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The hydrocarbon selectivity model for the Fischer-Tropsch synthesis on CO-Ni-ZrO_2 catalyst using Artificial Neural Network

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Abstract

A new hydrocarbon product distribution model for Fischer-Tropsch synthesis reaction has been studied on CO-Ni-ZrO2 catalyst in a fixed bed reactor. Artificial Neural Network technique in Fischer-Tropsch synthesis has been taken into consideration. Response surface methodology was applied to investigate the effects of operating variables (Temperature and space velocity) and optimization. The selectivity model was investigated for CH4, C2, C3, C4 and CO2. The R2 and R2 adj values indicated a good fit for all models. In a lower space velocity the amount of produced methane increases with increasing temperature. Ethylene and propylene selectivity increased with increasing temperature and was decreased with increasing space velocity. The optimal condition for the production of ethylene and propylene, was found to be in a space velocity of 7.86 (h-1) and the temperature of 530.14 K.

***Keywords*:** Artificial Neural Network, Fischer-Tropsch synthesis, Ethylene, propylene Selectivity model,

1. Introduction

Fischer-Tropsch (FT) synthesis is a process in which the synthesis gas (a mixture of hydrogen and carbon monoxide derived from natural gas and coal) is converted to a wide range of hydrocarbon products [1-5].However, FT synthesis is non-selective and produces a wide range of light gases and distillates, including olefins, paraffins and oxygenated products [6.7]. The diversity in composition of FT products reflects a complex set of surface reactions, where by CH_2 units formed by the hydrogenation of CO are "monomers" in a stepwise oligomerization process. At each stage of growth, the adsorbed hydrocarbon species may be desorbed, hydrogenated to form primary FT products, or react with another monomer to continue chain growth [8-10].

Given the much time and money spent on the tests and their effectiveness, the standard experimental design and statistical approaches can be used as an efficient tool in complex catalytic reactions selectivity modeling like FT synthesis. Statistical approaches and experimental design has been took into consideration in a lots of researches. Although Artificial Neural Network (ANN) techniques in FT synthesis is very rarely taken into consideration Adibet al, applied ANN and Genetic Algorithms for Modeling and Optimization of FT synthesis on the CO/Al_2O_3catalyst [11]. Chen and his colleagues, for the design and selection of a Co-Mo catalyst promoted with potassium to produce FT synthesis hydrocarbons used the fractional factorial design [12]. Calemma et al, investigated the effects of operating conditions on the production of FT synthesis hydrocarbons

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in the factorial design, and the good results were achieved [13]. Faryas and colleagues have studied the effect of potassium as an iron catalyst promoter and also the changes in temperature and pressure based on the average carbon number and distribution in FT synthesis using design of experiments and statistical analysis [14].Sharma and colleagues have developed artificial neural network models on Co/Al_2O_3-SiO_2 catalyst that subsequently dependence of degree of conversion and steady state concentrations of the main products of FT synthesis were modeled to operating conditions [15].Shiva and coworkers applied the combined response surface experimental design and artificial neural network to determine the macro-micro kinetic equations for the conversion of synthesis gas to light olefins over iron-cobalt catalyst [16].

In this study, by using experimental data from reference [17] a hybrid approach was used to model the FT synthesis liquid hydrocarbon products selectivity on a CO-Ni-ZrO_2catalyst. In this method, first using an ANN the behavior of the catalytic system has been simulated. Then using an experimental design in a suitable software and giving corresponding output from ANN, evaluation and development of statistical model for each of the products of the reaction was studied.

2. Modeling

2.1 Artificial Neural Network (ANN)

These networks are built with inspiration from the human brain. As the brain is a highly complex, nonlinear and parallel data processing system which is formed from structural units called neurons or neurons with strong connections, an ANN is made similar to human brain biological structure and the body neural network and Like the brain is able to learning, decision-making system and generalization. These networks do not require mathematical models and like humans learn experience and then extend this experiences [18].

