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MODELING, SIMULATION AND SYSTEMATIC ANALYSIS FOR HIGH-TEMPERATURE ADIABATIC FIX-BED PROCESS OF SNG WITH NOVEL CATALYSIS

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ABSTRACT

A novel systematic analysis framework based on modeling and simulation is provided for optimization of the methanation process using novel high-temperature tolerant catalysts. In this framework, the reactor is described by kinetic equation and energy balance. 3 schemes for methanation processes and 2 types of feedstock are investigated. In addition, different reaction temperature is considered for different schemes and different feedstock. Furthermore, the solution method is proposed for simulation and optimization the different process schemes. To compare the performance of different schemes, economic analysis including methane profit, steam profit, and compressing work consumption is investigated. Comprehensive considering different profit, the total profit for different schemes is provided and the optimal scheme is obtained.

Keywords: methanation, process optimization, simulation, SNG, profit analysis

NONMENCLATURE

Abbreviations	
Ind.	Industrial
Sim.	Simulation
Temp.	Temperature
Sch.	Scheme
Symbols	
y_{CH_4}	Mole fraction of CH_4
y_{CO_2}	Mole fraction of CO_2
ρ_p	Density of the catalyst particles
ε	Void fraction of the reactor bed
h	Height of the reactor
A	Cross-sectional area of the reactor
r_{CH_4}	Reaction rate of CH_4
r_{CO_2}	Reaction rate of CO_2
T	Temperature
G	Mass flux of gas mixture
C_{pm}	Heat capacity of gas mixture
ΔH_{Re}	Heat of reaction
p	Pressure
d_{ps}	Equivalent diameter of catalyst particles
μ	Viscosity
ρ_f	Density of gas
k	Split ratio
a	Recycle ratio
T_R	Temperature of reactor
W	Compressing work

1. INTRODUCTION

Natural gas is a type of clean energy and can be used in the power industries, transportation fuel, and urban gas [1]. Due to the energy security, carbon dioxide emissions, rapid urbanization, and variation of the price of natural gas in China, coal to synthetic natural gas (SNG) has attracted more attention [2-3]. The coal to SNG process consists gasification, air separation, water gas shift (WGS), and methanation units. Gasification is the process of non-catalytic converting coal into carbon monoxide and hydrogen by adding steam and oxygen under pressure. WGS is a thermodynamically limited reaction which has to operate at low temperatures, reducing kinetics rate and increasing the amount of catalyst required to reach valuable CO conversions. Methanation is the conversion of CO_x and H_2 to methane

CH_4 with strongly exothermic and catalytic reaction. The research on the coal to SNG technologies in recent years is mainly focused on the catalyst, reactor design, process development, and system integration & optimization [3]. Because of the strongly exothermic reactions in methanation unit, the catalysts with high temperature stability, selectivity, and activity for methanation process have been pursued. Extensive work has been done, including the research for selecting different metal-based catalysts, different preparation methods, different carriers for the catalyst and different promoters [3]. In our previous work, a novel kind of high temperature-tolerant methanation catalyst AM-830 was developed [4]. However, less literature is devoted to work on systematic analysis method for process optimal development with a novel catalysts. In this paper, a novel systematic analysis framework is provided and several feasible processes with the novel catalysts are optimized by the provided framework.

2. PROCESS DESCRIPTION AND SIMULATION

2.1 Process description

Several SNG technologies have been reviewed [5] and the typical fixed-bed processes are including Lurgi process [6], TREMP™ process [7], and Davy process [8]. In the typical methanation technologies, 4 adiabatic fixed-bed reactors are used. 2 reactors are operating in high temperature as main reactors and the other 2 reactors are running in low temperature to increase the conversion of CO. Hot gas recycle is adopted to control the main-reactor temperature by adjusting the ratio of recycle gas to the fresh syngas. Without loss generality, 4 adiabatic fixed-bed reactors technology is investigated and different configurations are considered in this work. The general flowsheet is shown in Fig 1. In this figure, S_i, E_i, and R_i denote stream, heat exchanger, and reactor. C is compressor. This process can be optimized by adjusting the split ratio k (S_{10}/S_0) and recycle ratio a (S_1/S_0). Therefore, three different methanation schemes based on the general flowsheet are introduced as shown in Fig 2. The detail information of the split ratio and the recycle ratio for different schemes are described in Fig 2.

