

# On Application of Computer Simulation Technology in Methanol Synthesis in the Coal Chemical Industry

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In this paper, we build a one-dimensional pseudo-homogenous mathematical model for the interpolate heat-exchange synthesis reactor in the methanol synthesis process in the coal chemical industry and embed Aspen Plus to conduct computer process simulation. The simulation results are well consistent with the measured values. We use this model to analyze the effects of inlet temperature, operating pressure and feed rate on the methanol concentration at the outlet of the reactor and at the same time analyze the effects of catalyst in different periods on the yield distribution of coarse methanol. The simulation results show that the operating pressure should be properly increased and the inlet flow should be properly controlled in the production process to ensure methanol yield.

## 1. Introduction

As a basic organic chemical material, methanol is widely used in various industrial production fields like medicine, fuel, coating and synthetic materials (Mondragon et al., 1982; Ratanakandilok et al., 2001). In 1923, the German company BASF synthesized methanol for the first time using carbon monoxide and hydrogen at 300~400°C and 30~50MPa through zinc-chromium catalyst. Currently, there are mainly two ways to produce methanol - coal-based and natural gas-based (Yoon and Erickson, 2008; Halmann and Steinfeld, 2006; Ozaki et al., 1986). The coal-to-methanol process is usually composed of coal gasification, transformation, purification, synthesis and rectification. The synthesis section is the core part of the whole methanol production process. However, the methanol synthesis reactor is often unstable. The inlet temperature, flow, pressure and drum-steam pressure of the synthetic gas all have great effects on the quality of coarse methanol, and it is also very difficult to control the temperature of the synthesis reactor (Iwai et al., 2002); Trop et al., 2014; Bimer et al., 1993).

In light of the above issues, it is necessary to simulate and optimize the synthesis process of coal-based methanol to find the production bottlenecks so as to improve production and at the same time provide guidance to the actual production operation.

## 2. Simulation and analysis of the methanol synthesis section

In this paper, we use Aspen Plus to simulate the whole process. The interpolate heat-exchange methanol synthesis reactor is adopted in the methanol synthesis process, so a one-dimensional pseudo-homogenous mathematical model needs to be established for the methanol synthesis reactor.

### 2.1 Methanol synthesis reaction

Major reactions involved in the methanol synthesis process include (Cagniant et al., (1994); Zhang and Gao, 2015, Zhang et al., 2016):



## 2.2 Mathematical model for the methanol synthesis reactor

The interplate heat-exchange methanol reactor is adopted in the synthesis section. However, the existing models in Aspen Plus cannot effectively express this reactor form. Therefore, in this paper, we establish a one-dimensional pseudo-homogenous mathematical model for the interplate heat-exchange reactor and use the user model interface provided by Aspen Plus to connect with the whole synthesis process, which can not only show the features of the reactor, but also utilize many optimized functions of Aspen Plus like the powerful database and sensitivity analysis.

Casale methanol synthesis reactor is adopted in the synthesis section, which uses plate type heat exchange. The heat exchange plates are arranged vertically in the reactor, through which boiler water is transferred. In the process, the byproduct is medium pressure steam. Between the plates is catalyst packing. The catalyst bed in the whole methanol synthesis reactor is of an axial structure, in which, the heat exchange plates are directly immersed in the catalyst bulk materials. This structure allows high gas space velocity and can easily remove the heat, leading to even higher heat transfer efficiency of the reactor. And because of the large amount of catalyst loaded, the production capacity is also greatly improved. Therefore, in this paper, we assume that there is no radial temperature difference and concentration difference and use a simplified one-dimensional model. We take a cake-like element from the axial reactor for the material and energy balance calculations and obtain the one-dimensional pseudo-homogenous mathematical model, as shown below.

$$\frac{dy_{CO}}{dl} = \frac{A\rho_b}{N_T} [r_{CO}(1-2y_{CO}) - 2r_{CO}y_{CO}] \quad (4)$$

$$\frac{dy_{CO_2}}{dl} = \frac{A\rho_b}{N_T} [r_{CO_2}(1-2y_{CO_2}) - 2r_{CO}y_{CO_2}] \quad (5)$$

$$\frac{dT_b}{dl} = \frac{1}{N_T C_{p,b}} [A\rho_b \alpha (\Delta H_{R,CO} r_{CO} + \Delta H_{R,CO} r_{CO_2}) - K_{bW} S (T_b - T_w)] - Loss \quad (6)$$

$$\frac{dT_w}{dl} = \frac{K_{bW} S}{N_{T,W} C_{p,W}} (T_b - T_w) \quad (7)$$

Boundary conditions: when  $L=0$ ,  $T_b = T_b^0$ ,  $y_{CO} = y_{CO}^0$  and  $y_{CO_2} = y_{CO_2}^0$ .

