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# NEURAL NETWORK PREDICTION OF THE FISCHER-TROPSCH SYNTHESIS OF NATURAL GAS WITH Co (III)/$Al_2O_3$ CATALYST

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**Abstract:** Application of Co (III)/$Al_2O_3$ catalyst in Fischer-Tropsch synthesis (FTS) was studied in a wide range of synthesis gas conversions and compared with ANN Simulation results. Present study applies Neural Network model to predict composition of $CH_4$, $CO_2$ and CO of the Fischer–Tropsch Process of Natural Gas, while the input vector was 4-dimension vector including four variables from operating pressure, operating temperature, time and ratio of $CO/H_2$ of 70 different experiments and the output were composition of $CO_2$, CO and $CH_4$. The MLP algorithm has been applied for the training and the test set was applied to evaluate the performance of the system including R2, MAE, MSE and RMSE. The results exposed that the predicted values from the model were in good agreement with the experimental data. The paper indicates how Neural Network, as a promising predicting technique, would be effectively used for FTS.

***Keywords:*** *Neural Network; Fischer–Tropsch; Natural Gas; Catalyst; CO (III); $Al_2O_3$.*

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## INTRODUCTION

Fischer-Tropsch synthesis (FTS) is an industrially important process for the conversion of syngas ($H_2$/CO) derived from carbon sources such as coal, peat, biomass, and natural gas into hydrocarbons and oxygenates [1-3]. FTS enables the production of virtually sulfur and aromatic free transportation fuels and chemical feedstock from carbon sources alternative from crude oil. Depending on FTS feedstock and desired products, either Cobalt or Iron catalyst are applied industrially [4]. Cobalt-based catalysts are highly active, although Iron may be more suitable for low-hydrogen-content synthesis gases such as those derived from coal due to its promotion of the water-gas-shift reaction. Alumina is often used as a support for cobalt FTS catalysts due to its favorable mechanical properties, but an alumina-supported catalyst has a limited reducibility due to a strong interaction between the support and the cobalt oxides [5]. The cobalt species, which strongly interact with the support, are generally inactive in CO hydrogenation due to their low reducibility. This can be improved to a certain extent by adding metal or metal oxide promoters, such as Pt, Re,$ZrO_2$, etc [6].

Cobalt catalysts are more active for Fischer-Tropsch synthesis when the feedstock is natural gas. Natural gas has high hydrogen to carbon ratio, so the water-gas-shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower quality feed stocks such as coal or biomass. Several reactions are required to obtain the gaseous reactants required for FTS catalysis. First, reactant gases entering a FTS reactor must first be desulfurized to protect the catalysts that are readily poisoned. The other major class of reactions is employed to adjust the $H_2$/CO ratio:

Water gas shift reaction provides a source of hydrogen:

$$H_2O + CO \xrightarrow{yields} H_2 + CO_2$$

For FTS plants that start with methane, another important reaction is steam reforming, which converts the methane into CO and $H_2$:

$$H_2O + CH_4 \xrightarrow{yields} CO + 3H_2$$

The Fischer-Tropsch synthesis (FTS) synthesis is a complex reaction giving rise to numerous gas, liquid and solid phase products. Thus, modeling FTS synthesis phenomenologically i.e., via mass, energy and momentum balance equations becomes difficult [7,8]. Catalyst design is a tedious and a complex process involving many steps, many variables and complex interactions among these variables, making the experimental studies quite expensive and time consuming [9]. In recent years, the artificial neural network (ANN) based modeling approach has opened a new avenue for developing empirical models. Based on the property of artificial neural network, the relation between catalytic performances (such as the selectivity of reaction and the conversion of reactant) and the components of catalyst could be expressed effectively.

