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Optimization of methanol yield and carbon dioxide utilization in methanol synthesis process

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Abstract. The method of CO_2 hydrogenation to methanol can effectively reduce carbon emission and has wide application prospects in chemical industry and environment. Therefore, methanol synthesis is an important way to save energy, reduce emission and transform energy utilization. In this paper, the mathematical model of methanol synthesis reactor is established. Under the condition of controllable cooling temperature, the optimization is carried out with maximum methanol yield and CO_2 utilization rate. The results show that the methanol yield can be increased by 6.57% and CO_2 utilization rate can be increased to 39.1% by adjusting the cooling temperature control strategy. The comparative study found that the optimal cooling temperatures all show up and down variations, with local minima and maxima. In addition, an industrial application method of methanol yield maximization cooling strategy is proposed. When the stage cooling at different temperatures is adopted, the methanol yield could be increased by 5.38%.

Keywords: methanol synthesis; methanol yield; CO_2 utilization rate.

1. Introduction

According to the report published by the Global Carbon Project, the world's total carbon dioxide emissions from fossil fuels will reach 36.8 billion tons in 2023, the total emissions were up 1.1 percent from last year [1]. Carbon dioxide is the common greenhouse gas, which is mainly produced by burning fossil fuels. A large amount of CO2 emissions will produce greenhouse effect, leading to global warming and other environmental problems. To effectively deal with the issue of climate change and achieve the goal of 'carbon peak and carbon neutrality', it is necessary to accelerate the energy transition. As a source of carbon raw materials, carbon dioxide can be synthesized into liquid fuels such as methanol by hydrogenation. Methanol is liquid at normal temperature and pressure, which is easy to store and transport. Methanol can be used as fuel directly to replace liquid fuel such as gasoline and diesel, and it can also be converted into hydrogen through methanol reforming technology to supply fuel cells to generate electricity [2, 3]. Due to the wide application of methanol, the study of efficient methanol synthesis technology not only has a wide application prospect in the field of chemical industry and environment, but also an important method to realize the development of energy transformation.

Methanol synthesis methods are mainly divided into high-pressure synthesis and low-pressure synthesis, and copper-based catalysts are widely used in the synthesis reaction. Methanol synthesis is an endothermic and reduced volume reaction, so higher pressure and lower temperature are conducive to methanol formation. However, low temperature will affect the activity of catalyst, reduce the reaction rate, and lead to the decrease of methanol yield. Therefore, reasonable temperature control strategy is the key factor for efficient operation of methanol synthesis reactor. Some scholars have studied the optimal temperature distribution of methanol synthesis process with maximum methanol yield as the optimization goal. Jahanmiri et al. [4] optimized the external temperature distribution of methanol synthesis reactor and solved the optimal temperature curve by using control variable parameterization method. The temperature profile was considered as a cubic polynomial of reaction length ($T = A + Bz + Cz^2 + Dz^3$) in optimization, and methanol yield was greatly improved by using the optimal temperature profile. Kordabadi et al. [5] applied genetic algorithm to study the maximum methanol yield of methanol synthesis reactor, obtained the optimal bed temperature distribution under

different catalyst deactivation degrees. Lim et al. [6] studied the maximum yield of methanol synthesis reactor by optimizing variables such as inlet temperature, wall temperature distribution, and CO2 fraction, and the results showed that the methanol yield could be significantly improved by optimizing temperature and CO2 fraction.

The research on the optimal temperature profile for maximizing methanol yield mainly involves parameterization or discretization of the optimization temperature variable [4-6]. Therefore, the optimization result may be affected by the form of the parametric equation or the number of discrete points. CO2 utilization is also an important index in the synthesis of methanol, but there are fewer research reports on the optimal configuration for maximum CO2 conversion rate, and there is a lack of comparative studies on different optimization results. In this paper, a mathematical model will be developed to optimize the cooling temperature distribution, considering the two conditions of maximum methanol yield and CO2 utilization rate. By comparing the temperature and flow rate variations of different reactors, the influencing factors to improve the methanol yield and CO2 utilization are investigated. The reactor performance can be effectively improved by utilizing the optimal cooling control strategy, which provides theoretical guidance for industrial design and application.

