWSIM with results from the literature. The study developed in [15] was used for validation. The process DWSIM was adapted according to the simulation developed in ASPEN PLUS. Table 7 details the comparison of the results; as it can be seen, the percentage errors do not exceed 5%. The existence of the error between the values obtained and those of the literature is justified by the thermodynamic model used (SRK-MVHS) and by the volume of the reactor that is not defined in [15].

Table 7. DWSIM simulation validation.

Component	Input Flow Entrada (kg/h)	Output Flow [6] (Kg/h)	Output Flow DWSIM (kg/h)	Error (%)
Methanol	0	59,300	58,297.99	1.69%
Water	0	33,700	32,559.83	3.38%
Carbon dioxide	88,000	5820	5710.52	1.88%
Carbon monoxide	0	510	524.53	2.85%
Hydrogen	12,100	870	833.46	4.19%

4.2. ANN Topology

This section defines how the ANN was structured through the analysis of the correlation coefficient (R) and the RMSE.

4.2.1. Methods Used for Selection of ANN Training Algorithm

This study employs a MATLAB library, NNTOOL, which provides three different training algorithms: Levenberg–Marquardt (LM), Bayesian regularization (BR) and scaled conjugate gradient backpropagation (SCG). These methods were used because they are capable of obtaining lower RMSE than some other algorithms [50–52].

A trial and error test was carried out, varying the training algorithm and number of neurons in the hidden layer. As in other prediction studies, for example, those developed by Wang et al. [38,53], R and RMSE were evaluated to determine the appropriately ANN structure R and RMSE results of the analysis are provided in Table 8.

Table 8. Pearson's correlation coefficient (R) and root mean square error (RMSE) values for trial and error using Levenberg–Marquardt (LM), Bayesian regularization (BR) and scaled conjugate gradient backpropagation (SCG) algorithms.

# Neurons	LM		BR		SCG	
	R Global	RMSE	R Global	RMSE	R Global	RMSE
500	0.318	1.26	0.956	0.012	0.206	1.72
100	0.497	0.18	0.924	0.068	0.861	0.042
50	0.939	0.022	0.939	0.045	0.936	0.013
12	0.944	0.0085	0.940	0.009	0.891	0.010
6	0.935	0.0048	0.938	0.036	0.907	0.010
3	0.932	0.0087	0.933	0.01	0.650	0.037

After the training process, the results detailed in Table 8 conclude: the most suitable training algorithm to predict the methanol flow are LM and BR. The minimum RMSE value and maximum R value are: 0.0085 and 0.944 when LM algorithm is used (training time: 10.2 min), while when BR is applied the minimum RMSE is 0.009 and maximum R is 0.940 (training time: 60.5 min).

The RMSE and R values are similar in both algorithms. However, in this study LM was used because it requires less training time (6 times less), this agrees, with what is established by Tabbussum et al. [54]; Cheng et al. [55]; Negash et al. [56] which indicate that Bayesian Regularization takes more time to generate results.

4.2.2. Selection of Neurons in the Hidden Layer

Figures 6–8 show the evolution of R-values for the training, validation, test, and global phase using 500, 100, and 12 neurons, respectively. The global R-value using 500 neurons is: 0.318 and the RSME = 1.26 (Table 9). These results suggest that the network is not suitable for methanol flux prediction. On the other hand, in 100 neurons the value of R = 0.49 and the RMSE = 0.18. In this case, the value of R in the training phase is 0.99, indicating an adequate correlation between the observed data and those predicted by the network. However, the value of R in the validation and testing phase drops to 0.25 and

0.076; these values indicate that the ANN is overtrained, losing the ability to generalize its predictions. When 12 neurons were used (Figure 9), it is observed that the value of R both in the training, validation, test, and global phases are: 0.948, 0.940, 0.942, and 0.944, respectively, and according to Table 9, the value of the RSME is 0.0085; these results indicate that ANN has a good predictive ability.