We use Fortran language to build this model and use the fourth-order Runge~Kutta method to solve it. The fourth-order Runge~Kutta method is as follows.

If  $y' = f(x, y)$  and  $y(x_0) = y_0$ , then

$$k_1 = f(x_i, y_i)$$

$$k_2 = f\left(x_i + \frac{h}{2}, y_i + \frac{h \times k_1}{2}\right)$$

$$k_3 = f\left(x_i + \frac{h}{2}, y_i + \frac{h \times k_2}{2}\right)$$

$$k_4 = f(x_i + h, y_i + h \times k_3)$$

$$y_{i+1} = y_i + \frac{h}{6} (k_1 + 2k_2 + 2k_3 + k_4)$$

## 2.3 Call to the user subroutine of the synthesis reactor by Aspen Plus

To achieve the combination of Aspen Plus and external Fortran subroutine, we must first write the Fortran subroutine with the parameter names and forms, etc. that are consistent with the Aspen specifications. Then we follow the steps below to complete the call to the external subroutine interface of Aspen Plus:

- (1) Activate Aspen Plus Simulation Engine, enter "aspcomp filename.f" into the popup edit box to compile the Fortran file, and then input "asplnk filename.dll" to generate link files.
- (2) Enter the names and paths of the compiler-generated .opt and .dll files into the .opt file and save it.
- (3) Enter the path of the .opt file in the Run/Setting/Engine Files/Linker in the menu bar in the Aspen Plus simulated file.

(4) Insert the subprogram name and its internal array values in the corresponding position of the Aspen Plus module that calls the subroutine.

## 2.4 Process description

The flow chart for the methanol synthesis section is shown Figure 1.

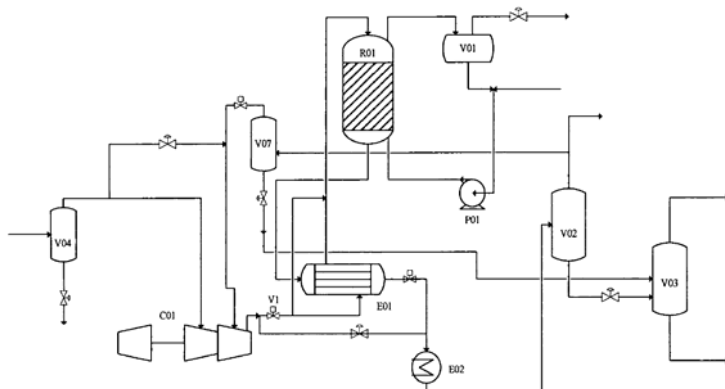


Figure 1: Industrial flow sheet of methanol synthesis process

The syngas from the combined compressor C01 is preheated in the feed/effluent heat exchanger E01 and then mixed with the E01 bypass gas to the inlet temperature for synthesis reaction and then routed from the top of the methanol synthesis reactor R01. In R01, under the action of the synthetic catalyst, CO, CO<sub>2</sub> and H<sub>2</sub> react with each other to produce coarse methanol. The reactant gas from the outlet of R01 is cooled down in the feed/effluent heat exchanger E01, where a part of methanol is condensed. Then the reactant gas passes through the methanol water cooler E02 for cooling. Through the separator V02, coarse methanol is separated from the gas-liquid mixture and routed to the flash tank V03 for flashing. The coarse methanol is depressurized to 0.6MPa to flash off most of the gases dissolved in methanol. The flashed coarse methanol is sent to the coarse methanol tank.

The desalted water in the heat exchange plates of the methanol synthesis reactor R01 removes the reaction heat from the synthesis reactor and then enters the steam pocket to produce steam. The boiler water inside the steam pocket is mixed with the boiler feed water coming externally after being heated in the steam heating furnace and then routed to the inlet of the hot water circulation pump for recycling.

## 3. Simulation results and analysis

### 3.1 Simulation results

Through the methanol synthesis reactor model established in this paper and the embedded Aspen program, we carry out simulation and obtain the axial temperature of the synthesis reactor bed and the concentration distribution of the components, as shown in Table 1.