2. System description and reaction model

2.1 Reactor model

The main reactions that occur during methanol synthesis are as follows [7]:

$$CO_2+3H_2 \rightleftharpoons CH_3OH+H_2O \quad \text{(R1)}$$

$$CO_2+H_2 \rightleftharpoons CO+H_2O \quad \text{(R2)}$$

$$CO+2H_2 \rightleftharpoons CH_3OH \quad \text{(R3)}$$

Among the above reactions, there are 3 main reactions, but only two of them are independent chemical reactions. In this study, CO2 hydrogenation reaction (R1) and reverse water gas shift reaction (R2) are selected as independent chemical reactions. Fixed bed reactor is a common reactor model in industry because of its simple structure and easy manufacture, and the structure of methanol synthesis the packed bed reactor is shown in Figure 1. Table 1 lists the parameter values of reference reactor. The catalyst is filled in the tube, and the cooling medium of constant temperature is outside the tube. Here, it is assumed that the reaction gases can be regarded as ideal gases, and the gas is a piston flow without axial back-mixing, so it can be treated as a one-dimensional piston flow reactor model.

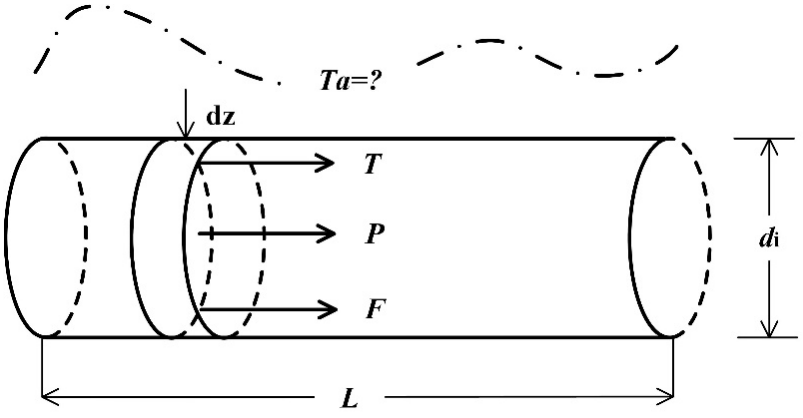


Figure 1. Schematic diagram of reactor structure

Table 1. Parameters and values of reference reactor [8]

Parameter	Symbol	Value	Unit
Inlet temperature	T_{in}	493.2	K
Cooling temperature	T_{w}	523	K
Inlet pressure	P_{in}	85	bar
Inlet flow rate	F_{in}	0.0033	mol/s
CO2 molar fraction	X_{CO_2}	0.03	-
H2 molar fraction	X_{H_2}	0.82	-
CO molar fraction	X_{CO}	0.04	-
H2O molar fraction	X_{H_2O}	0.005	-
CH3OH molar fraction	X_{CH_3OH}	0.005	-
N2 molar fraction	X_{N_2}	0.1	-
Reactor diameter	d	0.016	m
Reactor length	L	0.15	kg/m^3
Catalyst density	ρ_c	1775	-
Bed porosity	ε	0.5	m
Catalyst particle diameter	d_p	0.016	m

2.2 Conservation equation

2.1.1 Mass conservation equation

According to the reaction equation, for each reaction component, the net reaction rate can be defined as [9]:

$$\frac{dF_{CO_2}}{dz} = -\rho_b A_c (r_1 + r_2) \tag{2}$$

$$\frac{dF_{H_2}}{dz} = -\rho_b A_c (3r_1 + r_2) \tag{3}$$

$$\frac{dF_{CH_3OH}}{dz} = \rho_b A_c r_1 \tag{4}$$

$$\frac{dF_{CO}}{dz} = -\rho_b A_c r_2 \tag{5}$$

$$\frac{dF_{H_2O}}{dz} = \rho_b A_c (r_1 + r_2) \tag{6}$$

Where F_k is the flow rate of k component gas, r_1 and r_2 is the CO2 hydrogenation and reverse water vapor shift reaction rate, respectively. ρ_b is the catalyst bed density, $\rho_b = \rho_c(1-\varepsilon)$, and A_c is the cross-sectional of reactor.

2.1.2 Momentum conservation equation

The pressure drop of gas flow in a tubular reactor can be expressed as [10]:

$$\frac{dP}{dz} = -\left[\frac{150\mu(1-\varepsilon)}{d_p} + 1.75G\right] \times \frac{1-\varepsilon}{d_p \varepsilon^3} v \tag{7}$$

Where μ and v are the dynamic viscosity and velocity of the reaction gas, $v = FRT/(PA_c)$, G is the surface mass flow rate of reaction mixture.

