AN OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY STRATEGY FOR FISCHER-TROPSCH SYNTHESIS USING CO/AL_2O_3 CATALYST IN A MICROSTRUCTURED REACTOR

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Abstract - In this study, the process of Fischer-Tropsch (FT) synthesis using Co/Al_2O_3 catalyst in a microstructured reactor was optimized by using response surface methodology (RSM) for minimizing methane selectivity and maximizing the alkene (C2-C4) selectivity. Different optimization strategies were employed to find out the best combination of process conditions with optimal product selectivity with best optimal conditions (T=491K, P=2.0 MPa, SR=2.05 with GHSV setting at 3000 h^{-1}) were achieved.

Keywords - Fischer-Tropsch synthesis; cobalt catalyst, Process optimization;

I. INTRODUCTION

Although Fischer-Tropsch (FT) synthesis was discovered over 90 years ago, it still remains one of the most interesting topics in energy conversion and fuel processing field due to its flexibility and advantage of converting natural gas, biomass, and coal into synthetic fuel and bulk chemicals based upon dynamic supply-demand market[1-6]. The product produced from FT synthesis is complex[7]. Therefore, its selectivity such asmethane (C1 selectivity) and small olefin (C2-C4 alkene selectivity) are often the interests of optimization for FT synthesis[8, 9]. The response surface methodology (RSM) is a set of mathematical and statistical techniques seeking to optimize an objective function that is affected by multiple factors using design of experiments (DoE) methods and statistical analysis[10]. Optimization by response surface methodology (RSM) for minimizing C1 selectivity and maximizing alkene selectivity using Co/Al_2O_3 catalyst for FT synthesis, to the best of our knowledge, has also seldom been investigated before, this initiates our work for this paper.

II. EXPERIMENTAL SECTION

The detailed configuration of microchannel reactor, approaches for liquid product collections and catalyst loading together with operational parameters could be found in our previous reports[11]. The CO conversion and hydrocarbonselectivitywere calculated as the followings:

$$X_{CO}\% = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100 \quad (1)$$

$$Selectiviy\% = \sum_{i=2}^{4} \frac{n_i S_{A_i}}{(F_{CO,in} - F_{CO,out}) - F_{CO_2,out}} \times 100 \quad (2)$$

where S_{A_i} refers to the molar flow rate of hydrocarbon (mol.h^{-1}), $F_{CO_2,out}$ CO_2 molar flow rate from outlet (mol.h^{-1}), X_{CO} CO conversion (%), $F_{CO,in}$ CO molar flow rate from inlet(mol.h^{-1}), and $F_{CO,out}$ CO molar flow rate from outlet (mol.h^{-1}).Three independent variables was investigated to study the response pattern and to determine the optimal combination of FT temperature (°C),total pressure (MPa), andthe syngas H_2/CO ratio (-) during FT synthesis in a microstructed reactor. The range and levels of variables are shown in Table 1.

Table 1. Three factors with the responses (CO conversion,methane selectivity and small alkene selectivity) of independent variables, where X_1 is temperature (K), X_2 is pressure (MPa), X_3 is syngas ratio (-).

Runs	Code values			Experimental Xco/%	Experimental CH_4 selectivity/%	Experimental Y_{alkene} /%
	X_1	X_2	X_3			
1	493	2	2.11	45.3	9.2	4.6
2	493	2	2.04	32.4	12.9	6.4
3	493	2	2.25	56.4	7.4	3.6
4	493	2	2.11	52.6	8.0	3.9
5	493	2	1.48	37.3	11.2	5.5
6	493	2	1.45	40.2	8.6	5.1
7	483	2	2.03	38.3	10.9	5.3
8	483	2	1.98	29.1	14.3	7.0
9	483	2	1.44	25.7	16.3	8.0

