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Determination of the Product Selectivity Model from the Fischer Tropsch Synthesis in a Fixed Bed Reactor

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The Fischer-Tropsch synthesis is a catalytic process that can produce a fuel similar to fossil fuels using primary sources such as agricultural waste and carbon sources that can convert into synthesis gas by superheated steam. All fuel derivatives can be supplied through the Fischer-Tropsch reaction. The synthesis produces a variety of hydrocarbons *via* parallel and sequential reactions. However, achieving a particular product requires different operating conditions. It is worth noting that the terms of time and cost will increase by any change in operating conditions even on the laboratory scale, so it will not be cost-effective. For this purpose, in this study, adopting the method of modeling was investigated for the manufacturing the products of the Fischer-Tropsch process on Cobalt-based catalyst under the following operating conditions: TOS = 20-150 h, T = 190-225 °C, P = 2-6 MPa and H_2/CO ratio of 1-5. Then, the models of selectivity and the optimal conditions for the reaction products were determined.

Keywords: Cobalt based catalyst, Fischer Tropsch synthesis, Fixed bed reactor, Selectivity of products, Optimal conditions

INTRODUCTION

The production of liquid fuel resulting from the synthesis of natural gas through the Fischer-Tropsch (FT) process is one of the most important operations in the industry due to easy transportation [1-3]. In addition, the fuel manufactured from FT is clean, aromatic-free and environmentally friendly [4-7]. Catalysts play a very important role in the FT synthesis. So, it is very important to select the suitable catalyst. Amongst the catalysts used in the FT synthesis (nickel, ruthenium, iron, and cobalt), cobalt metal is generally considered to be the most suitable catalyst to convert natural gas to liquid fuel (GTL) [8,9]. Cobalt characteristics such as high activity, great economic value, the choice of a wide range of products at low temperatures and high resistance against deactivation have made it useful for the FT synthesis [10]. In order to diminish catalyst deactivation costs (sintering, accumulation, *etc.*), as well as the increase in selectivity of favorable products, different supports and promoters were applied [11]. Traditionally, in this synthesis, supports such as TiO_2, Al_2O_3, and SiO_2 are utilized for the cobalt catalyst [12,13]. By identifying the presence of cobalt on these supports, it was found that Co/SiO_2 catalyst surface area is larger than Co/TiO_2 and Co/Al_2O_3. In addition, the reduction of the cobalt catalyst is better performed on the silica base, therefore the CO conversion rate on the Co/SiO_2 catalyst is the largest [14]. Chuong Xing examined the various methods of preparing the Co/SiO_2 catalyst [15]. Wenping Ma analyzed the effect of catalyst size on reaction kinetic on the Co/SiO_2 catalyst, and Mohsen Mansouri also investigated the catalyst kinetics in the presence of Cerium [16,17]. Ya-Ping Li illustrated the effect of zeolite on silica support [18]. C. Pirola studied the

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effect of Pt and Ru promoters on Co/SiO_2 catalyst [19]. Subsequently, A.P. Savost Yanov also adopted alumina as a promoter for the Co/SiO_2 catalyst. He stated that the extraordinary percentage of CO conversion and the highest production of heavy products would be obtained in the presence of 1% Al_2O_3. The use of 1% weight of alumina exceedingly increases the surface area of the cobalt catalyst on the silica support [20]. Lastly, in another work, Yanov reported the effect of reaction conditions on the performance of the $CO-Al_2O_3/SiO_2$ catalyst [21]. All studies were qualitatively performed on the silica-support cobalt catalyst in FT synthesis. No comprehensive and quantitative model have been so far presented to examine the catalyst performance. It should have also been considered that the FT synthesis is very sensitive to the conditions applied during the process. Determining the suitable operating conditions is also used to attain the optimum amount of excellent output in reactors, so that after reacting in the desired conditions, reactors can be designed based on the required temperature and pressure. To this end, several tests were conducted on catalysts to determine the desired conditions. In the FT synthesis, reduction of the catalyst in any previous shift in the operating conditions is essential, so performing the experiments are costly and time-consuming. The creation of a model that is proportional to laboratory data allows prediction of the catalyst performance in different conditions. The main purpose of this study was to determine the selectivity models for these four products of CO_2, CH_4, C_2-C_4 and C_{5+} based on time on stream (TOS), temperature, pressure and H_2/CO ratio factors on the $Co-Al_2O_3/SiO_2$ catalyst, by utilizing the data presented in Reference [21]. The proposed models determine the best possible conditions for manufacturing each product.