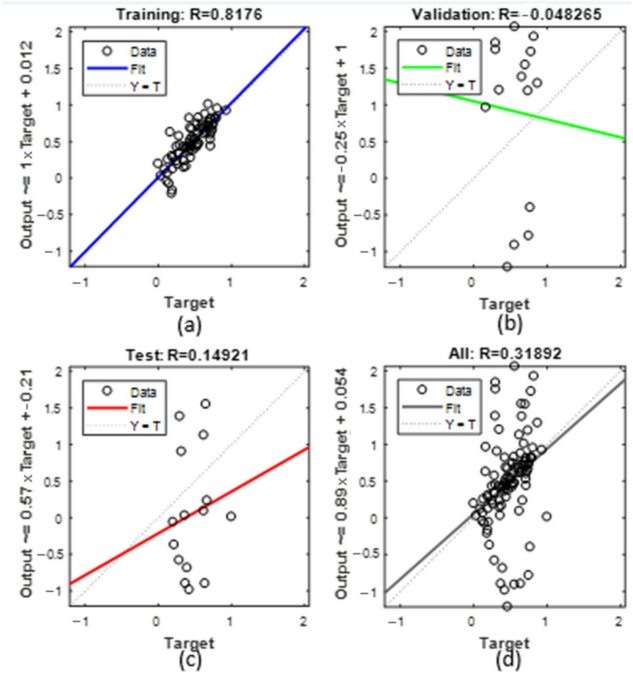

Figure 6. Regression and correlation coefficient using 500 neurons in the hidden layer for stage (**a**) the training phase, (**b**) validation, (**c**) testing, and (**d**) overall.

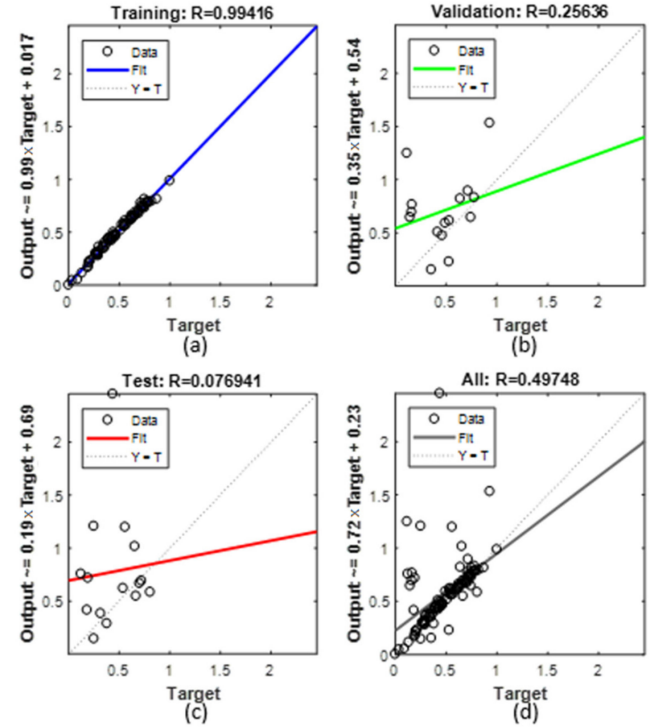

Figure 7. Regression and correlation coefficient using 100 neurons in the hidden layer for stage (**a**) the training phase, (**b**) validation, (**c**) testing, and (**d**) overall. Using 100 neurons in the hidden layer.

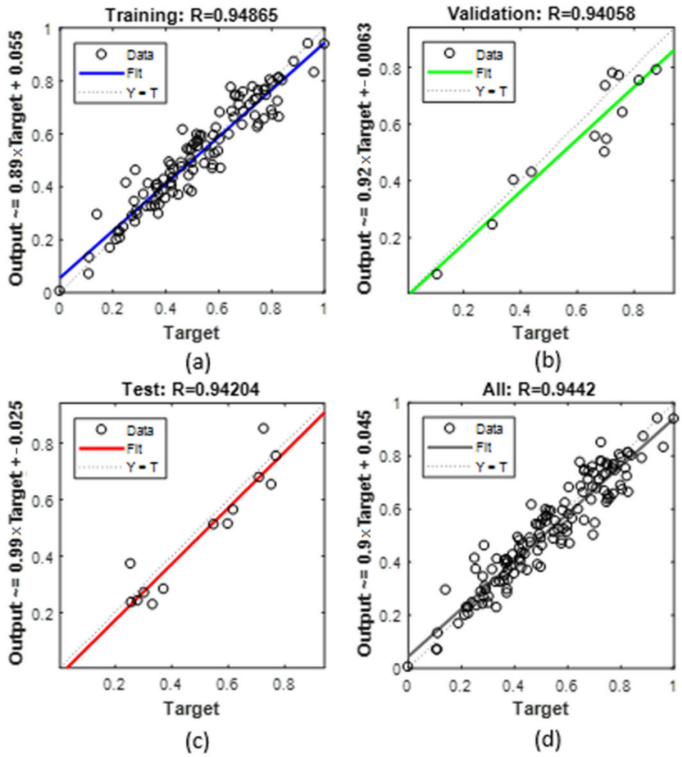

Figure 8. Regression and correlation coefficient using 12 neurons in the hidden layer for stage (**a**) the training phase, (**b**) validation, (**c**) testing, and (**d**) overall.