There are many researches in various fields that applied these methods for nonlinear system identification. The neural networks has been applied for modeling the green house effect, simulation $N_2O$ emissions from a temperate grassland ecosystem, and assessment of flotation experiments [10] . Authors in [11] applied a combination of fuzzy model and neural networks in order to identify a complex

dynamic system. Wai and Chen also used a neuro-fuzzy model for the robot manipulator dynamic identification [12]. Sadrzadeh applied a neuro-fuzzy model coupled with a mathematical model for the prediction of zinc ions separation from wastewater using electrodialysis [13]. Erguo li and his colleague used a neuro-fuzzy system in order to construct a quality predictive model for injection process [14]. Evgueniy Entchev and Libing Yang applied an adaptive neuro-fuzzy interface system to predict solid oxide fuel cell performance in residential micro-generation installation [15]. In addition, the flow rate of dirty amine of an adsorption column in the Khangiran gas refinery was predicted using neural network and genetic algorithm [16]. A comparison of ANN and neuro-fuzzy model has been done recently to delineate the best model for the prediction of parameters. Yasin Varol and his coworker compared ANN and neuro-fuzzy models to predict the flow fields and temperature distributions due to natural convection in a triangular enclosure in [17]. Singh applied the neuro-fuzzy and ANN models for the prediction of Cadmium Removal [18]. The structural organization of network could show the complexity of catalyst system, and the weight matrix could show the interactions between different components [19].

Present study aims to develop an ANN model in order to predict the experimental results of Fischer–Tropsch process with Co (III)/Al catalyst.

## EXPERIMENTAL

### Catalyst Preparation

One-tenth mole of ammonium heptamolybdate (Aldrich) was dissolved in one liter of distilled water. The color of the solution was white. The catalyst support the aluminum oxide (400 mesh alumina) was added to the solution, with 11 g of alumina per 3 grams of the complex. The solution was stirred by a high speed mechanical stirrer for 10 hours as heptamolybdate anion was chemisorbed on the surface of aluminum oxide particles. Deposition of complex anion on the catalyst support is a very crucial step in precatalyst formation. At this time 0.2 mole of hexaammoniumcobalt (III) chloride (Aldrich) $[(NH_3)_6Co]\ Cl_3$ complex (burnt orange to red crystals) was dissolved in sufficient distilled water. Next, as the solution was stirring, the cobalt complex was added drop wise to the solution. The stirring continued for five more hours. Formation of an even pale pink color on the catalyst support and a colorless solution indicated that the following reaction had occurred:

$$2[(NH_3)_6Co]\ Cl_3 + [(NH_4)_6Mo_7O_{24}]: Al_2O_3 \rightarrow 6NH_4Cl + [(NH_3)_6Co]\ {}_2[Mo_7O_{24}]: Al_2O_3 \text{ (palepink)}$$

The precatalyst was filtered. The filtrate was colorless; indicating that no cobalt complex remained in the solution and all had reacted with the molybdate complex on the catalyst support. The precatalyst was washed with distilled water to remove all ionic co-products. The precatalyst was insoluble and unreactive in water at 0-100 $^oC$. The precatalyst was gently dried in an oven. The formation of the pink $[(NH_3)_6Co]_2Mo_7O_{24} : Al_2O_3$ precatalyst was demonstrated by both the developed color of the alumina as well as by potassium bromide disc infrared spectroscopy which indicated the presence of $(NH_3)_6Co^{3+}$ ion by $NH_3$ spreading modes and the Mo=O units of $Mo_7O_{24}^{6-}$ ion by strong Mo=O stretching absorption. The partial reduction of cobalt/molybdate precatalyst was performed in a quartz tube at elevated temperature (400-450$^oC$) under a steady flow of

hydrogen gas at ambient pressure for 24 hours. During reduction, the color of the precatalyst changed from pale pink to dark black. The following procedure for syngas catalysis was followed: The reactor was allowed to equilibrate at desired temperature; syngas with certain composition and pressure was injected, and then the stirring motor was turned on; after the selected time, the syngas product was passed through a condenser to condense out the water vapor. The condenser was cooled by a salt and ice mixture. Then the syngas was stored in the sample collector for gas chromatography analysis. There was no oily material observed above the water; the water was weighed.

The chromatograph was used to analyze the products. A Varian Aerograph Model 90 P with a carbosieve B 60/80 mesh column and thermal conductivity detector (TCD), with helium as carrier gas was used for CO, $CO_2$, and $CH_4$.