2.1.3 Energy conservation equation

Considering the fluid heat transfer of heat outside the tube and the heat absorption and release process of different reaction processes, the energy equation can be written as: [9]:

$$\frac{dT}{dz} = \left[\pi d U (T_a - T) - \rho_b A_c (r_1 \Delta_r H_1 + r_2 \Delta_r H_2)\right] / \sum \left(F_k C_{p,k}\right) \tag{8}$$

Where U is the total heat transfer coefficient, which can be approximated as a constant. $\Delta_r H_1$ and $\Delta_r H_2$ are the reaction enthalpies of R1 and R2.

2.3 Chemical reaction rate equation

Bussche et al. [11] tested the kinetics of methanol synthesis based on Cu-based catalysts, and the reaction mechanism model obtained was widely used. The reaction rate equation can be expressed as follows [11]:

$$r_1 = k_1 p_{CO_2} p_{H_2} \left(1 - \frac{p_{CH_3OH} p_{H_2O}}{p_{CO_2} p_{H_2}^3 K_{p_1}}\right) / D^3 \tag{9}$$

$$r_2 = k_2 p_{CO_2} \left(1 - \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2} K_{p_2}}\right) / D \tag{10}$$

Where k_1 and k_2 are the reaction rate constant, K_{p_1} and K_{p_2} are the equilibrium constants for reaction 1 and reaction 2, respectively. They are determined by the thermodynamic properties of the reaction and can be expressed as [11]:

$$\log_{10} K_{p_1} = \frac{3066}{T} - 10.592 \tag{11}$$

$$\log_{10} K_{p_2} = -\frac{2073}{T} + 2.029 \tag{12}$$

2.4 Performance index

The methanol yield of the reactor is expressed by the difference between the import and export flow rates of methanol:

$$\Delta F_{CH_3OH} = F_{CH_3OH,out} - F_{CH_3OH,in} \tag{13}$$

The utilization rate of CO2 can be written as:

$$Y_{CO_2} = \left(F_{CO_2,in} - F_{CO_2,out}\right)/F_{CO_2,in} \tag{14}$$

3. Solution method

Disregarding the temperature-induced catalyst deactivation problem, the reactor tube external cooling temperature is freely controllable, and the problem can be transformed into solving the optimal configuration problem. T_a is first obtained by fitting the guess point data and proceeding to discretize the variable to be solved into n points:

$$T_a = \left[T_a(1)\ T_a(2)\cdots T_a(i)\ T_a(i+1)\ \cdots T_a(n)\right] \tag{15}$$

Various constraint equations (2-8) are also discretized, while setting the constraint that the flow rate of methanol increases monotonically along the z-axis in a positive direction:

$$F_{CH_3OH}(i+1) > F_{CH_3OH}(i) \tag{16}$$

The optimization objective is the maximum methanol yield, which can be written as:

$$\mathrm{Max}\left(\Delta F_{CH_3OH}\right) = \mathrm{Max}\left(\sum_{i=1}^{n} \rho_b A_c r_1(\mathrm{i})\mathrm{d}z\right) \tag{17}$$

The maximum CO2 utilization rate is equivalent to the minimum exit flow rate:

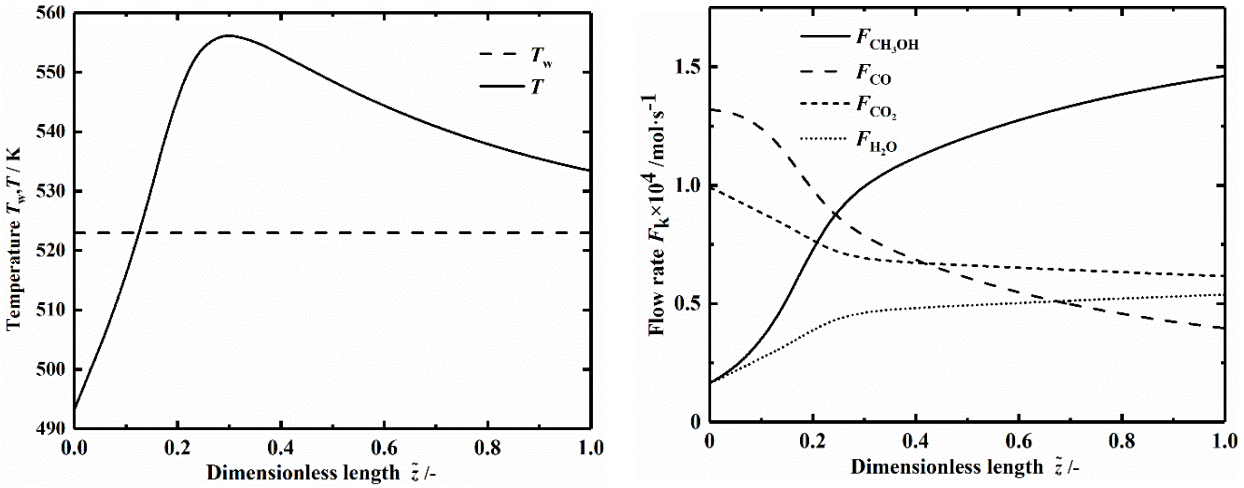
$$\mathrm{Max}\left(Y_{CO_2}\right) = \mathrm{Max}\left(\left(F_{CO_2}(1) - F_{CO_2}(n)\right)/F_{CO_2}(1)\right) \tag{18}$$