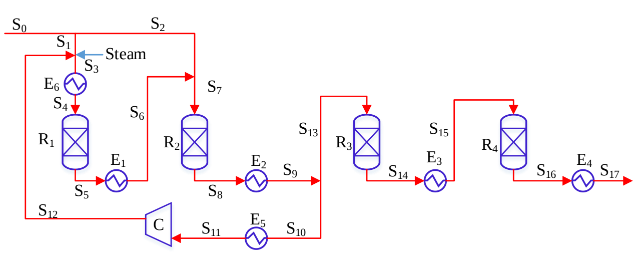


Fig 1 General flowsheet of methanation process.

2.2 Modeling

In methanation process, reactants and products are including CO, H_2, H_2O, CH_4, and CO_2. To describe this process, two independent reactions are considered and the two key components are CH_4 and CO_2. The kinetics of the novel catalysts are used from reference [4].

$$\mathrm{CO} + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{(Re.1)}$$

$$\mathrm{CO} + H_2O \rightarrow CO_2 + H_2 \qquad \text{(Re.2)}$$

To simplify the process, some assumptions are introduced:

(1) The reactor can be treated as one dimensional steady-state pseudo-homogeneous plug-flow reactor as the reference [9].

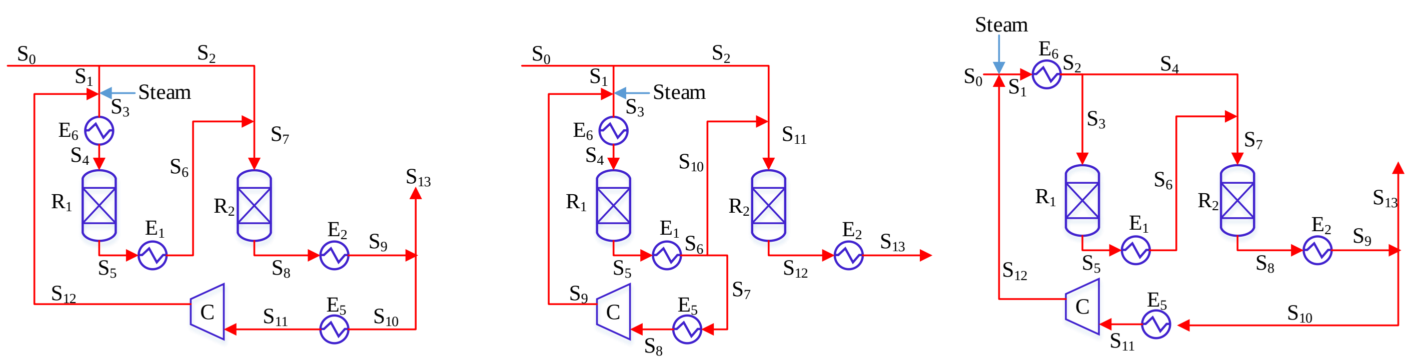
(2) The pressure drop should be satisfied $\Delta p \leq 0.15 p_0$ [10].

2.2.1 Mass balance

Mass balance of two key components is given as:

$$\frac{dy_{CH_4}}{dh} = \frac{(1-\varepsilon)\rho_p A}{F_0} \frac{(1+2y_{CH_4})^2}{1+y_{CH_4,0}} r_{CH_4} \qquad (1)$$

$$\frac{dy_{CO_2}}{dh} = \frac{(1-\varepsilon)\rho_p A}{F_0} \frac{(1+2y_{CH_4})}{1+2y_{CH_4,0}} \left(r_{CO_2} + 2y_{CO_2} r_{CH_4}\right) \qquad (2)$$



Recycle ratio: S_{10}/S_0
Split ratio: S_1/S_0
(a) Scheme 1

Recycle ratio: S_7/S_0
Split ratio: S_1/S_0
(b) Scheme 2

Recycle ratio: S_{10}/S_0
Split ratio: S_3/S_1
(c) Scheme 3

Fig 2 Three different schemes for methanation process.

2.2.2 Energy balance

Temperature equation can be obtained according to energy balance.

$$\frac{dT}{dh}=\frac{(1-\varepsilon)\rho_p}{GC_{pm}}\left[r_{CH_4}(-\Delta H_{Re.1})+r_{CO_2}(-\Delta H_{Re.2})\right] \quad (3)$$

2.2.3 Pressure equation

According to Ergun equation [11], pressure drop can be described as:

$$\frac{dp}{dh}=-\left[\frac{150\mu(1-\varepsilon)}{d_{ps}G}+1.75\right]\frac{G^2}{\rho_f d_{ps}}\frac{1-\varepsilon}{\varepsilon^3} \quad (4)$$

The compressor model, mixer model, and parameters of physical property are incorporated into the reactor model as reference [12].