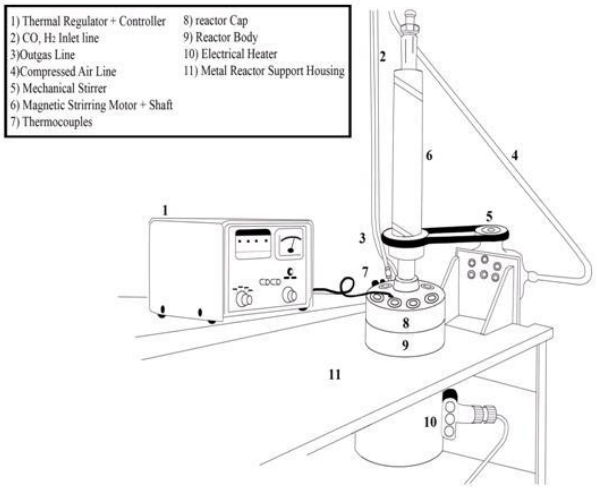


Figure1: Stainless Steel Autoclave Reactor Used for Syngas Evaluation

## Reactor System

The catalyst evaluation was carried out in one liter volume stainless steel autoclave reactor. In gas and out gas lines were also made of 316 stainless steel tubing. This reactor was equipped with electrical heater, magnetic stirring motor, and magnetic stirrer. The magnetic stirring motor was driven by air flow. The temperature of the reactor was controlled by a thermocouple model F2M Scientific 240 temperature programmer (Hewlett Packard). The autoclave reactor was convenient to use at medium to high pressure 150 bars and at temperature up to 350$^{o}$C. The autoclave reactor was manufactured by Autoclave Engineers, Inc., Erie PA. USA. The experimental setup is shown in the Figure 1.

## MODELING

In this study the modular artificial neural networks were created by using computer codes written in MATLAB Back-propagation algorithm with delta rule of error correction was used as the learning algorithm to adapt the weights [20]. The commonest type of artificial neural network consists of three layers of units: a layer of "input" units is connected to a layer of "hidden" units, which is connected to a layer of "output" units. (See Figure 2)

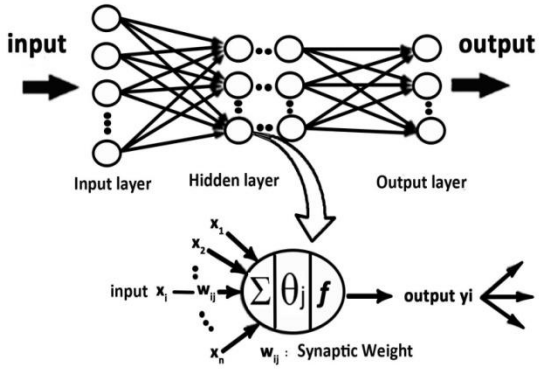


Figure2: Architecture of the ANN Model [20]

Figure 2 illustrates a typical full-connected network configuration. Such an ANN consists of a series of layers with a number of nodes. As one of the most widely implemented neural network topologies, in

this paper, the multilayer perceptron (MLP) is employed [21,22]. The network calculates a set of output data from the given set of input data. Then the difference between thus calculated output data and the given output data is propagated backward through the network to adjust the weight of connections between the neurons. This procedure is iterated until the calculated output data become close to the given output data [23]. In artificial neural network (ANN) all feed-forward neural networks (such as MLP and RBF) can be represented by the following equation:

$$\hat{y}(x,\alpha,\beta)=\sum_{j=1}^{M}\alpha_j\varphi_j(x,\beta_j) \qquad (1)$$

Where $\varphi_j(\cdot)$ can be chosen as any arbitrary non-linear function. The model is always linear with respect to $\alpha_j s$ but may be non-linear with respect to the $\beta_j s$.

Figure 2 represents a feed-forward neural network with a single hidden layer for a Multiple Input Single Output (MISO) system.

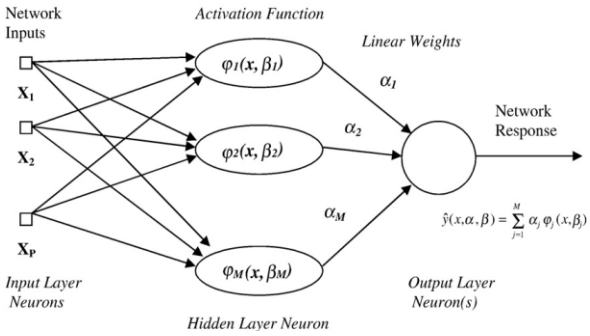


Figure3: Architecture of the Three-layered Feed-Forward Neural Network with a Single Hidden Layer for a MISO system [16]