CATALYST PREPARATION

The catalyst preparation method is available in Reference [21]. To obtain the $Co-Al_2O_3/SiO_2$ catalyst, the $NO_3.6H_2O$ cobalt was mixed with the alumina solution, then the solution was poured onto a silica support previously dried at 100 °C. Drying and calcination were conducted in temperatures of 100-120 °C and 300 °C, respectively, for 4 h. The reaction was carried out in a fixed bed reactor made of stainless steel. The catalyst was reduced with hydrogen gas at 400 °C and GHSV = 1000 h^{-1} for 4 h. Then, to evaluate the catalyst performance, it was evaluated under different operating conditions as follows: temperature of 190-225 °C, pressure of 2 and 6 MPa, H_2/CO ratio of 1-5, TOS of 20 to 150 h.

Method

As mentioned, the use of mathematical models to predict the selectivity of favorite products in each process saves time and costs of experiment. One of the mathematical models employed is response surface methodology (RSM). RSM is a collection of mathematical relations based on equation (1), which creates a logical relation between input variables (x) and responses (y). In fact, RSM links laboratory data from experiments to empirical models using mathematical relationships. For doing so, linear and quadratic equations are used to describe the system and the best laboratory conditions required. Presently, this method is employed for optimization and modeling in various areas. Marcos Almeida Bezerr [22] also described this method as a way to optimize chemistry. In this study, the steps to determine the selectivity models of products from the FT synthesis are represented schematically in Fig. 1;

$$y = \alpha_0 + \sum_{i=1}^{l} \alpha_i x_i + \sum_{i=1}^{l} \alpha_{ii} x_i^2 + \sum_{i}^{l} \sum_{j}^{k} \alpha_{ij} x_i x_j + \varepsilon \quad (1)$$

1) The determination of dependent variables (in this study, the products selectivity) and independent variables (in this study, time of stream, temperature, pressure and H_2/CO ratio).

2) Employing Eq. (1) to create a logical relationship between dependent and independent variables.

3) Evaluation of the models. It may not be possible to obtain satisfactory equations after evaluating experimental data with the generated models. The reliable method for evaluating the mathematical model is using ANOVA. For doing so, the F-value, P-value, R^2 and R^2_{adj} parameters were used. F-value is the ratio of variables that can be defined through the model to variables not reported by the model and employed to determine the P-value. The P-value helps determine the significance of the model obtained statistically in the analysis of variance. To use this parameter, a- value is needed to be defined for the model to

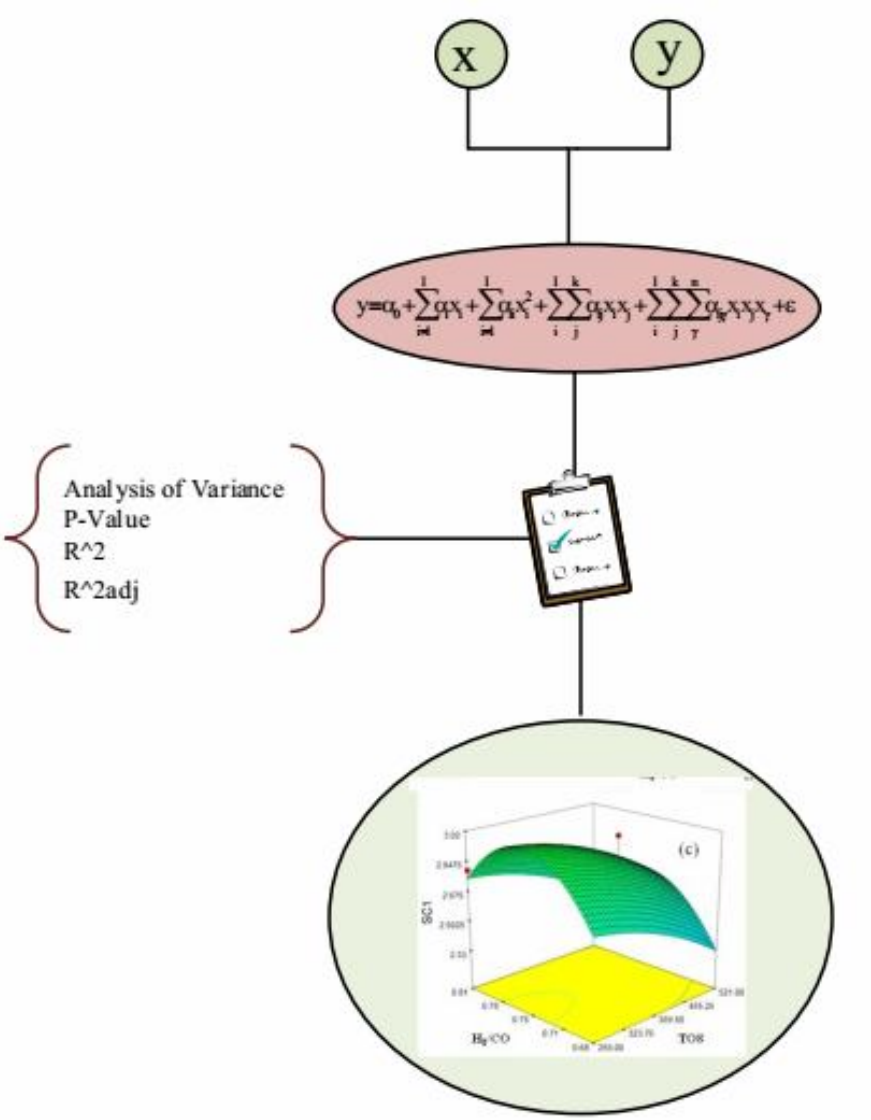

Fig. 1. Schematic of the response surface methodology (RSM) steps.