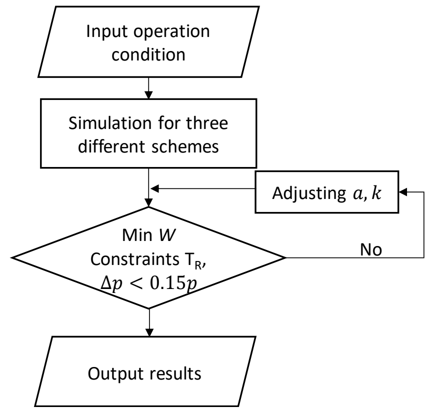


Fig 4 Influence of the recycle ratio.

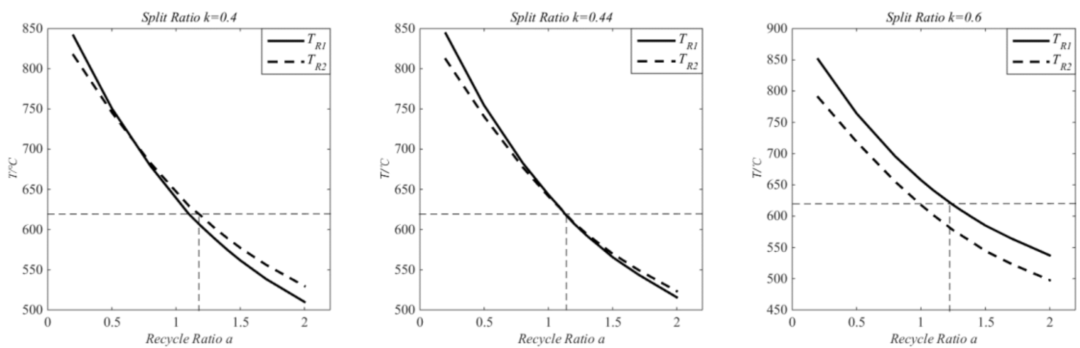


Fig 5 The effect of recycle ratio on the main reactors outlet temperature for Case 1 in Scheme 1.

2.3 Validation of the model

To valid this model, two cases with different feedstock are simulated. Flowrate in the two cases keeps the same and is 504,600 Nm^3/h. Operation pressure of Case 1 is 3.0MPa and Case 2 is 4.0MPa. Main composition of feedstock in Case 1 is H_2 (74.51%) and CO (24.18%). Main composition of feedstock in Case 2 is H_2 (63.8%), CO (20.02%), and CH_4 (14.94%). The model is solved by ode15s in MATLAB and the simulated results are provided in Table 1. By comparison of the component distribution in the industrial data with that in the simulation results, the proposed model and the kinetics of the novel catalysts can be validated.

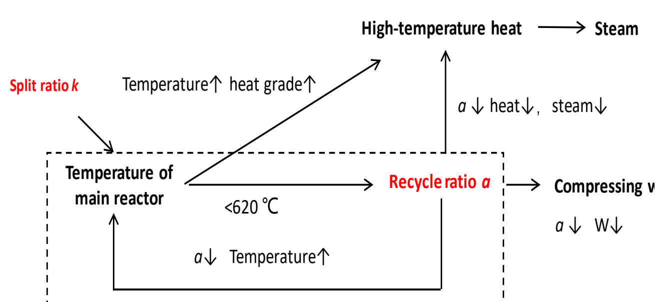


Fig 3 Influence of the recycle ratio.

Table 1 Comparison of industrial data with simulation results

Item		Case 1		Case 2	
		Ind. data	Sim. result	Ind. data	Sim. result
Inlet temp. of R_1 (℃)		300.0	300.0	300.0	300.0
Outlet temp. of R_1 (℃)		620.0	619.2	620.0	619.3
Inlet temp. of R_2 (℃)		300.0	300.0	300.0	300.0
Outlet temp. of R_2 (℃)		620.0	620.0	620.0	619.4
Inlet temp. of R_3 (℃)		280.0	280.0	280.0	280.0
Outlet temp. of R_3 (℃)		450.0	458.7	430.0	442.9
Inlet temp. of R_4 (℃)		250.0	250.0	250.0	250.0
Outlet temp. of R_4 (℃)		330.0	327.2	310.0	300.7
Composition of product (mole fraction, %)	H_2	2.22	1.71	1.41	2.42
	CO	0.01	0.13	50*	90*
	CO_2	0.83	0.59	0.50	0.27
	CH_4	94.01	94.76	97.42	96.26
	N_2	2.93	2.81	0.58	1.05

* The unit of this value is ppm.