Equation (17) and (18) are used as optimization objectives to solve the optimal temperature distribution profile, denoted as Case 1 and Case 2 reactor, respectively. In the process of solving the problem, the optimal temperature to be solved is discretized by spline interpolation, and the main function is solved by 'fmincon' function.

4. Numerical results and discussion

4.1 Reference reactor

Figure 2 shows the temperature and flow rate distribution curves in reference reactor. The temperature of reaction mixture *T* increases rapidly at inlet in figure 2(a), reaches a maximum value of 556 K at *z/L* = 0.3, and then gradually decreases to 533 K. CO_2 hydrogenation reaction has high reaction rate at inlet section, and releases a lot of reaction heat, resulting in a rapid increase of reaction gas temperature. The gas flow rate of each component changes rapidly at inlet, indicating that the reaction at inlet is relatively violent, and the synthesis of methanol mainly occurs in the first half of reactor. The methanol flow rate at reactor outlet reached 1.46×10^{-4} mol/s and the methanol yield is 1.29×10^{-4} mol/s. The outlet flow rate of CO_2 is 6.16×10^{-5} mol/s.

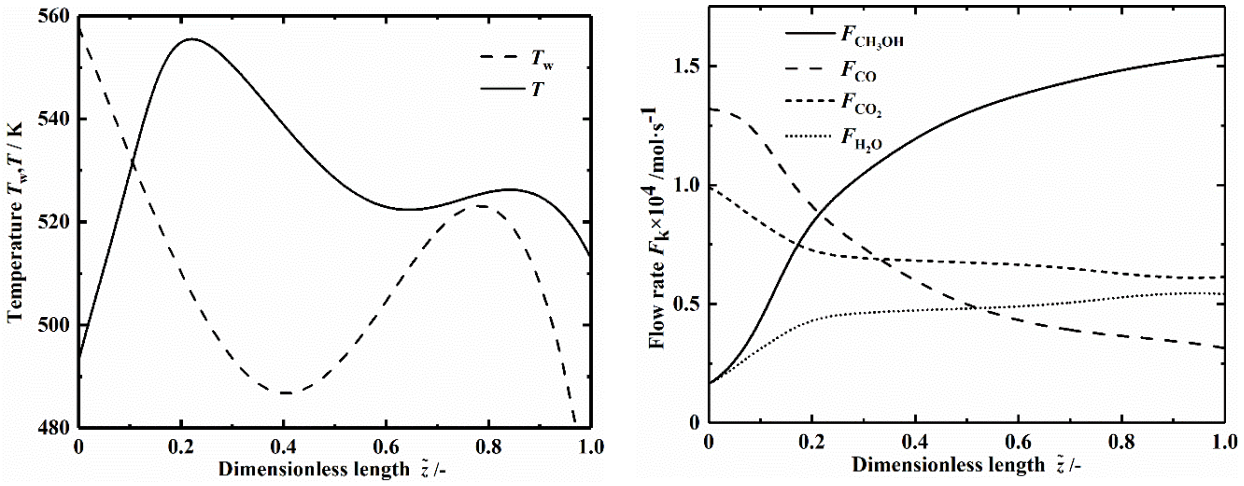


Temperature Flow rate

Figure 2. Temperature and flow rate distribution curves in reference model

4.2 Case 1 reactor

Figure 3 shows the temperature and flow rate distribution curves in Case 1 reactor. The optimized cooling temperature decreases rapidly at inlet position, reaches a local minimum of 486 K at z/L = 0.4, then increases to a local maximum of 523 K at about z/L = 0.8, and finally monotonically drops to 463 K at outlet. The changing trend of the mixed gas temperature at inlet is consistent with that of reference model, but it begins to decrease rapidly after reaching the maximum value, and remains relatively stable, rapidly decreases at the outlet section. The flow rate distribution of components is similar to the reference model, but the methanol flow rate at the outlet is 1.55×10^{-4} mol/s, and the methanol yield reaches 1.38×10^{-4} mol/s. The outlet flow rate of CO_2 is 6.14×10^{-5} mol/s.