10	483	2	1.39	26.5	15.8	7.7
11	483	1.5	2.03	32.3	12.9	6.4
12	483	1.5	1.98	24.7	16.9	8.3
13	483	1.5	1.44	25.9	13.3	7.9
14	503	2	1.95	58.0	7.2	1.5
15	503	1.5	2.03	43.4	9.6	2.1
16	503	2	1.50	45.7	9.1	1.9
17	503	2	2.02	55.4	7.5	1.6

III. RESULTS AND DISCUSSION

The experimental results associated with interaction between eachindependent variable are shown in Table 2.By applying multiple regression analysis to the experimental data, a model formethane selectivity and alkene selectivity can be expressed as the followings:

$$Y_{C_1} = 13.4 - 1.9X_1 - 0.6X_2 - 2.5X_3 + 0.03X_1X_2 + 0.7X_1X_3 - 0.3X_2X_3 + 0.1X_1^2 - 2.5X_2^2 - 0.03X_3^2 \quad (3)$$

$$Y_A = 7.4 - 0.9X_1 - 0.3X_2 - 1.5X_3 + 0.1X_1X_2 + 0.4X_1X_3 - 0.2X_2X_3 - 0.2X_1^2 - 0.5X_2^2 - 1.53X_3^2 \quad (4)$$

Where Y_{C_1} and Y_A are methane and alkene selectivity (C2-C4 olefin/%).The obtained model is found to be significant to the two chosen factors (methane selectivity and alkene selectivity).

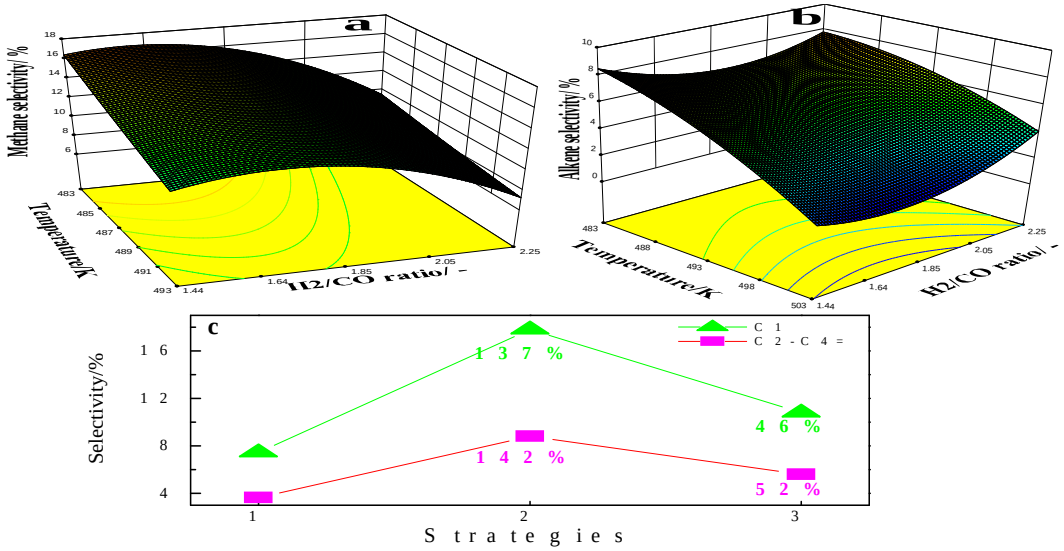

Figure 1. RSM optimization, where a) 3D surface responses for methane selectivity, b)3D surface responses for alkene selectivity, c) selectivity optimization using different optimization strategies.The optimal condition for the third strategy optimization was set at at T=490K, P=2.0 MPa, SR=2.07, GHSV=3000 h^{-1}.

The 3D response pattern of methane selectivity (%) and alkene selectivity (%) in responding to combination effects of independent variables are shown in Figure 1a and 1b. The ANOVA analysis result is shown in Table 2.