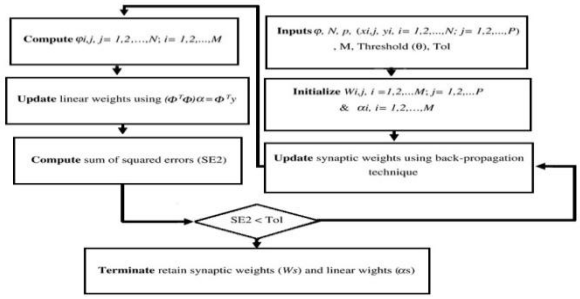


Figure 4: Learning Procedure for Training MLP Networks

Table 1: Comparison of Experimental Data with Predicted Values for $CH_4$, $CO_2$ and CO

| P (bar) | t (hr) | T (oC) | Ratio $CO/H_2$ | $CH_4$ | $CO_2$ | CO | Predicted $CH_4$ | Predicated $CO_2$ | Predicted CO |
|---|---|---|---|---|---|---|---|---|---|
| 9.1 | 12 | 250 | 0.25 | 51 | 28 | 21 | 49.39 | 28.21 | 21.96 |
| 20.8 | 12 | 250 | 0.25 | 72 | 14 | 14 | 73.02 | 16.36 | 12.35 |
| 34.7 | 12 | 250 | 0.25 | 86 | 5 | 9 | 86.71 | 5.51 | 6.89 |
| 48.6 | 12 | 250 | 0.25 | 81 | 7 | 12 | 80.95 | 7.54 | 13.01 |
| 34.7 | 23 | 200 | 0.5 | 64 | 25 | 11 | 63.31 | 24.23 | 11.62 |
| 34.7 | 23 | 200 | 0.25 | 80 | 14 | 6 | 80.34 | 13.85 | 2.58 |
| 34.7 | 23 | 200 | 0.167 | 93 | 1 | 6 | 93.61 | 1.75 | 10.51 |
| 34.7 | 1 | 150 | 0.25 | 0 | 4 | 96 | 0.34 | 4.21 | 96.76 |
| 34.7 | 1 | 170 | 0.25 | 26 | 14 | 60 | 26.08 | 14.46 | 59.78 |
| 34.7 | 1 | 200 | 0.25 | 64 | 20 | 16 | 63.37 | 14.82 | 17.26 |
| 34.7 | 1 | 250 | 0.25 | 75 | 12 | 13 | 75.05 | 12.48 | 13.33 |
| 34.7 | 1 | 300 | 0.25 | 81 | 7 | 12 | 80.95 | 6.80 | 12.70 |
| 34.7 | 10 | 170 | 0.25 | 35 | 18 | 47 | 35.35 | 17.10 | 48.97 |
| 34.7 | 20 | 170 | 0.25 | 46 | 27 | 27 | 46.65 | 27.09 | 27.44 |
| 34.7 | 0.5 | 200 | 0.25 | 57 | 20 | 23 | 57.71 | 18.94 | 24.04 |
| 34.7 | 1 | 200 | 0.25 | 64 | 20 | 26 | 63.37 | 19.82 | 26.26 |
| 34.7 | 2 | 200 | 0.25 | 64 | 21 | 10 | 64.66 | 14.57 | 11.77 |
| 34.7 | 5 | 200 | 0.25 | 74 | 16 | 10 | 73.29 | 15.87 | 11.77 |
| 34.7 | 10 | 200 | 0.25 | 73 | 17 | 10 | 73.29 | 17.88 | 10.28 |
| 34.7 | 15 | 200 | 0.25 | 81 | 10 | 8 | 79.08 | 12.14 | 7.49 |
| 34.7 | 23 | 200 | 0.25 | 80 | 14 | 6 | 80.34 | 14.85 | 6.58 |
| 34.7 | 32 | 200 | 0.25 | 87 | 5 | 8 | 87.00 | 5.54 | 8.38 |
| 34.7 | 36 | 200 | 0.25 | 88 | 6 | 60 | 88.13 | 6.88 | 61.34 |
| 34.7 | 1 | 250 | 0.25 | 75 | 12 | 13 | 75.05 | 12.48 | 13.33 |
| 34.7 | 10 | 250 | 0.25 | 84 | 7 | 9 | 84.68 | 12.15 | 9.82 |
| 34.7 | 20 | 250 | 0.25 | 89 | 5 | 6 | 89.09 | 5.53 | 6.01 |
| 34.7 | 0.5 | 300 | 0.25 | 80 | 6 | 14 | 79.37 | 6.97 | 13.91 |
| 34.7 | 1 | 300 | 0.25 | 81 | 7 | 12 | 80.95 | 6.80 | 12.70 |
| 34.7 | 10 | 300 | 0.25 | 85 | 5 | 10 | 84.42 | 5.10 | 10.07 |
| 34.7 | 20 | 300 | 0.25 | 89 | 4 | 7 | 89.06 | 4.02 | 6.63 |