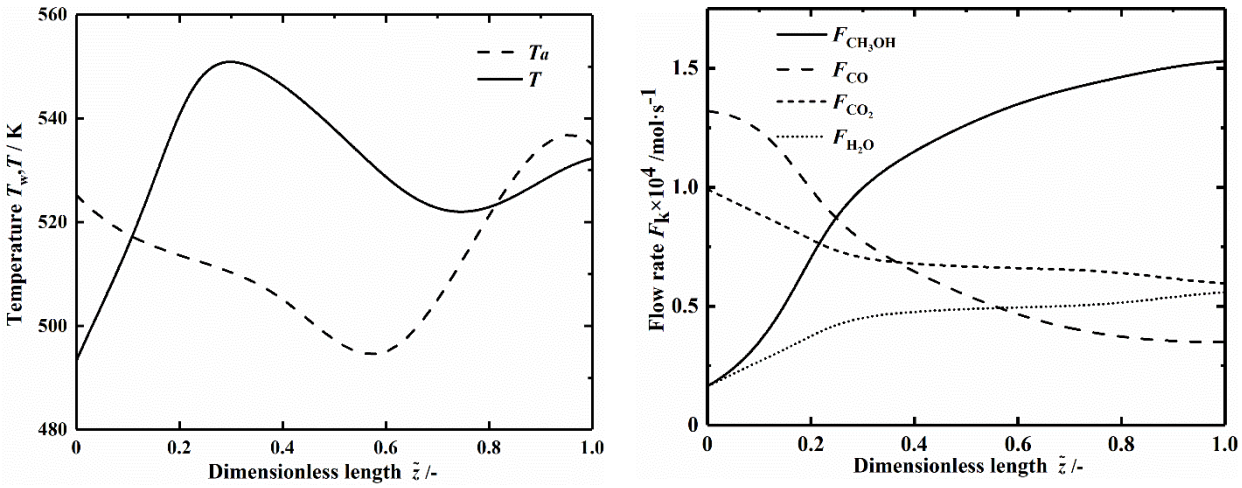


Temperature Flow rate

Figure 3. Temperature and flow rate distribution curves in Case 1 reactor

4.3 Case 2 reactor

Figure 4 shows the temperature and flow rate distribution curves in Case 2 reactor. The optimized cooling temperature decreases gradually from 525 K at the inlet to a local minimum of 495 K, followed by a sharp increase to a local maximum of 536 K, with a slight decrease at the outlet. The temperature of the gas mixture reaches the hot spot 551 K at z/L = 0.3, then drops to 522 K and rises again slowly. The methanol flow rate at the outlet is 1.53×10^{-4} mol/s, and methanol yield reaches 1.36×10^{-4} mol/s, the outlet flow rate of CO_2 is 5.96×10^{-5} mol/s.



Temperature Flow rate

Figure 4. Temperature and flow rate distribution curves in Case 2 reactor

4.4 Discussion

Table 2 lists the values of performance indicators in different reactor. Compared with reference value, the methanol yield in Case 1 and Case 2 reactor increased by 6.57% and 4.61%, and the CO2 utilization rate increased to 38.1% and 39.8%, respectively. It is concluded that optimizing the cooling temperature with the objective of maximum methanol output or maximum CO2 utilization will both enhance the reactor performance.

Figure 5 gives the temperature comparison in different reactors. The optimized cooling temperatures T_a all show up and down fluctuation changes and have local minima and maxima points. The cooling temperature of the Case 1 reactor shows a sharp change at the inlet and outlet, with higher values at the inlet and lower values at the outlet. The Case 2 reactor have the lowest value for the hot spot temperature of the reaction gas, the CO2 utilization rate is increased at the same time as the temperature is lowered, thus facilitating the maintenance of good catalyst activity during long-term operation.