2.1.1 Structure of Artificial Neural Network

Neural networks are composed of three layers including an input layer, an intermediate layer (hidden layer) and output layer. Input layer receives the input data and regard to the strength of association with the next layer, sends the input signal to the subsequent layer. The middle layer and the number of its neurons must be carefully selected to give the appropriate output. Neuron is the smallest unit of an ANN which forms the neural network functions. Outline of an ANN is shown in Fig.1.

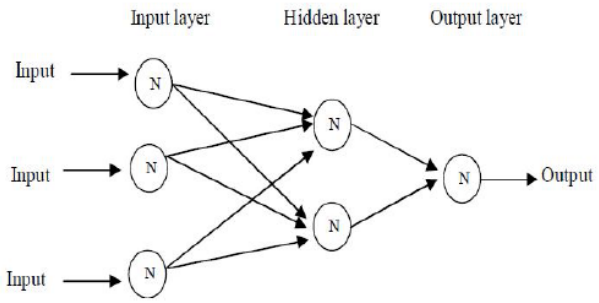

Fig.1 Artificial Neural Network structure [19]

2.1.2 Artificial Neural Network Training

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ANN should be configured in such a way that with the set of inputs, a set of desired outputs will be created. There are different methods for determining the strength of the connection. One of these ways is to determine directly using prior knowledge. Another method is neural network training using teaching patterns and letting it change the weights based on educational legislation.

According to the trial and error, the system will compare their results with the results given by experts as long as they reach a certain level of accuracy. With each experiment the weights assigned to the inputs will change until the desired results be obtained [20].

Using training algorithms and empirical data the network is trained. Various training algorithms have been developed according to the different applications of ANN. In this study LM^5 algorithm is used to train the networks. MSE function was also used for all networks.

To evaluate the performance and behavior of neural networks, the correlation coefficient (R) which is the most recognized method of regression analysis in neural networks has been used in this research. This coefficient is achieved through the correlation below [21].

$$R = 1 - \left(\frac{\sum_{i=1}^{N}(a_i - p_i)^2}{\sum_{i=1}^{N} p^2}\right)$$

Where p_i is the output of the network and a_i is the experimental value. It should be noted that how much the coefficient is closer to one, implies higher adaptation of experimental data with the predicted values associated with them.

In this study, the network consists of one hidden layer with two input neurons was used. Input variables are temperature and space velocities and the selectivity of products were considered as the outputs of the networks. Among the 21 experimental data, 15 data for training the network, 3 data for testing and 3 data were used to assess the network. Specifications of the trained network are listed in Table 1.

Table 1: Specifications of the trained network

Trained Networks	**Number of Neurons**		
	Input Layer	**Output Layer**	**Hidden Layer**
SelectivityCH_4	2	1	6
SelectivityC_2	2	1	8
SelectivityC_3	2	1	7
SelectivityC_4	2	1	8
SelectivityC_5^+	2	1	7
SelectivityCO_2	2	1	7

2.2 Experimental design and mathematical modeling

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In this study, Response surface methodology RSM method analysis were applied to investigate the effects of operating variables and optimization. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [22].Given that there are two process variables, experimental design of Box-Wilson Design (BWD) was selected to develop a statistical model. Three operations and process factors - Temperature (513-533 K) and space velocity (5-25 h^{-1}) in the atmospheric pressure - were considered as variables of the system and the selectivity of the products was determined as the process response. Analysis of variance (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The response surface methodology technique was applied to understand the interaction of various variables (temperature and space velocity) and then used to find the optimum conditions of the main variables that affect the response and also provide an equation to predict the selectivity of the products in other conditions with a high confidence of accuracy.

3. Results and Discussion

To evaluate the effect of process temperature and space velocity on the selectivity of hydrocarbon models, Box-Wilson Design (BWD) was applied consisting of 13 experiments. (5 repeat the test with a choice of 1.5 for α). The design and the whole extreme values are reported in Table 2.

Table 2: Experimental conditions and results of Box-Wilson Design (BWD) for CO-Ni-ZrO_2 catalyst.