## RESULTS AND DISCUSSION

Table 1 shown data experimental data and predicted data for Co (III)/$Al_2O_3$ catalyst in Fischer-Tropsch synthesis (FTS). This table show, the results predicted by Neural Networks are in a relatively good agreement with the experimental data.

In this research, there are 70 various data for the Fischer–Tropsch synthesis of Natural Gas with Co (III)/$Al_2O_3$ catalyst system. Table 2 shows neural network features for Fischer–Tropsch synthesis system.

Table 2: Neural Network Features

| Network Type | Feed-forward Back Propagation |
|---|---|
| Training Function | Trainlm (Levenberg marquardt) |
| Number of Layer | 3 |
| Number of neurons in first Layer | 7 |
| Number of neurons in Second Layer | 9 |
| Transfer function in first Layer | tanhyperbolic |
| Transfer function in second Layer | tanhyperbolic |
| Regression for training | 0.991 |
| Regression for validation | 0.996 |
| Regression for testing | 0.913 |

Figure 5, 6 and 7 shows comparison of the predicted value with the neural network and measured of the experimental data for $CH_4$, $CO_2$ and CO of the Fischer–Tropsch Process of Natural Gas.

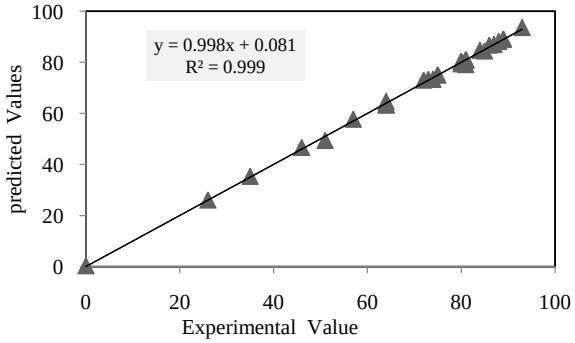


Figure 5: Comparison of the Predicted with the Neural Network and Measured of the Experimental Data for $CH_4$

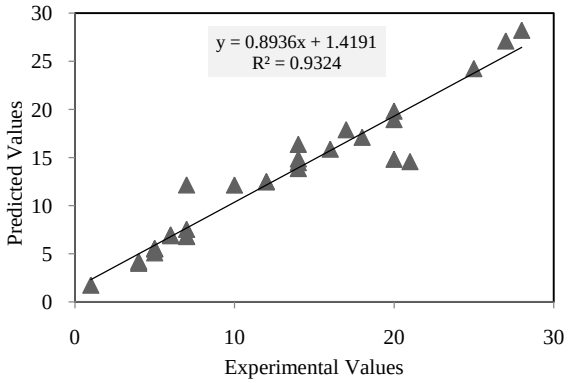


Figure 6: Comparison of the Predicted with the Neural Network and Measured of the Experimental Data for $CO_2$

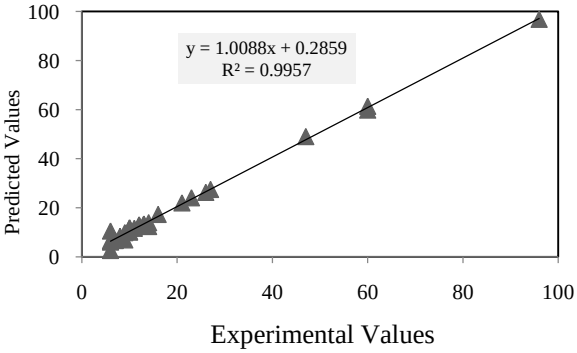


Figure 7: Comparison of the Predicted with the Neural Network and Measured of the Experimental Data for CO

Figure 8 shows the network which has seven neurons in the first hidden layer, and Figure 9 network which has nine neurons in second hidden layer, generating least error, so due to this minimum error, for predicting $CH_4$, $CO_2$ and CO, this network has been used for simulating.