specify thedistance between the pivots of the center of the design in the central composite design, which is usually equal to 0.05. If the P-value is less than the a-value, it indicates that the parameter is significant from the statistical point of view. R^2 represents the unstable quantity of the obtained model that can be more reliable (closer to one) with increasing laboratory data (Eq. (2)). Indeed, the dependence of R^2 on the number of data has created another parameter (R^2_{adj}) to be described for the dispersion of the values calculated by the model. R^2_{adj} is the adjusted equation of R^2, and when its value is closer to 1, the model will be more consistent with experimental data (Eq. (3)).

$$R^2 = 1 - \frac{SS_{error}}{SS_{total}} = 1 - \frac{\Sigma\left(y_i - \hat{y}_i\right)^2}{\Sigma\left(y_i - \bar{y}\right)^2} \quad (2)$$

$$R^2_{adj} = 1 - \frac{MS_{error}}{MS_{total}} = 1 - \left(\frac{\Sigma\left(y_i - \hat{y}_i\right)^2}{\Sigma\left(y_i - \bar{y}\right)^2}\right)\left(\frac{n-1}{n-p-1}\right) \quad (3)$$

Table 1. Limit of the Independent Variable of the Process8

Independent variable	Symbols	Confine	
		Min	Max
TOS (h)	X1	20	150
T (°C)	X2	190	225
P (MPa)	X3	2	6
H_2/CO	X4	1	5

Table 2. Dependent Variables, and Independent Variable Coefficients of Selectivity Equations

	Dependent variables			
Independent variable coefficients	CO_2 (Y1)	CH_4 (Y2)	C_2-C_4 (Y3)	C_{5+} (Y4)
a0	58.4	169	170	-287
a1	-0.143	2.65	0.41	-2.92
a2	-0.579	-2.51	-2.14	5.14
a3	0.43	15.25	31.8	-47.7
a4	-0.435	13.15	4.91	-17.71
a5 × 10^{-3}	0.059	-1.3	0.22	1.21
a6 × 10^{-3}	1.47	7.63	6.34	-15.3
a8	0.06	-0.883	-0.449	1.27
a9 × 10^{-3}	0.58	-10.87	-2.09	12.4
a10 × 10^{-3}	4.5	-48.5	19.6	24.7
a12 × 10^{-2}	-0.27	-6.39	-15.22	21.96

4) Determination of optimal conditions. To do so, three-dimensional graphs are drawn in the response surface methodology, which can be seen in Figs. 2-8.

RESULTS AND DISCUSSION

To predict the catalyst behavior, it should be evaluated under different operating conditions. Using different mathematical models leads to less cost and less time to fulfill different conditions. In this study, the mathematical equations were obtained by RSM method for selectivity of the products that obtained from the Fischer-Tropsch synthesis on the Co-Al_2O_3/SiO_2 catalyst. The independent variables and their operating range are shown in Table 1. The general selectivity equation for all products was in the form of Eq. (4). The coefficient of each independent variable are also shown in Table 2. Table 3 shows the analysis of variance (ANOVA) for the correctness and

Table 3. ANOVA Analysis for CO_2, CH_4, C_2-C_4, C_{5+}

	Y1		Y2		Y3		Y4	
	F-value	P-value	F-value	P-value	F-value	P-value	F-value	P-value
Model	9.90	0.0055	51.89	<0.0001	8.64	0.0079	16.91	0.0013
X1	3.30	0.1194	1.13	0.3284	2.95	0.1366	0.42	0.5396
X2	3.55	0.1084	3.70	0.1028	0.63	0.4571	1.30	0.2971
X3	2.06	0.2016	2.38	0.1741	0.97	0.3632	1.06E-005	0.9975
X4	0.89	0.3812	206.72	<0.0001	8.59	0.0263	57.72	0.0003
X1X2	0.58	0.4754	3.39	0.1151	0.068	0.8031	0.77	0.4133
X1X3	1.90	0.2177	3.78	0.1000	0.33	0.5858	0.17	0.6945
X1X4	-	-	-	-	-	-	-	-
X2X3	0.32	0.5926	2.75	0.1482	8.43	0.0272	5.66	0.0549
X2X4	-	-	-	-	-	-	-	-
X3X4	-	-	-	-	-	-	-	-
$X1^2$	1.00	0.3553	9.37	0.0222	1.4E-003	0.9711	1.42	0.2780
$X2^2$	3.01	0.1335	2.37	0.1746	0.88	0.3840	1.65	0.2467
$X3^2$	-	-	-	-	-	-	-	-
$X4^2$	0.80	0.4042	3.51	0.1102	0.51	0.5006	1.32	0.2948
	$R^2 = 94.29\%$		$R^2 = 98.86\%$		$R^2 = 93.50\%$		$R^2 = 96.57\%$	
	$R^2_{adj} = 84.77\%$		$R^2_{adj} = 96.95\%$		$R^2_{adj} = 82.67\%$		$R^2_{adj} = 90.86\%$	