Table 1: Profiles of temperature and mole fraction along axial direction of reactor

Reactor height (m)	T <sub>b</sub> (°C)	T <sub>w</sub> (°C)	CO (mol%)	CO <sub>2</sub> (mol%)	CH <sub>3</sub> OH (mol%)	H <sub>2</sub> (mol%)	H <sub>2</sub> O(mol%)	α
0.00	193.00	220.00	0.1040	0.0237	5.0E-04	0.6833	3.300E-03	0.757
1.00	217.58	220.00	0.0976	0.0239	8.54E-03	0.6780	3.600E-03	0.601
2.00	233.22	220.00	0.0902	0.0239	0.0183	0.6714	4.024E-03	0.514
3.00	241.16	220.00	0.0831	0.0240	0.0279	0.6650	4.468E-03	0.476
4.00	243.96	220.00	0.0766	0.0241	0.0366	0.6591	4.867E-03	0.463
5.00	244.01	220.00	0.0708	0.0242	0.0444	0.6539	5.200E-03	0.463
6.00	242.00	214.01	0.0655	0.0243	0.0514	0.6492	5.470E-03	0.472
7.00	235.73	202.15	0.0605	0.0244	0.0580	0.6449	5.704E-03	0.502
8.00	226.20	188.51	0.0556	0.0245	0.0645	0.6406	5.945E-03	0.552
9.00	213.92	173.70	0.0511	0.0246	0.-705	0.6366	6.201E-03	0.623

The temperature of the catalytic bed is raised from 193°C to a hot-spot temperature of 244°C and reduced to 214°C at the outlet. The temperature does not fluctuate much, which helps prolong the service life of the catalyst, and in this temperature section, the catalyst can maintain high activity. The boiler water reaches the saturated temperature at a bed height of 5m.

We use the User2 module in Aspen Plus to embed the reactor model into the whole process and adopt the PSRK property method for simulation. The results are in good agreement with the factory measured data. The calculated values and measured values of the components of coarse methanol at the bottom of V2003 are shown in Table 2.

Table 2: Comparison between simulated and measured values of components in crude methanol

Composition	CH <sub>3</sub> OH (mol%)	H <sub>2</sub> O (mol%)	CO <sub>2</sub> (mol%)	CO (mol%)	H <sub>2</sub> (mol%)	N <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)
Measured value	90.23	8.810	-	-	-	-	-
Simulation value	91.10	8.554	0.3041	39 ppm	298 ppm	71 ppm	226ppm
relative error	0.95%	2.99%	-	-	-	-	-

The results show that the relative errors in methanol and water content are only 0.95% and 2.99%, respectively. It can be seen that the simulation process has well expressed the actual production process and can be used as the basis for further analysis.

### 3.2 Sensitivity analysis on major operating parameters

#### 3.2.1 Effect of the feed gas inlet temperature

When the feed gas inlet temperature of the reactor is raised from 180°C gradually to 250°C and other conditions remain unchanged, the simulation results are shown in Figure 2.

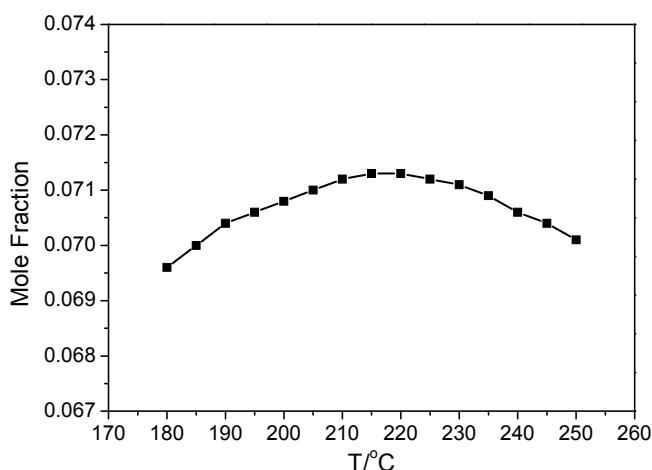


Figure 2: Mole fraction of methanol in outlet of reactor at different inlet temperature

It can be seen from the figure that the molar fraction of methanol at the outlet of the reactor has a tendency to increase first and then decrease with the increase of the inlet temperature, and the amplitude is very small, with the difference between the maximum and minimum values being only about 0.002. This is because the cooling water in the heat exchange plate transfers the reaction heat away in time and there is sufficient heat exchange between the catalyst bed and the heat exchange system, so that the bed temperature distribution is less affected by the inlet temperature. Therefore, adjusting the primary and secondary line fraction through valve V1 to indirectly control the reactor inlet temperature has little effect on increasing the concentration of the exported methanol and reducing the hot-spot temperature, but it can keep the temperature near the top of the reactor within a range at which the catalyst is highly active.