Table 9. R and RMSE values for trial and error using LM algorithm.

# Neurons	R Train	R Validation	R Test	R Global	RMSE
500	0.817	0.048	0.149	0.318	1.26
100	0.994	0.256	0.076	0.497	0.18
50	0.976	0.917	0.686	0.939	0.022
12	0.948	0.940	0.942	0.944	0.0085
6	0.933	0.947	0.936	0.935	0.0048
3	0.943	0.915	0.920	0.932	0.0087

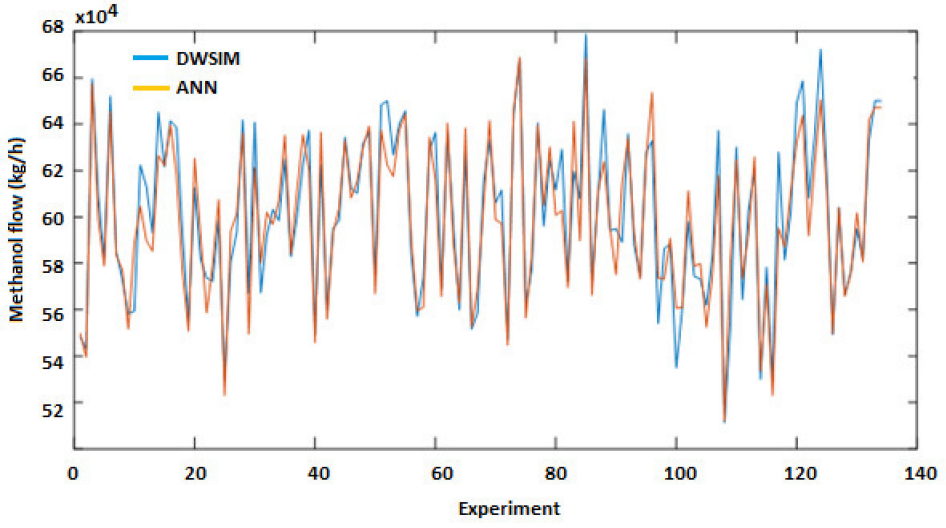

Figure 9. Comparative graph of the experimental data (DWSIM) and ANN predictions regarding methanol flux (kg/h).

Through these experiments, we defined that the network topology is a layer with four input neurons, a hidden layer with 12 neurons, and an output layer with a neuron based on the above analysis. This is consistent with the previous research, which highlights that a hidden layer may be sufficient in most practical applications of ANN [27]. The designed ANN is of the simple perceptron type and is trained with the Levenberg–Marquardt algorithm using the MATLAB tool NNTOOL version R2018a. The overall parameters are:

Population size: 153
Maximum iteration: 1000
Epochs: 11
Time: 10.2 min
Performance: 0.00236
Gradient: 0.000407
Mu (Control parameter): 0.0001

4.3. Prediction Model of Methane Flow Topology

Figure 9 shows the comparison between predictions (ANN) and the values defined by simulation (DWSIM). It is possible to appreciate the approximation between observations and predictions. The average percentage error of the predictions is: 2.55%. Therefore, the network prediction is acceptable since there is an excellent correlation between the input and output data of the ANN. It can be concluded that the developed model approaches the data of the observations, proving that the ANN is a robust model and suitable for predicting the flow of methanol by ANN hydrogenation plants.

4.4. Verification of the ANN Model

To evaluate the reliability of the performance of the ANN designed during the training, validation and testing phase, unknown data pairs were created by the ANN to verify their predictive capacity. For this, a set of 10 random data (P, T, mass flows) simulated in DWSIM has been generated to collect new observations based on the new operating conditions. To verify the prediction capacity, the ANN designed to predict the methanol flux at the exit of the hydrogenation plant was used. The comparison between the observations and the predictions is shown in Figure 10. The overlap between them allows us to deduce that the designed ANN has a good capacity and precision of prediction of the methanol flow at the exit of the carbon dioxide hydrogenation plant. The graphic analysis was complemented with an ANOVA analysis in order to guarantee that the designed ANN is reliable and suitable as a prediction tool.