evaluation of the models obtained. In all of the models obtained, the values of R^2 and R^2_{adj} are close to 1, so the P-values for all models are less than 0.05, indicating that the models are statistically significant.

$$Y_{i,1\le i\le 5} = a0 + a_1X1 + a_2X2 + a_3X3 + a_4X4 + a_5X1^2 + a_6X2^2 + a_7X3^2 + a_8X4^2 + a_9X1X2 + a_{10}X1X3 + a_{11}X1X4 + a_{12}X2X3 + a_{13}X2X4 + a_{14}X3X4 \quad (4)$$

Selectivity of CO_2

It can be seen that the CO_2 selectivity model is statistically significant according to the F-value (9.9). In this model, temperature has the most important effect compared to the other factors. The carbon dioxide selectivity will increase with increase in temperature, pressure and time on stream. By increasing the H_2/CO ratio, the CO_2 selectivity will first decrease and then slightly increase. Figure 2 shows the interaction between the three X_1X_2, X_1X_3 and X_2X_3 factors, where X_1X_3 has the highest impact on the model. Figure 3 shows the trend of the impact of TOS, T, P and H_2/CO factors on CO2 selectivity.

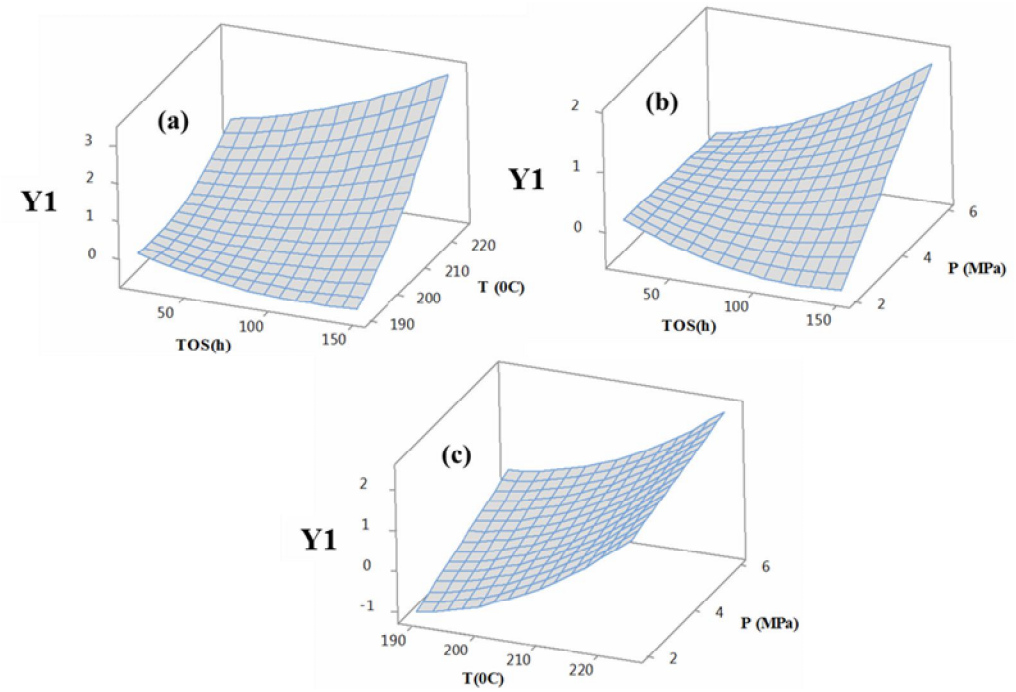

Fig. 2. Effect of the interaction of TOS, T and P on CO_2 selectivity model (Y1) in (a) P = 4 MPa, H_2/CO = 3, (b) T = 205 °C, H_2/CO = 3, (c) TOS = 85 h, H_2/CO = 3.