3. PROCESS ANALYSIS AND OPTIMIZATION

3.1 Operation analysis

As described before, temperature of the main reactor is controlled by adjusting the recycle ratio. If the recycle ratio varies, the main reactor temperature, steam quality, quantity of steam, and consumption of the compressing work in this process are influenced and the relationship is given in Fig 3. In addition, the recycle ratio is constrained by the outlet temperature of the main reactor and split ratio. So a constraint optimal problem can be constructed to obtain a minimum recycle ratio.

The optimization problem including objective and constraints to ensure process safety and profit can be described as:

Objective: $\min W$

Constraints:
$$0 < k < 1$$
$$610 \le T_{R1} \le 700$$
$$610 \le T_{R2} \le 700$$
$$\Delta p < 0.15p$$

The solution method of this optimization problem is given in Fig 4.

3.2 Optimal configuration

When split ratio k is set as 0.40, 0.44, and 0.60, the relationship of the temperature of main reactors T_R with recycle ratio for Case 1 in Scheme 1 is listed in Fig 5. From this figure, minimum recycle ratio can be obtained with different split ratio when the constraints are satisfied. Furthermore, the relationship of minimum recycle ratio with different split ratio for Case 1 in Scheme 1 is provided in Fig 6. So we can determinate the optimal recycle ratio for Case 1 in Scheme 1 is 1.13 when the split ratio is 0.44 and the temperature of main reactor is 620℃.

By the same way, the optimal recycle ratio with the corresponding constraints in the different Schemes can be obtained and the results are presented in Table 2. In addition, the split ratio is given in Table 3. It is clearly seen that the recycle ratio of Scheme 1 is smaller than that of other Schemes in Case 1 and Case 2.

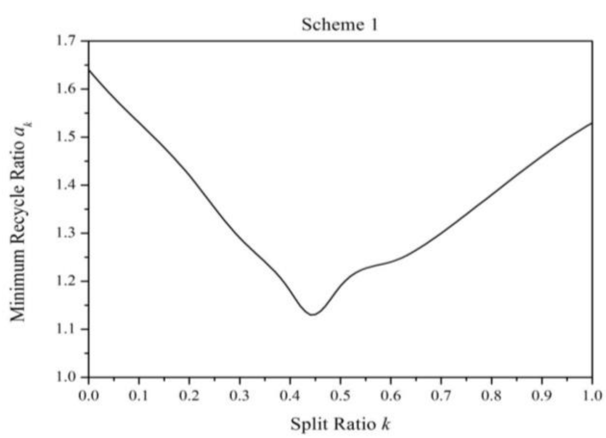


Fig 6 The effect of split ratio on the recycle ratio in Scheme 1 (Case 1, T_R=620℃).

Table 2 Optimal recycle ratio for different Schemes

T_{R1} (℃)	Case 1 Sch. 1	Case 1 Sch. 2	Case 1 Sch. 3	Case 2 Sch. 1	Case 2 Sch. 2	Case 2 Sch. 3
610	1.20	2.19	1.93	0.79	1.39	1.40
620	1.13	2.09	1.83	0.74	1.29	1.30
630	1.08	1.94	1.73	0.69	1.19	1.20
640	1.03	1.83	1.62	0.64	1.10	1.12
650	0.96	1.72	1.52	0.59	1.01	1.05
660	0.90	1.60	1.43	0.55	0.92	0.97
670	0.85	1.50	1.34	0.51	0.85	0.90
680	0.80	1.40	1.27	0.46	0.77	0.84
690	0.75	1.30	1.20	0.42	0.70	0.78
700	0.71	1.20	1.12	0.38	0.63	0.72

By analysis the results of Table 2 and 3, we can obtain the optimal configuration for the three different schemes as following:

Scheme 1: $\mathrm{k} = 0.35 - 0.45,\ \mathrm{T_{R1}} = \mathrm{T_{R2}}$.
Scheme 2: $\mathrm{k} = 0.60 - 0.85,\ \mathrm{T_{R1}} = \mathrm{T_{R2}}$.
Scheme 3: $\mathrm{k} = 0.55 - 0.60,\ \mathrm{T_{R1}} > \mathrm{T_{R2}}$.

The operational flexibility of the Scheme 3 is relative small by comparison the result of the optimal configuration. The optimal problem is only considering the consumption of the compressing work.