Table 2. Comparison of values of indicators for different reactors

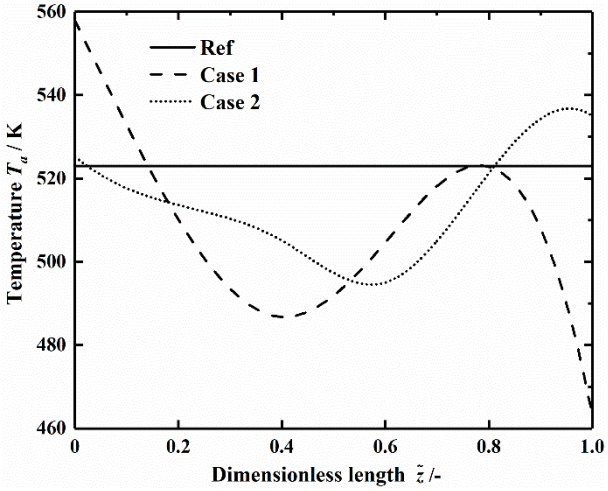
Reactor	Methanol yield (mol/s)	CO2 utilization rate (-)
Reference	1.30×10^{-4}	37.7%
Case 1	1.38×10^{-4}	38.1%
Case 2	1.36×10^{-4}	39.8%

Figure 6 gives the flow rate comparison in different reactors. Compared to the reference model, the methanol flow rates in Case 1 all maintain a high growth rate, while the methanol flow rate in Case 2 starts to grow faster in the second half of the reactor. The CO_2 flow rate in the Case 2 reactor shows a sharp decrease near the outlet and exceeds that of the reference and Case 1 reactors.

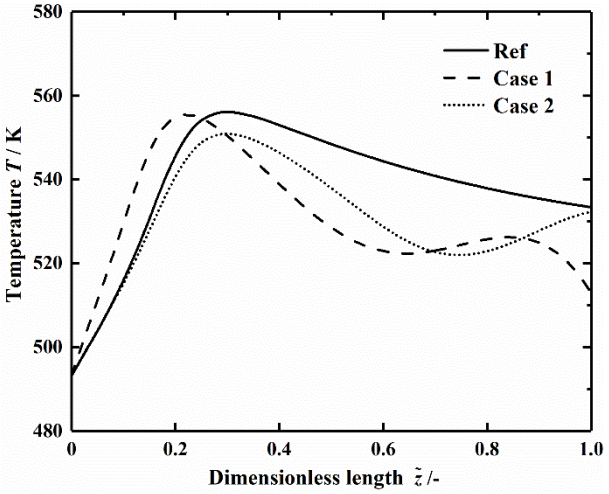
4.5 Engineering Applications

To make the optimized temperature distribution curves more practical, the method of segmenting cooling can be used to approach the optimized profile. At the same time, different saturated boiling medium temperatures can be achieved by adjusting the pressure in industry. Figure 7 shows the temperature curve distribution of two-stage cooled reactor. The intersection points of the optimized temperature curve and the constant temperature curve 523 K (at z/L=0.14) is taken as the demarcation point, and the average value of the curve data points is taken as the modified cooling temperature.

That is, the cooling temperature of 540.4K is used at the z/L<0.14 position, and the cooling temperature of 503.9K is used at remaining position. Table 3 compares the parameter values of the two-stage cooling reactor with those of the reference reactor. It is calculated that the methanol yield is increased by 5.38% by using the method of stage cooling. With the increase of cooling stage, the temperature profile is more and more close to the optimal profile curve, but at the same time, but the input cost of the corresponding equipment also increases. Therefore, decision makers need to comprehensively measure the relationship between equipment input cost and methanol yield output in industrial applications.