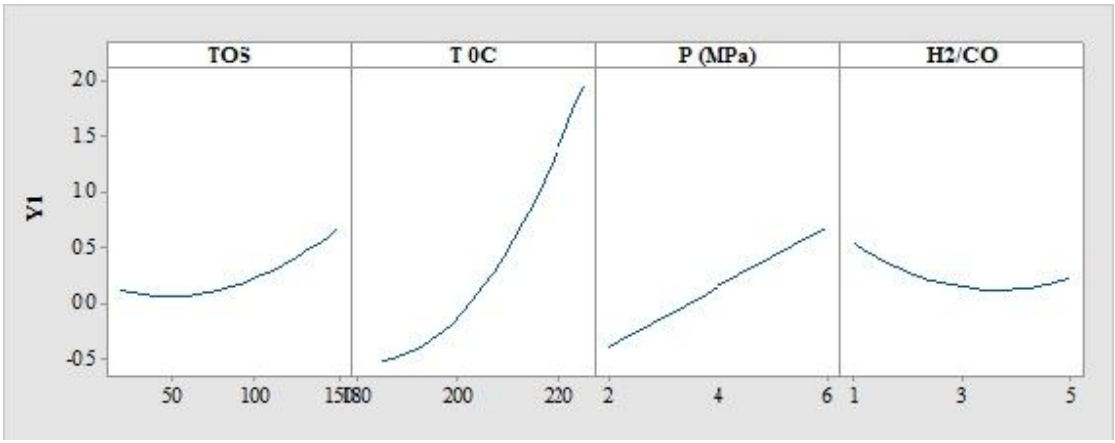

Fig. 3. The effect of TOS, T, P and H_2/CO ratio parameters on CO_2 selectivity model (Y1).

Selectivity of CH_4

The model obtained for methane is consistent with experimental data. The F-value is 51.89 for this model, indicating that the obtained model is statistically significant. Figure 4 shows the trend of TOS, T, P and H_2/CO factors on methane selectivity. The selectivity of methane decreases with increase in temperature and pressure, but the selectivity of CH_4 will increase with increase in the H_2/CO ratio. By increasing the time on stream, the methane selectivity increases and then decreases. Subsequently, the effect of

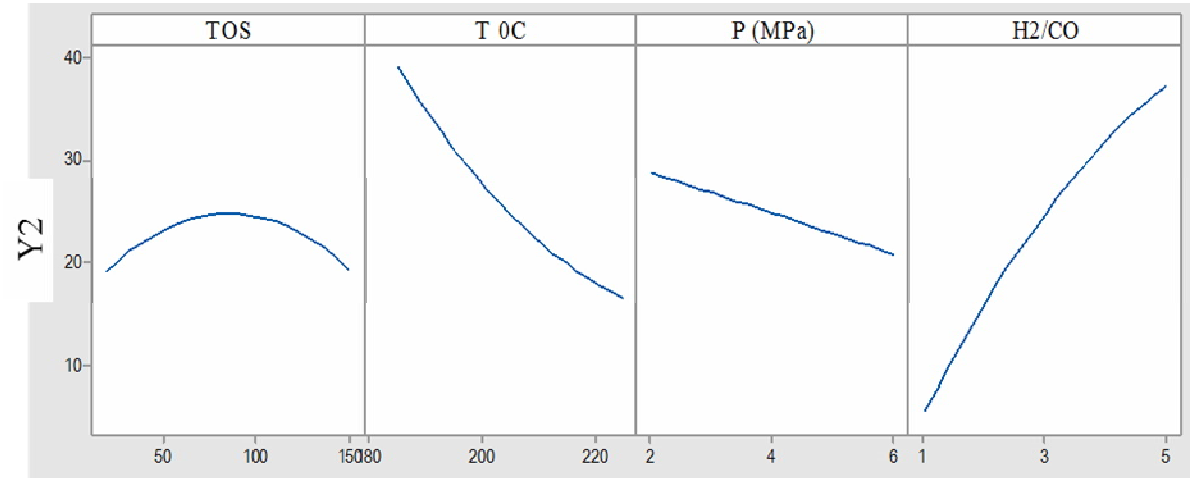

Fig. 4. The effect of TOS, T, P and H_2/CO ratio parameters on CH_4 selectivity model (Y2).