Test	Temp. (K)	GHSV (h^{-1})	Selectivity					
			CH_4	C_2	C_3	C_4	C_5^+	CO_2
1	513	15	4.1319	1.2778	3.6525	7.132	12.2157	76.4287
2	530.14	7.86	14.0109	3.6055	10.3276	1.5186	21.6624	34.899
3	523	15	5.6511	1.7378	3.9682	8.4857	12.0885	72.6228
4	523	15	5.6511	1.7378	3.9682	8.4857	12.0885	72.6228
5	523	15	5.6511	1.7378	3.9682	8.4857	12.0885	72.6228
6	523	25	0.8961	0.32	0.8509	28.0613	1.5629	93.9566
7	515.86	22.14	1.8655	0.5644	0.9591	1.0961	3.6215	33.9569
8	533	15	7.3307	2.2039	5.2547	8.1257	10.0846	75.6544
9	530.14	22.14	2.1486	0.3726	1.9949	20.2615	2.5966	91.9578
10	523	5	11.7922	3.4091	10.6881	17.0991	28.336	38.854
11	523	15	5.6511	1.7378	3.9682	8.4857	12.0885	72.6228
12	523	15	5.6511	1.7378	3.9682	8.4857	12.0885	72.6228
13	515.86	7.86	6.7164	1.4188	9.4945	11.5323	13.4234	96.2074

WHSV: Weight hourly Space Velocity

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Three replicates of the central points were performed along the design space in order to estimate the experimental error and checking of the analysis repeatability. The experimental plan is also shown in Table 1. It can be seen that the responses of this design are selectivity of CH_4 (CH_4 sel), C_2 (C_2 sel), C_3 (C_3 sel), C_4 (C_4 sel), C_5^+ (C_5^+ sel) and CO_2 (CO_2 sel). The maximum C_2 and C_3 selectivity is desired.

3.1. ANOVA analysis

To select a model that meets the needs of this research, it is necessary to carefully evaluate the data and analyze them. In this regard, many equations (such as cubic, Quadratic, 2FI) have been investigated. Effective terms are identified and applied in the final selectivity equations. The terms that appear in the equation and causes the disorder identified as the meaningless terms and removed from the equation. Finally, with the conducted investigation the desired selectivity model can be achieved. The results of ANOVA (analysis of variance) for product selectivity models can be observed in Table 3.

Table 3: ANOVA results of product selectivity models

Selectivity Model	Sum of Squares	R^2	R^2_{adj}	P-Value
CH_4	161.79	0.9985	0.9974	<0.0001
C_2	12.02	1	1	<0.0001
C_3	127.76	0.9796	0.9727	<0.0001
C_4	654.62	1	1	<0.0001
C_5^+	633.23	1	1	<0.0001
CO_2	5349.94	1	1	<0.0001

As indicated in Table 2, models are statistically significant and acceptable because of the optimum amount of P-Value. The R^2 and R^2adj values which are significant for all models also indicate a good fit of the data by the model. Table 4 shows the final equations for the selectivity of these products.

Table 4: Final equations for products selectivity

Selectivity	Model
CH_4	$-580.12505 + 1.13955A + 49.55418B - 0.096258AB - 1.0717B^2 + 0.000021AB^2$
C_2	$-8490.64399 + 32.16077A + 1063.14535B - 4.04082AB - 0.030436A^2 - 33.20299B^2 + 0.003838A^2B + 0.12652AB^2 - 0.0001205A^2B^2$
C_3	$-21.17559 + 0.072687A - 1.13942B + 0.019927B^2$
C_4	$-138071 + 529.02A + 19548.69954B - 74.75395AB + 0.50662A^2 - 700.09207B^2 + 0.071451A^2B + 2.67245AB^2 - 0.00255A^2B^2$
C_5^+	$-94912.25339 + 360.94307A + 10540.486B - 40.05968A - 0.34301A^2 - 291.93634B^2 + 0.038053A^2B + 1.10946AB^2 - 0.0011A^2B^2$

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CO_2	$+86255.16655 - 320.63376A + 5806.4202B - 22.81653AB + 0.29779A^2 - 728.477B^2 + 0.022415A^2B + 2.78704AB^2 - 0.002666A^2B^2$

A: Temperature and B: Space velocity

3.2. Optimization of reaction conditions

To investigate the optimal conditions for the FT synthesis hydrocarbon products selectivity, three-dimensional response surface plot is used. Three-dimensional response surface plot, allowing the ratio of products selectivity changes to the process variables to be well defined. Fig.2indicates the dependence ofCH_4 selectivity towards temperature and space velocity.