Table 2. ANOVA analysis for C1 selectivity (r^2 0.97, Adjust r^2 0.94, Predicted r^2 0.94, adequate precision 16), and alkene selectivity ($r^2$0.98, Adjust r^2 0.93, Predicted r^2 0.92, adequate precision 16)

Source	C1selectivity/%					Alkene selectivity/%				
	DF	Sum of squares	Mean square	F-value	Prob>F	DF	Sum of squares	Mean square	F-value	Prob>F
Model	9	168.2289	21.0283	4.8802	0.0155	9	87.590	10.9250	15.0860	0.0002
X_1	1	24.6877	24.6877	5.7295	0.0376	1	5.1300	5.1300	7.0015	0.0252
X_2	1	4.2570	4.2570	0.9880	0.3208	1	0.6650	0.6650	0.9690	0.3260
X_3	1	10.9193	10.9193	2.5346	0.1340	1	3.4200	3.4200	4.6550	0.0548
X_1X_2	1	0.0067	0.0067	0.0019	0.9210	1	0.1900	0.1900	0.2565	0.5857
X_1X_3	1	4.1449	4.1449	0.9624	0.3266	1	1.5200	1.5200	2.1280	0.1640
X_2X_3	1	0.4085	0.4085	0.0950	0.7223	1	0.1900	0.1900	0.2945	0.5642
X_1^2	1	0.3059	0.3059	0.0713	0.7520	1	3.4200	3.4200	4.6550	0.0548
X_2^2	1	0.1169	0.1169	0.0029	0.0000	1	1.9950	2.8500	3.1635	0.0972
X_3^2	1	5.4141	5.4141	1.2569	0.2691	1	1.9000	1.9000	2.5650	0.1322
Residue	7	32.7465	4.0936			7	5.5100	0.6650		
Lack of	5	31.8298	5.3048	10.9982	0.0775	5	5.3200	0.8550	16.1500	0.0120

fit						
Pure Error	2	0.9168	0.0000	0.0000	2	0.1900
Cor total	16	200.9744			16	93.1950

It was found that the term X1 (temperature) was among the most significant factor to the response (C1 and alkene selectivity), which was reflected from probability factor. The obtained R^2 was close to the experimental R^2 for both C1 and alkene selectivity, indicating a good agreement between experimental data and predicted values. In this work, three strategies were employed for optimization, the first one was by setting the C1 selectivity as the significant parameter to minimize without restricting the alkene selectivity. The second one was by setting the C2-C4 selectivity as the significant parameter to maximize without restricting the C1 selectivity. The third one was by setting the optimization goal by both minimizing the methane selectivity and maximizing the alkene selectivity, while other process parameters vary within reaction conditions. The optimal conditions obtained from these three different optimization strategies are shown in Figure 1c. In strategy 1, of which the C1 was restricted to minimum while alkene selectivity and other process parameters varied within range of experimental plan, the optimal operational condition was achieved as the following: T=493K, P=2 MPa, SR=2.25with GHSV setting at 3000 h^{-1}. In strategy 2, of which the C2-C4 alkene selectivity was restricted to maximum while C1 selectivity and other process parameters varied within range of experimental plan, the optimal operational condition was obtained as the following: T=483K, P=1.5 MPa, SR=1.55with GHSV setting at 3000 h^{-1}. In strategy 3, of which C1 was restricted to minimum while C2-C4 alkene selectivity was restricted to maximum, and other process parameters varied within range of experimental plan, the optimal operational condition wasachieved as the following: T=491K, P=2.0 MPa, SR=2.05with GHSV setting at 3000 h^{-1}. Apparently, different optimization strategies will produce different selectivity. By both considering reasonable minimum methane and maximum alkene selectivity, the optimal condition (T=491K, P=2.0 MPa, SR=2.05with GHSV setting at 3000 h^{-1}) is achieved with methane and alkene selectivity reaching 10.8% and 5.6%, respectively.

CONCLUSION

The RSM was used to optimize product selectivity from FT synthesis using Co/Al_2O_3 catalyst by employing different optimization strategies. It was found that the third optimization strategy yielding the best optimal condition (T=491K, P=2.0 MPa, SR=2.05with GHSV setting at 3000 h^{-1}),of which the methane and alkene (C2-C4) selectivity could be 10.8% and 5.6%, respectively.

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