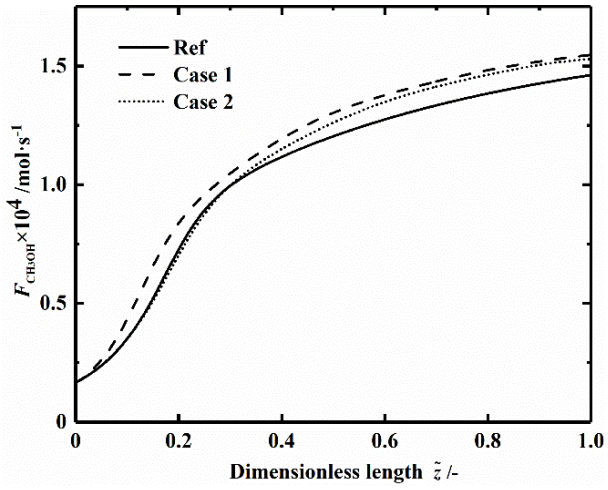


Cooling temperature

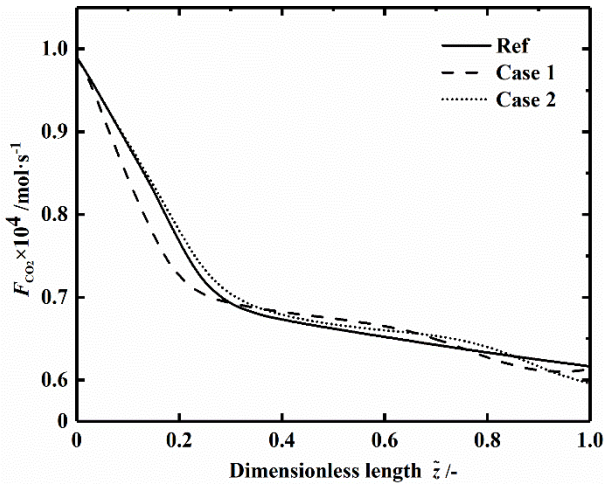


Reaction gas temperature

Figure 5. Comparison of temperatures in the reactor

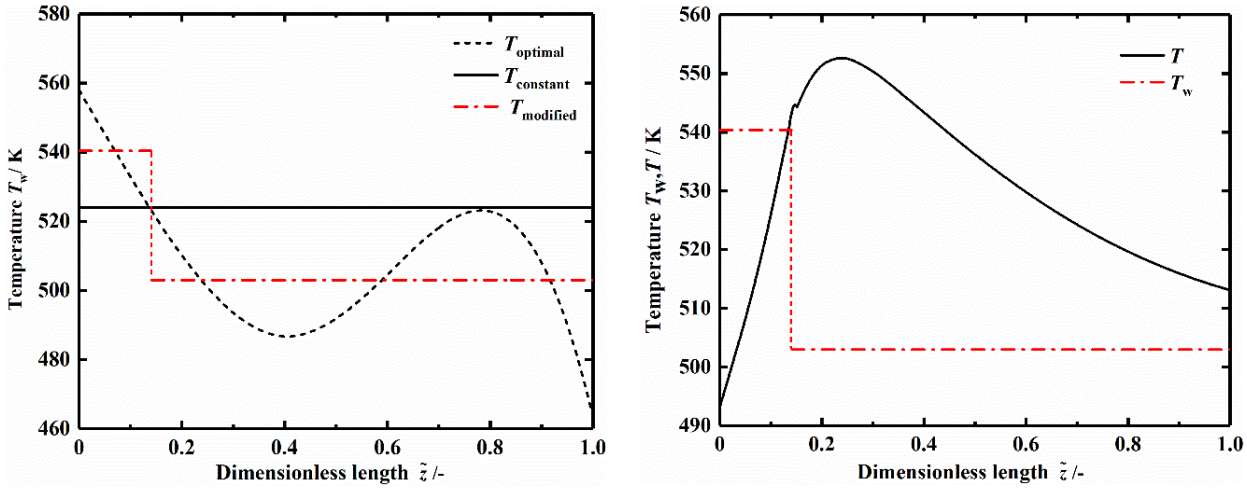


Methanol



CO_2

Figure 6. Comparison of methanol and CO_2 flow rates in the reactors



(a) Two-stage cooling temperature (b) Application temperature

Figure 7. Temperature curve distribution of the two-stage cooled reactor

5. Summary

In this paper, a reactor model for methanol synthesis is developed to optimize the cooling temperature distribution under the objectives of maximum methanol yield and maximum CO2 utilization, and the following conclusions are obtained.

Compared to the reference model, the optimized methanol yield can be increased by 6.57%, while the CO2 utilization rate is increased from 37.7% to 39.8%.

The optimal cooling profiles under both optimization objectives show upward and downward fluctuations. the optimal cooling temperature of Case 1 varies sharply at the inlet and outlet, and the reaction gas temperature of Case 2 has a lower temperature hotspot.

The optimum temperature distribution can be approximately achieved by using the stage cooling method, and the methanol yield can be increased by 5.38% after application.

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