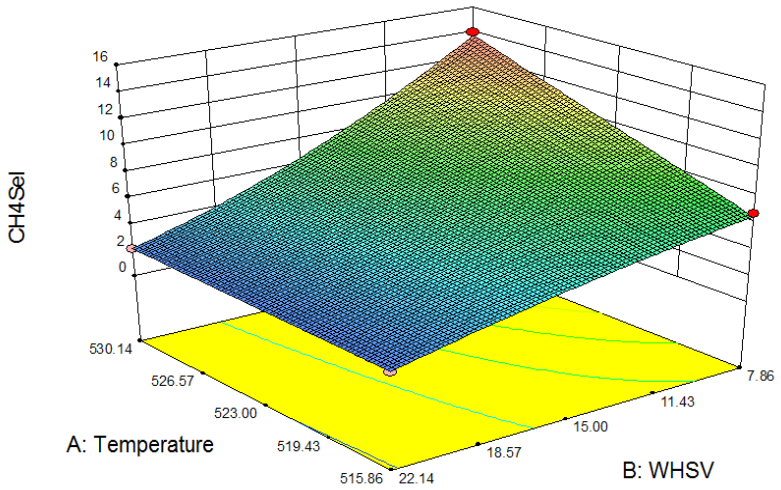

Fig. 2 CH_4 selectivity towards temperature and space velocity in atmospheric pressure.

Fig.2 shows that the maximum amount of methane is at high temperatures and low space velocity and it is because of the thermal decomposition of heavier products. The amount of methane will significantly reduce when the space velocity is increased. In Fig. 2, it can be clearly seen that with the increase of space velocity, temperature has little influence on the selectivity of CH_4, because the space velocity increases, the effect of temperature is very light and is considered negligible. However, in low space velocity methane selectivity increases with increase in temperature and reaches its highest value.

As can be seen in Fig.3, the trend of produced ethylene changes is similar to the changes of methane respect to the temperature and space velocity and the maximum amount of ethylene is produced at low space velocities and high temperatures. The main reasons for this subject may be thermal failure of the heavy products caused by increase in temperature.

Fig.3 also shows that at high temperatures, with increasing space velocity, ethylene selectivity decreases. However, at lower temperatures, increasing the amount of space velocity to about 31/13 (h^{-1}) has a negligible effect on the amount of ethylene selectivity and by increasing the temperature, higher selectivity will be achieved by increasing the space velocity.

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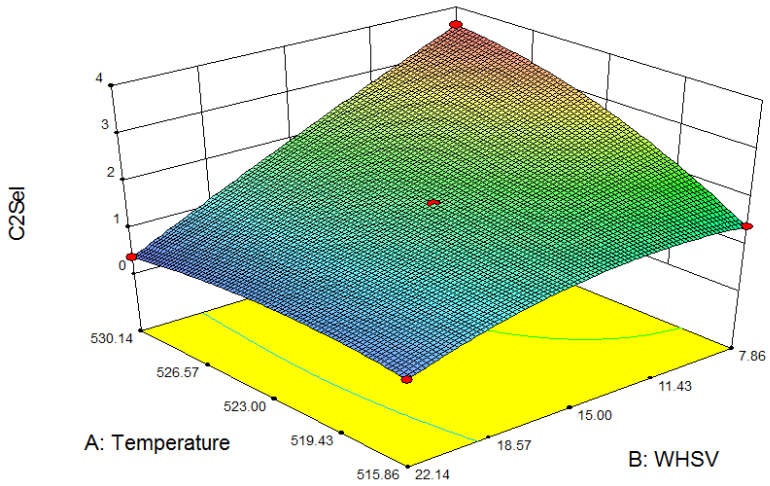

Fig. 3 C_2 selectivity towards temperature and space velocity in atmospheric pressure.