Table 3 suitable split ratio for different Schemes

T_{R1} (℃)	Case 1 Sch. 1	Case 1 Sch. 2	Case 1 Sch. 3	Case 2 Sch. 1	Case 2 Sch. 2	Case 2 Sch. 3
610	0.44	0.83	0.61	0.42	0.75	0.60
620	0.44	0.82	0.60	0.42	0.74	0.60
630	0.44	0.81	0.60	0.42	0.73	0.59
640	0.44	0.80	0.59	0.41	0.71	0.59
650	0.43	0.79	0.58	0.40	0.69	0.59
660	0.43	0.78	0.58	0.40	0.68	0.58
670	0.42	0.77	0.57	0.39	0.66	0.58
680	0.42	0.75	0.57	0.38	0.64	0.57
690	0.42	0.74	0.57	0.38	0.62	0.57
700	0.42	0.73	0.56	0.37	0.60	0.57

3.3 Profit analysis

3.3.1 Steam profit

Because of the strongly exothermic reactions, the reaction heat can be utilized to increase the profit of the methanation unit. According to the process as shown in Fig 1, the scheme of steam network is applied for heat recycle as Fig 7. Different grade steam will be generated due to different process schemes. To compare the profit conveniently for different schemes, the steam is converted into power and the Rankine cycle is adopted. The equivalent power is calculated and the isentropic efficiency of Turbine is set as 0.75 according to reference

[13]. The price of power is 0.64 RMB/kWh and the steam profit is shown in Table 4. Comparing the steam profit for different operating condition, we can know that the performance of the lower temperature of the main reactor is better than that of the higher temperature of the main reactor. The condition of Case 1 is better than the condition of Case 2. In all cases, the performance of Scheme 3 is the best in Case 1 condition when the outlet temperature of main reactor 1 is operating at 610℃.

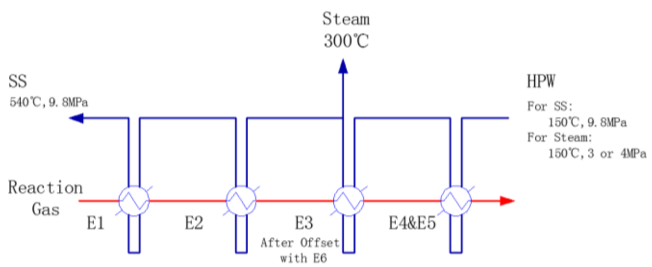


Fig 7 Scheme of steam generation.

Table 4 Steam Profit for different schemes

T_{R1} (℃)	Steam profit (10^9 RMB)					
	Case 1			Case 2		
	Sch. 1	Sch. 2	Sch. 3	Sch. 1	Sch. 2	Sch. 3
610	4.46	4.85	4.94	3.83	3.56	3.98
620	4.41	4.72	4.91	3.79	3.43	3.97
630	4.37	4.56	4.88	3.74	3.27	3.95
640	4.33	4.42	4.83	3.69	3.15	3.92
650	4.27	4.27	4.78	3.62	2.99	3.88
660	4.20	4.12	4.73	3.57	2.86	3.86
670	4.14	3.97	4.68	3.52	2.72	3.82
680	4.08	3.83	4.64	3.44	2.57	3.77
690	4.02	3.65	4.59	3.38	2.43	3.74
700	3.95	3.51	4.52	3.30	2.28	3.70

3.3.2 Methane profit

The methane profit of different schemes in two kinds of feedstock (Case 1 and Case 2) with different operating temperature of the main reactor 1 is provided in Table 5. The price of methane is set as 1.86 RMB/m^3 according to reference [14]. The profit of Case 2 in different schemes is higher than that of Case 1 in different schemes. The reason is that the content of methane of Case 2 in the feedstock is higher than the content of methane of Case in the feedstock. The methane profit of Scheme 3 is better than the methane profit of other two schemes in Case 1 or Case 2. There is not significantly difference for the methane profit in different main reactor temperature with the same scheme and feedstock. The reason is that the conversion of CO and selectivity of CH_4 keep the same in the novel catalysts AM-830.