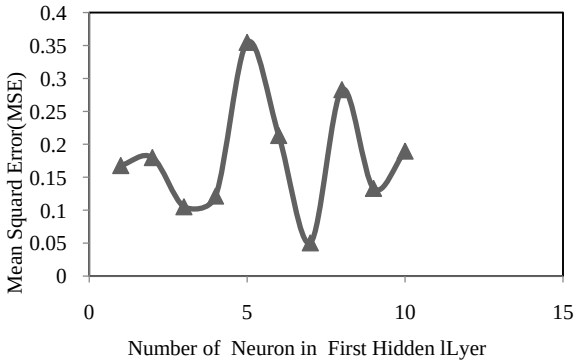


Figure 8: Training Error versus Number of Neurons in First Hidden Layer

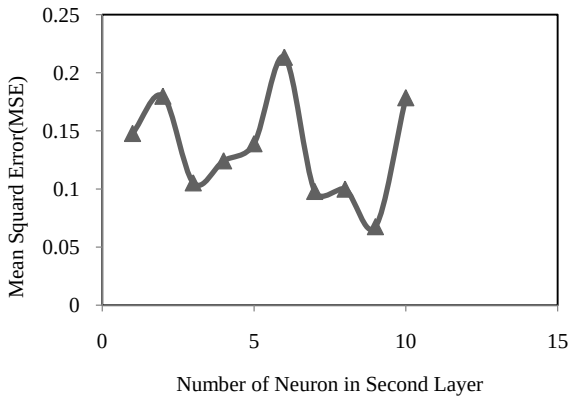


Figure 9: Training Error versus Number of Neurons in Second Hidden Layer

Table 3 reveals Mean absolute error (MAE), Mean square error (MSE), Root Mean square error (RMSE) and Mean absolute percentage error(MAPE) for Fischer–Tropsch synthesis of Natural Gas with Co (III)/$Al_2O_3$ catalyst Respectively. MAE, MSE and RMSE are defined as below:

$$\text{Mean absolute error(MAE)} = \frac{\sum_{i=1}^{n}|y'_i - y_i|}{n} \quad (2)$$

$$\text{Mean square error(MSE)} = \frac{\sum_{i=1}^{n}(y'_i - y_i)^2}{n} \quad (3)$$

$$\text{Root mean square error(RMSE)} = \sqrt{\frac{\sum_{i=1}^{n}(y'_i - y_i)^2}{n}} \quad (4)$$

Where $y_i$ is the ith actual value and $y'_i$ is the ith predicted value for the train and test data.

Table 3: MAE, MSE, RMSE and MAPE for CH4, CO2 and CO which Modeled by ANN

| Comp. | Method | MAE | MSE | RMSE |
|---|---|---|---|---|
| $CH_4$ | ANN | 0.49 | 0.43 | 0.66 |
| $CO_2$ | ANN | 1.11 | 3.77 | 1.94 |
| CO | ANN | 1.01 | 2 | 1.41 |

## CONCLUSION

This paper presents an application of the ANN in the prediction of the Fischer-Tropsch Synthesis's products. Fischer-Tropsch based on the operating pressure, temperature of the reaction, time and ratio of $CO/H_2$. From the presented results it is proved that ANNs can be used with satisfactory accuracy for the prediction of the composition of the Fischer-Tropsch products. This study helps application engineers determine the CO, $CO_2$ and $CH_4$ concentration and conversion of them easily without exhaustive experiments, thus saving both money and time. The ANN model based on a back propagation algorithm was developed which has a two hidden layers and 4–7-9–3 neuron configuration. The performance of the ANN Prediction and experimental results was measured using the mean-squared error (MSE), Mean Absolute Error (MAE), and Root Mean-squared Error (RMSE) and the correlation Coefficients ($R^2$) values. The developed ANN model showed a good regression analysis with The $R^2$ in the range of 0.92 to 0.99. As the regression coefficients indicate the ANN approach could be considered as an alternative and practical technique to evaluate the composition of the Fischer-Tropsch products based on the operating pressure, temperature of the reaction, time and ratio of $CO/H_2$ with a high degree of accuracy.

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