Three-dimensional diagram of C_3 selectivity changes with respect to two variables, temperature and space velocities are shown in Fig. 4. As is evident in all parts of the graph, increasing the temperature enhances the selectivity of propylene and increase in space velocity reduces the selectivity. The reason of propylene increase can be interpreted by the fact that by increasing the temperature the inclination for thermal failure of heavier hydrocarbons enhances which lead to the formation of light products. Also the space velocity has the greatest effect on propylene selectivity.

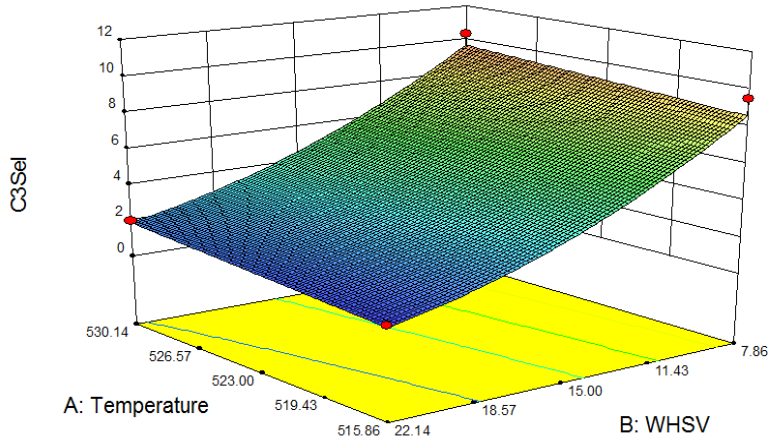

Fig. 4 C_3 selectivity towards temperature and space velocity in atmospheric pressure.

Fig. 5 illustrates the C_4 selectivity towards temperature and space velocity and the influence of temperature of the selectivity can be divided into two stages. First, increasing the selectivity of C_4 respect to boosting the temperature and then C_4 selectivity diminishing stage. At low space velocity, by increase in temperature the first stage is in the range of less than second stage. However, the increase in the space velocity increases the range of first stage while the second area is reduced. The reason for this is that in the beginning of the temperature increasing, the decomposition of heavy hydrocarbons increases the amount of C_4 and followed by a marked rise in temperature, the probability of C_4 decomposition is increased and its selectivity is reduced. It can be also seen

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that the maximum amount of C_4 production occurs at the temperature of 527 K and The space velocity of 14/22 (h^{-1}).

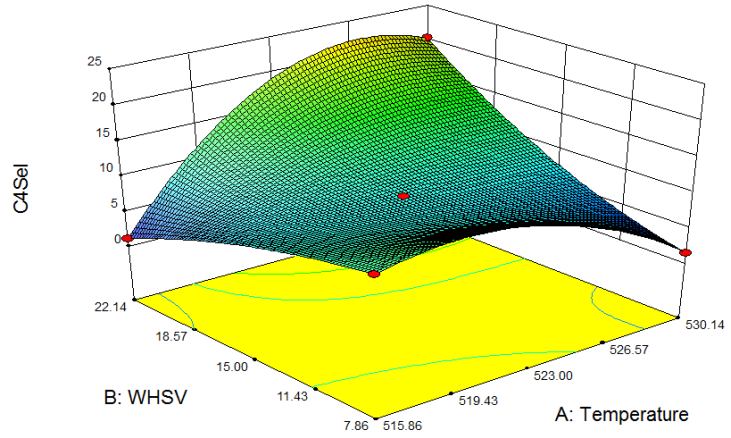

Fig. 5 C_4 selectivity towards temperature and space velocity in atmospheric pressure.