Table 5 Methane profit for different schemes

T_{R1} (℃)	Methane profit (10^9 RMB)					
	Case 1			Case 2		
	Sch. 1	Sch. 2	Sch. 3	Sch. 1	Sch. 2	Sch. 3
610	17.69	17.68	17.69	25.68	25.63	25.71
620	17.68	17.68	17.69	25.68	25.62	25.71
630	17.68	17.66	17.69	25.68	25.61	25.71
640	17.67	17.65	17.69	25.69	25.60	25.70
650	17.65	17.64	17.69	25.70	25.63	25.70
660	17.63	17.62	17.69	25.72	25.63	25.70
670	17.61	17.59	17.69	25.72	25.62	25.70
680	17.59	17.57	17.69	25.72	25.60	25.70
690	17.57	17.53	17.68	25.71	25.59	25.70
700	17.53	17.49	17.67	25.69	25.56	25.70

3.3.3 Compressing work consumption

If the recycle ratio is different in the process, the compressing work consumption is different. The less compressing work consumption is required in a scheme, and the operating cost for this scheme is lower. Correspondingly, the profit of the scheme is different with different recycle ratio. Therefore, compressing work consumption for different schemes is analyzed with different feedstock in various operating temperature of the main reactor and the results are provided in Table 6. From the results of Table 6, it is clear to see that the performance of different schemes for Case 2 feedstock is super to that of different schemes for Case 1 feedstock.

Table 6 Compressing work consumption

T_{R1} (℃)	Compressing work consumption (10^9 RMB)					
	Case 1			Case 2		
	Sch. 1	Sch. 2	Sch. 3	Sch. 1	Sch. 2	Sch. 3
610	0.18	0.33	0.25	0.09	0.16	0.13
620	0.16	0.29	0.22	0.08	0.13	0.11
630	0.15	0.24	0.20	0.07	0.11	0.09
640	0.13	0.21	0.17	0.06	0.09	0.08
650	0.11	0.18	0.15	0.06	0.07	0.07
660	0.10	0.15	0.13	0.05	0.06	0.06
670	0.09	0.13	0.11	0.04	0.05	0.05
680	0.08	0.11	0.10	0.04	0.04	0.04
690	0.07	0.10	0.09	0.03	0.03	0.04
700	0.06	0.08	0.08	0.03	0.02	0.03

3.3.4 Total profit

By comprehensive considering the steam profit, methane profit, and compressing work consumption, the total profit for different schemes can be obtained and the results are listed in Table 7. From this table, it is obvious that the profit of Scheme 3 is higher than the other two schemes in the same feedstock and same operating temperature. For different feedstock, the profit of Case 2 is super to that of Case 1 in the same scheme. For the same feedstock and the same scheme, lower operating temperature of the main reactor is benefit than relative high operating temperature of the main reactor.

Table 7 Total profit for different schemes

T_{R1} (℃)	Total profit (10^9 RMB)					
	Case 1			Case 2		
	Sch. 1	Sch. 2	Sch. 3	Sch. 1	Sch. 2	Sch. 3
610	21.96	22.19	22.38	29.42	29.04	29.57
620	21.93	22.11	22.38	29.39	28.92	29.58
630	21.91	21.98	22.37	29.35	28.77	29.56
640	21.86	21.86	22.35	29.31	28.66	29.54
650	21.81	21.73	22.32	29.27	28.55	29.52
660	21.74	21.58	22.29	29.24	28.43	29.50
670	21.66	21.43	22.26	29.20	28.30	29.46
680	21.58	21.29	22.22	29.12	28.14	29.42
690	21.52	21.08	22.18	29.05	27.98	29.40
700	21.42	20.92	22.11	28.97	27.81	29.36

4. CONCLUSIONS

Several methanation schemes with the novel catalysts AM-830 were investigated to improve the performance on the basis of simulation and optimization. In addition, two cases with different feedstock and different operating pressure were considered for the methanation process. The optimal recycle ratio was obtained for different schemes in various operating condition. Furthermore, economic performance of different schemes with two feedstock in various temperature of the main reactor were systematically analyzed. The economic performance included methane profit, steam profit, and compressing work consumption. Comprehensive consideration of the different profit and consumption, total profit for different schemes was obtained. The contribution were summarized as follows:

(1) The mathematical model of methanation process integrated reactor with kinetic equation and heat utilization was presented.

(2) Optimization method for minimum recycle ratio of different schemes was introduced.

(3) Systematic analysis of the profit for different schemes was performed. In case 1 and case 2, total profit of Scheme 3 is super to other 2 schemes. In case 1, the total profit of Scheme 3 is higher about 1.9% than the total profit of Scheme 1 in different operating temperature. In case 2, the total profit of Scheme 3 is higher approximate 1.8% than the total profit of Scheme 2 in different operating temperature.

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