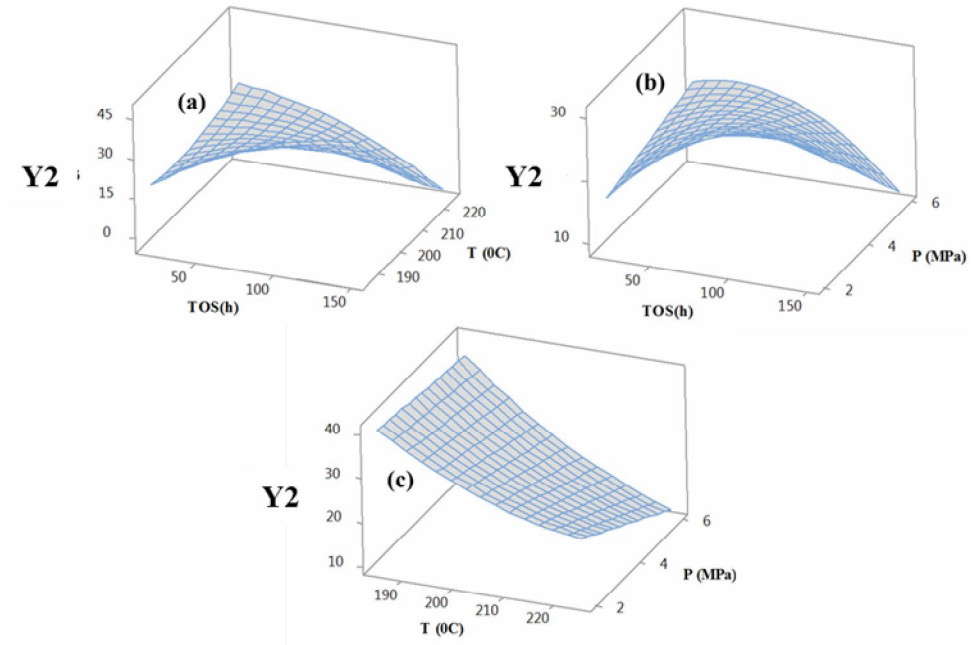

Fig. 5. Effect of the interaction of TOS, T and P on CH_4 selectivity model (Y2) in (a) P = 4 MPa, H_2/CO = 3, (b) T = 205 °C, H_2/CO = 3, and (c) TOS = 85 h, H_2/CO = 3.

interaction between the three factors of X_1X_2, X_1X_3 and X_2X_3 on the methane selectivity is shown in Fig. 5.

Selectivity of C_2-C_4

The effect of each parameter on the selectivity of light hydrocarbons is shown in Fig. 6. By increasing the time on stream, the pressure and the H_2/CO ratio, the selectivity of the light products will increase, and decrease of Y3 will occur by increasing the reaction temperature. The three X_1X_2, X_1X_3 and X_2X_3 factors affecting the C_2-C_4

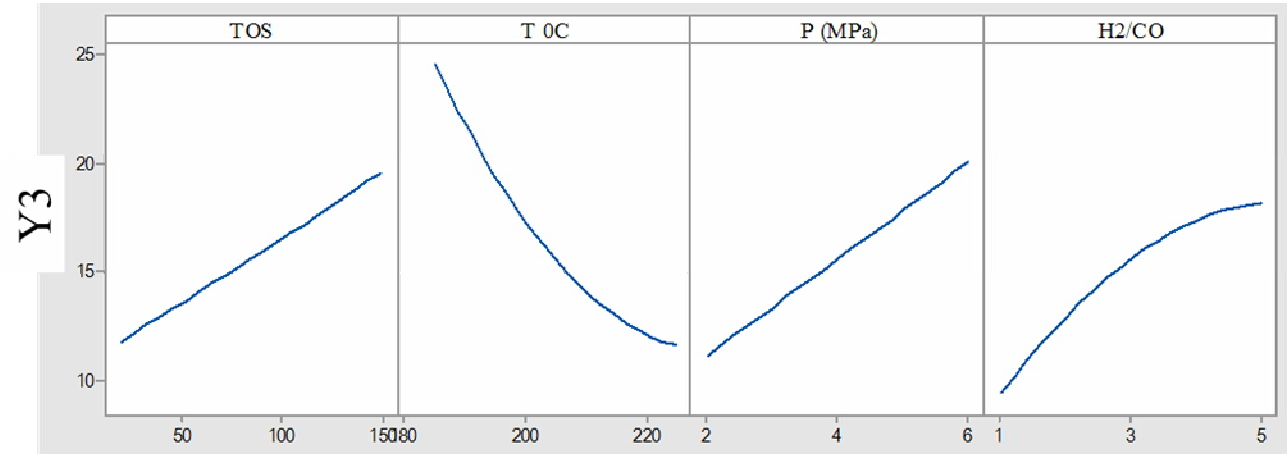

Fig. 6. The effect of TOS, T, P and H_2/CO ratio parameters on C_2-C_4 selectivity model (Y3).