Fig.6 shows theC_5^+ selectivity changes respect to the temperature and space velocity. It can be observed that at low space velocity with increasing temperature, the C_5^+ selectivity increases and reaches its maximum value at a temperature of 525 K. The higher the temperature, the higher is the desire to increase its selectivity is reduce the possibility of thermal decomposition. The higher increase in temperature enhances the possibility of thermal decomposition and lead to the decrease in selectivity. It can also be inferred from Figure 6 that at space velocities higher than 15 (h^{-1}) temperature has a very little effect on C_5^+selectivity and remains almost constant.

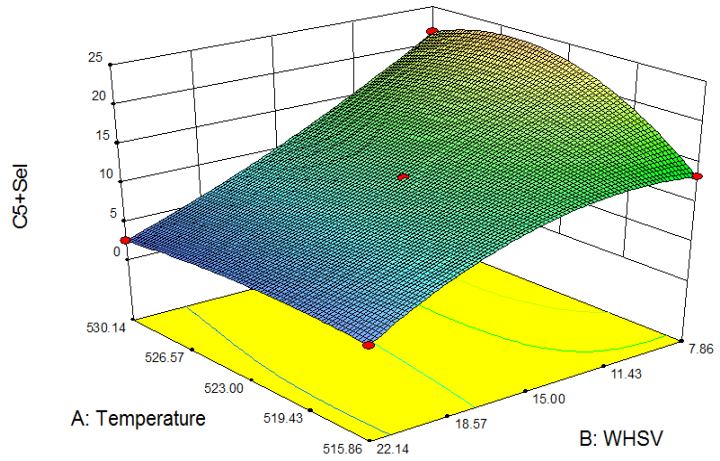

Fig. 6 C_5^+ selectivity towards temperature and space velocity in atmospheric pressure.

Fig.7 shows the response curve of CO_2 selectivity with respect to temperature and space velocities. It can be inferred that at low space velocity with increasing temperature, CO_2 selectivity has been decreased and this trend has been changed so that completely reversed in high space velocity. Fig.7 also shows that the highest amount of CO_2production occurs at a temperature of approximately 527 K and a high space velocity.

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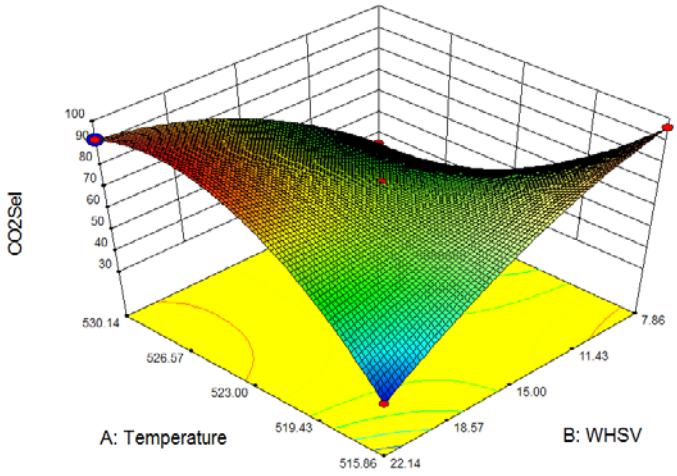

Fig. 7 CO_2 selectivity towards temperature and space velocity in atmospheric pressure.

4. Conclusions

In this study selectivity model of the Fisher - Tropsch synthesis reaction products on CO-Ni-ZrO_2catalyst in a fixed bed reactor was investigated. The results of selectivity model indicate that in a lower space velocity 86/7 (h^{-1}) the amount of produced methane increases with increasing temperature. However, its value decreases with increasing space velocity. Ethylene and propylene selectivity increased with increasing temperature and was decreased with increasing space velocity. Therefore, the optimal condition for the production of ethylene and propylene, was found to be in a space velocity of 86/7 (h^{-1}) and the temperature of 14/530 K.CO_2 selectivity was also observed to be proportional to the temperature at higher space velocity while at lower space velocity there was an inverse relation with temperature.

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