#### 3.2.2 Effect of the reactor operating pressure

When the operating pressure at the top of the reactor is gradually increased from 4.4MPa to 5.5MPa and the other conditions remain constant, the simulation results are shown in Figure 3.

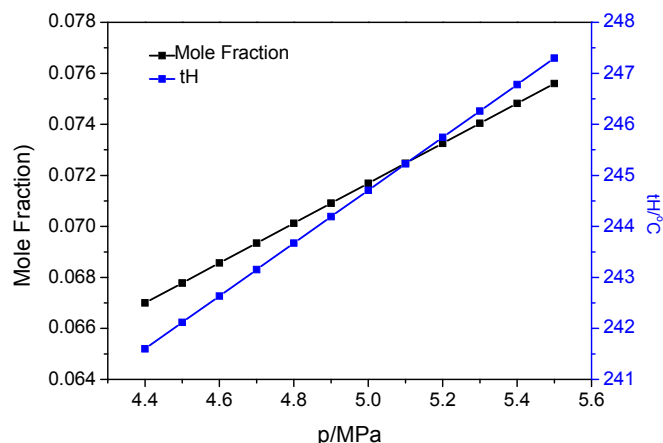


Figure 3: Mole Fraction of methanol and hot-spot temperature at different pressure of bed

As can be seen from the figure, with the increase in pressure, the exit concentration of methanol is increased significantly, and the bed hot-spot temperature is also increased. The average pressure is increased by 1MPa, the mole fraction of methanol increased by 0.01, and the bed hot-spot temperature increased by 4°C. From the dynamics point of view, the pressure is increased and the reaction rate is accelerated. From the chemical equilibrium point of view, the pressure is increased and the reaction equilibrium moves towards the generation of methanol. Therefore, improving the operating pressure of the reactor helps increase the exit concentration of methanol. But taking into account the effect of hot-spot temperature on the catalyst activity, the operating pressure of the reactor cannot be excessively high.

### 3.3 Effects of catalyst in different periods

When the service time of the catalyst is increased from 0h to 8000h, the activity of the catalyst decreases over time. If the operating conditions remain constant, the production of coarse methanol at the outlet of the flash tank V2003 is shown in Figure 4.

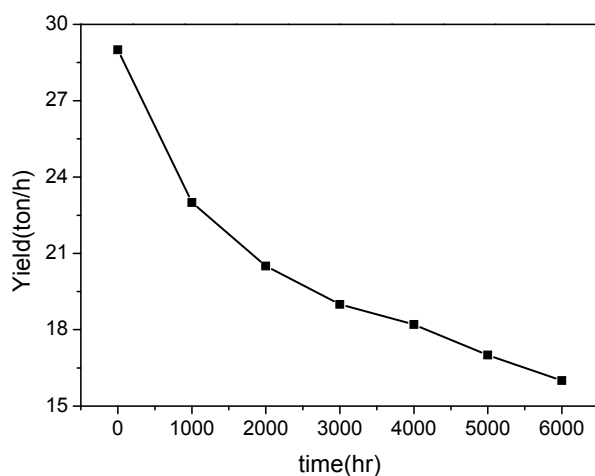


Figure 4: Yield of methanol at different time

As can be seen from the figure, as the catalyst service time increases, the flow of coarse methanol at the bottom of the reactor gradually decreases. Therefore, when the production proceeds to the later stage of the catalyst, we should take measures such as increasing the operating pressure to ensure methanol yield.

## 4. Conclusions

In this paper, we use the Aspen Plus user defined program to write the methanol synthesis reactor model and imbed Aspen Plus to conduct simulation and analysis, which solves some common problems in the methanol production in the coal chemical industry. The conclusions are as follows:

(1) We verify the model by comparing the concentrations of the components in coarse methanol at the outlet of V03 and find that the one-dimensional pseudo-homogenous mathematical model established for the interplate heat-exchange methanol synthesis reactor can well express the actual production behaviors.

(2) The operating pressure of the synthesis reactor has a great effect on the methanol yield. The concentration of methanol at the outlet of the reactor increases with the rise of the operating pressure, but considering the rise of the hot-spot temperature, the operating pressure cannot be too high.

(3) Inlet stream temperature has little effect on the methanol concentration, but with the increase of flow, the methanol yield goes in the opposite direction with the concentration, so while ensuring the yield of coarse methanol, we should also control the inlet temperature appropriately.

(4) At the late stage of the catalyst, the catalyst become less active, so the operating pressure should be increased to ensure methanol yield.

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