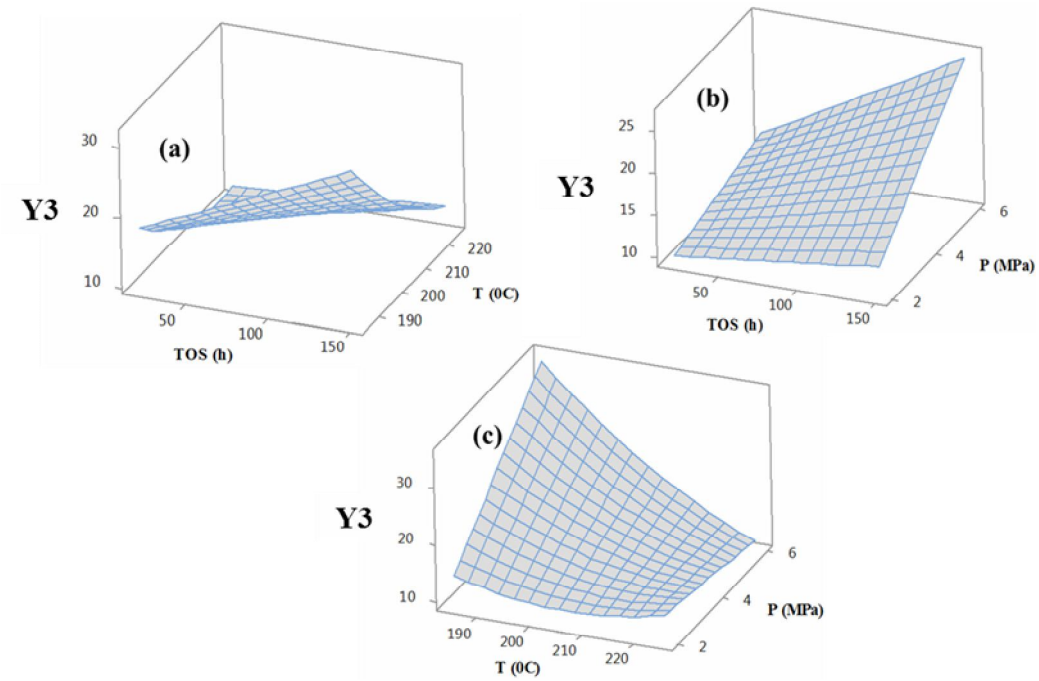

Fig. 7. Effect of the interaction of TOS, T and P on C_2-C_4 selectivity model (Y3) in (a) P = 4 MPa, H_2/CO = 3, (b) T = 205 °C, H_2/CO = 3, and (c) TOS = 85 h, H_2/CO = 3.

selectivity model and their effects are seen in Fig. 7.

Selectivity of C_{5+}

Figure 8 indicates the change of the time on stream, temperature, pressure and H_2/CO ratio factors. The impact of the pressure on the C_{5+} selectivity is very low. The C_{5+} selectivity will decrease with increase in the H_2/CO ratio. The effect of the reaction temperature is ascending on the selectivity of heavy hydrocarbons. As the time on stream increases, the C_{5+} selectivity decreases and then increases.

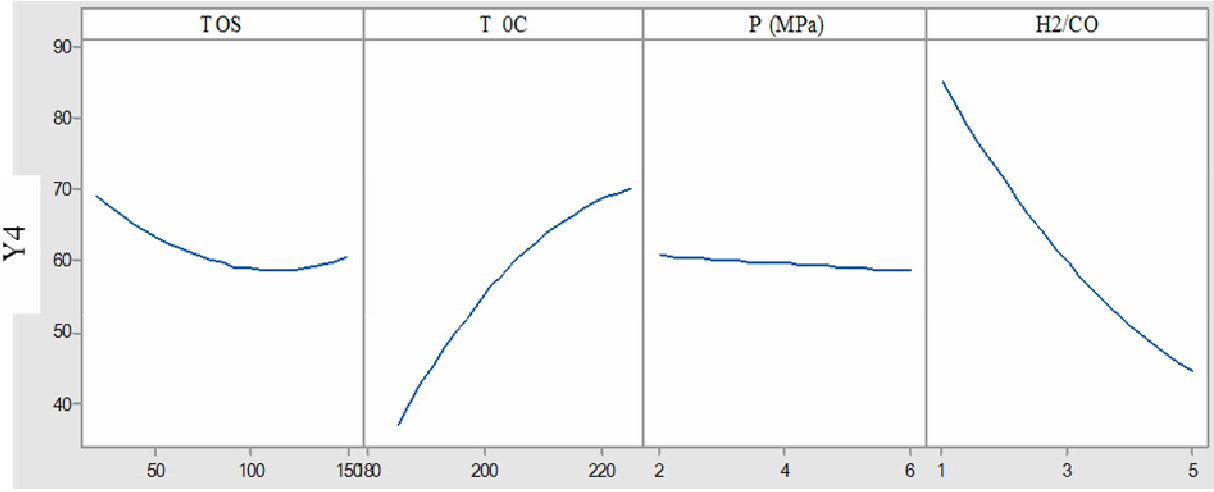

Fig. 8. The effect of TOS, T, P and H_2/CO ratio parameters on C_{5+} selectivity model (Y4).