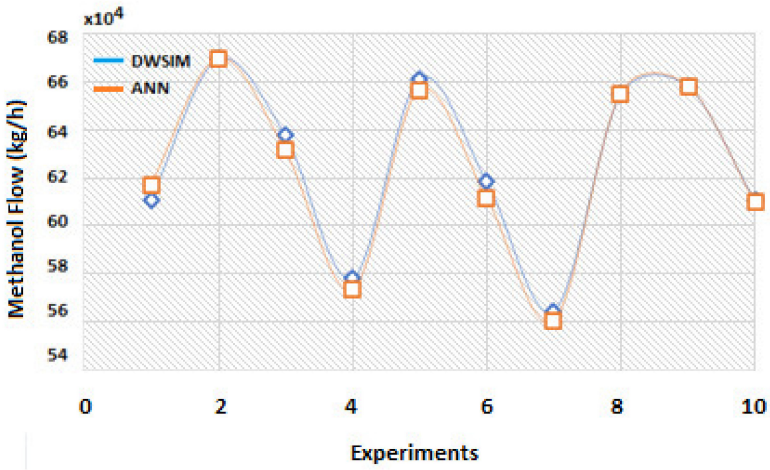

Figure 10. Comparison between observations (DWSIM-blue) and predictions of ANN (orange) methanol flow.

In this research, the ANOVA was used to statistically validate the ANN. The results of the ANOVA are summarized in Table 10. According to the statistical test employed,

the *p*-value of F-ratio is greater than 0.05. The ANOVA analysis shows no statistically significant difference between the predictions and observations (experimental data). For this reason, the constructed ANN is statistically valid for predicting the methanol flow in the dehydrogenation plant. In addition, as seen in Table 11 measuring the average percentage errors (%E) between predictions and observations, the %E is lower than 1.5%.

Table 10. Analysis of variance (ANOVA) results ANN model.

Source	DF	Middle Square	F-Reason	*p*-Value
Between groups	1	231,849	0.02	0.8968
Intra groups	18	1.34×10^7		
Total (Corr.)	19			

Table 11. Percentage error values between predictions (ANN) and experimental data.

Pressure (Bar)	Temperature (°C)	Flow H_2 (kg/h)	Flow H_2 (kg/h)	Flow CH_3OH ANN	Flow CH_3OH Exp. Data	%E
67	206	92,000	18,000	61,087.27	61,678.39	0.968
69	203	100,000	20,000	66,943.53	66,956.09	0.019
70	202	97,000	15,000	63,806.52	63,155.75	1.020
73	210	80,000	19,000	57,800.02	57,333.64	0.807
64	203	100,000	18,000	66,143.67	65,640.04	0.761
71	206	87,000	19,000	61,887.38	61,187.57	1.131
59	200	86,000	13,000	56,438.23	56,022.78	0.736
68	208	97,000	20,000	65,456.97	65,522.59	0.100
69	210	100,000	19,000	65,822.90	65,831.86	0.014
58	205	98,000	16,000	61,069.53	60,973.94	0.157

5. Conclusions

In this study, a neural network was designed to predict methanol flux in a carbon dioxide dehydrogenation plant from the simulation process in DWSIM. The designed neural network has a hidden layer with 12 neurons and was trained, validated and testing with a base of 153 data pairs with four input variables: pressure (P) and temperature (T) of the reactor, mass flow of CO_2 and H_2 and is capable of predicting the methanol flux as an output variable.

The ANN was trained with the Levenberg–Marquardt algorithm, has an RMSE of 0.0085, and has a total regression coefficient of 0.9442. The ANN was validated through a comparative statistical analysis (ANOVA) between the observations (DWSIM) and the values predicted by the network. The statistical test indicates that the network adequately predicts the flow of methanol with a significance level of 95%. Based on the results, it is deduced that the ANN designed in this study can be used as a prediction tool to improve the processes for obtaining methane from the dehydrogenation of carbon dioxide.

The advantage of using the ANN is the reduction of the calculation time to predict the methanol flow from the inputs to the model and implies fewer mismatches, in fact the current trend is for the ANN to be coupled to dynamic processes and used in a way. Extensive for process optimization. In addition, the ANN does not have a defined structure, other input parameters that have not been analyzed could be added to make the prediction more accurate. The disadvantage of the ANN is the need for continuous data collection to adapt to change and improve learning and prediction.

Further study will focus on the development of an ANN trained, validated and testing with a broader database, coupled with a genetic optimization algorithm to maximize methanol production and minimizing economic costs. Additionally, the optimization would include current trends including process performance, CO_2 conversion, and preheat/precool energy intensification using the mean impact value-based analysis. However, it will be necessary to obtain a broad base of experimental and/or industrial data from the methanol production process.

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