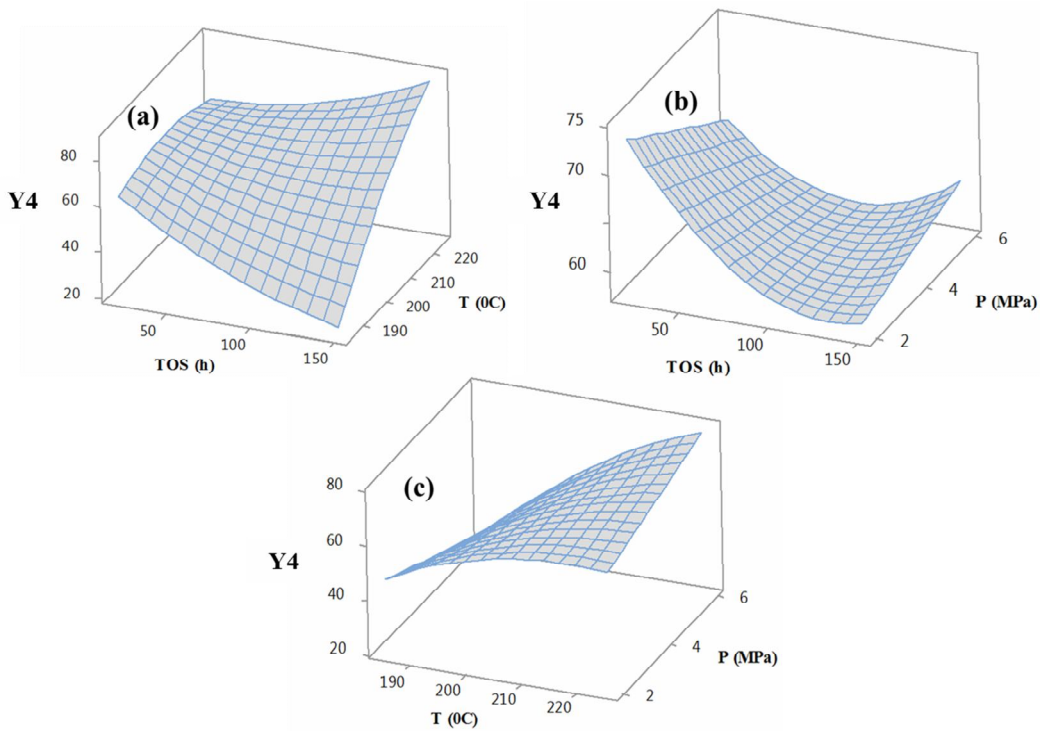

Fig. 9. Effect of the interaction of TOS, T and P on C_{5+} selectivity model (Y4) in (a) P = 4 MPa, H_2/CO = 3, (b) T =205 °C, H_2/CO = 3, and (c) TOS = 85 h, H_2/CO = 3.

Subsequently, Fig. 9 shows the effect of the interaction between X_1, X_2 and X_3 factors on the selectivity of heavy products.

Optimization

The purpose of optimization is to determine the reaction conditions for maximize the favorable product and

Table 4. Determining the Optimal Conditions for the FT Process Using RSM

			TOS (h)	T (°C)	P (MPa)	H_2/CO
One objective	CO_2	min	150	190	2	3.63
	CH_4	min	150	225	6	1
	C_2-C_4	max	150	185	6	5
	C_{5+}	min	150	185	6	5
Multi objective	C_2-C_4	max	150	190	4.7	1.1

reduce the side costs. One of the most powerful usages of RSM is to attain optimal conditions. In fact, the RSM method achieves the optimal conditions by establishing a logical relationship between input and output factors. One of the main goals of this study is to provide optimal reaction conditions in FT synthesis. This goal was achieved by using the obtained models. One-objective and multi-objective functions were performed for optimization of models. The optimization of each output was obtained by ignoring other outputs. The optimization of the whole process was calculated in order to maximize the production of C_2-C_4 hydrocarbons as well as the other products (Table 4).

CONCLUSIONS

Conversion of renewable energy sources is an activity that has attracted the attention of many scientists and investors around the world. The Fischer Tropsch synthesis is a catalytic process that can convert all carbon sources into fuel. Manufacturing diverse products in different operating conditions in FT synthesis has led scientists to test several catalysts under various operating conditions. However, the adoption of different operating conditions requires a lot of time and money. We can use the RSM methodology to minimize the number of experiments. Using a few laboratory data, a model for the product selectivity is computed, so there is no need to perform several tests in different operating conditions. In this study, the selectivity models were obtained for the Co-Al_2O_3/SiO_2 catalyst under operating conditions: TOS = 20-150 h, T = 190-225 °C, H_2/CO = 1-5 ratio at 2 and 6 MPa pressures, for these four products of CO_2, CH_4, C_2-C_4 and C_{5+}. By analyzing the obtained models, it was concluded that temperature has the greatest impact on product selectivity. In addition, the interaction occurred only between T and TOS, P and TOS, T and P. Consequently, the optimization of operating condition was applied to the models, the best-operating conditions were achieved in order to maximize the selectivity of C_2-C_4 and minimize the selectivity of other products which are defined by TOS = 150 h, T = 190 °C, P = 4.7 MPa, and H_2/CO = 1.1.

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