Three-dimensional numerical simulation of hydrogen production from coke oven gas reformer

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Abstract. The non-catalytic partial oxidation process is a simple and efficient gasification furnace conversion process. In this paper, a three-dimensional numerical simulation of a coke oven gas reforming furnace is carried out. This calculation uses the component transport model to simulate the combustion reaction in the furnace. The reason for the reactor is GRI-Mech 3.0. The calculation results show that when the syngas stays in the furnace for a short period of time, the increase of pressure is beneficial to the conversion of methane, and the H₂/CO ratio will increase slightly with the increase of pressure.

1. Foreword

Energy is the material basis for human survival and development. With the development of science and technology, the demand for fossil energy has increased. Natural gas is mainly composed of methane. Compared with coal, natural gas is a clean and efficient low-carbon base energy. In recent years, the exploitation of gaseous hydrocarbons in China has gradually accelerated, and the increasing output has stimulated the upgrading of natural gas application technology [1].

The use of natural gas to produce syngas (CO+H₂), and the production of ammonia, methanol and other chemicals as well as clean oil products are common process technologies in energy and chemical industry. After nearly a hundred years of development, a variety of different processes have been formed, including steam reforming process, non-catalytic partial oxidation process, catalytic partial oxidation process and carbon dioxide reforming process, among them, the non-catalytic partial oxidation synthesis process of natural gas [2] is increasingly favored because it does not require pretreatment of raw materials, simple equipment, and the molar ratio of H₂ and CO in syngas is close to the theoretical requirements of methanol and ethylene glycol synthesis.

For the above reasons, many researchers have invested in the research work of non-catalytic partial oxidation synthesis of natural gas. Vegendla S. N. P [3] uses OpenFOAM to solve the flow equation and couples the multi-inlet small flame combustion model to simulate the turbulent reaction of single-phase gas in the gasifier, by analyzing the flow rate and flame time scale, the effectiveness of the flame gasification model under gasification conditions is studied in detail. The CFD-flamelet simulation results are compared with the experimental values at the exit, which has good consistency; Li Xinyu et al [4] studied the characteristics of microwave oxygen diffusion flame on the non-catalytic partial oxidation hot model experimental device of natural gas, and explored the jet velocity, diffusion...
mode and the influence of O₂/ CH₄ on the flame morphology; the non-catalytic partial oxidation process has also been applied to small-scale distributed hydrogen production systems [5]. In recent years, many researchers have studied the realization of non-catalytic partial oxidation of natural gas in internal combustion engines, this process supplies hydrogen to a distributed hydrogen storage device while utilizing the heat generated during the reaction to output power to the outside of the system.

The content of this paper is to establish a three-dimensional model of a coke oven gas reforming furnace, simplify the GRI-Mech 3.0 methane chemical reaction mechanism model [6] and couple it with CFD software to analyze the reaction process and results of the non-catalytic partial oxidation reaction.

2. Calculation object

The structure of the reformer is shown in Figure 1. The total height of the furnace is 5.4m. The upper part of the furnace contains a circular O₂+H₂O inlet with a radius of 30mm and a circular coke oven gas inlet with an outer diameter of 1m, the furnace exit is located at the bottom of the furnace and is surrounded by a layer of refractory bricks.

![Figure 1. Reformer structure.](image)

At the inlet of the circular O₂+H₂O, O₂ and H₂O are mixed at a ratio of approximately 1:1, the mixing pressure is 1.8 MPa, and the temperature is 560 K; the main inlet of the coke oven gas is CH₄, H₂O, O₂, N₂, etc., the inlet pressure is 2.3 MPa, and the temperature is 890K.

3. Pre-emulation processing and setting

The model is divided by structure grid, and the calculation domain is divided into two regions. the upper part is an ordinary fluid domain, and the refractory brick at the exit of the furnace is set as a multi-empty medium area, and the porosity is set to 0.3, the viscous drag coefficients in the x, y, and z directions are set to 3e+07, 3e+07, and 3e+05, respectively, and the inertial drag coefficients are 15000, 15000, and 200, respectively.

This calculation uses the component transport model (Finite rate/vortex dissipation model) to simulate the combustion reaction in the furnace, and the finite rate model describes the chemical reaction process using the total package mechanism reaction:

\[
\frac{\partial}{\partial t} (\rho Y_s) + \frac{\partial}{\partial x_j} (\rho v_j Y_s) = \frac{\partial}{\partial x_j} \left( D \frac{\partial Y_s}{\partial x_j} \right) - w_s
\]  

(1)

The laminar finite-rate model uses the Arrhenius equation to calculate the reaction rate as the source term, ignoring the influence of turbulent pulsation, and is suitable for combustion with slow reaction rate and small turbulent pulsation. The reaction equation is:

\[
\frac{\partial}{\partial t} (\rho Y_s) + \frac{\partial}{\partial x_j} (\rho v_j Y_s) = \frac{\partial}{\partial x_j} \left( D \frac{\partial Y_s}{\partial x_j} \right) - w_s
\]  

(2)

\[
W = k C_A^a C_B^b = k_0 \exp \left( -\frac{E}{RT} \right) C_A^a C_B^b
\]  

(3)
Where $E$ is the activation energy of the reaction; $CA$ and $CB$ are the reactant concentrations; $a$ and $b$ are the chemical reaction measures; $k_0$ is the previous factor.

The eddy dissipation model is based on the fast combustion hypothesis, that is, the chemical reaction rate is faster than the turbulent diffusion rate, and the combustion process is controlled by the mixing of fuel and oxidant, the eddy dissipation model is suitable for turbulent flow with high Reynolds number and rapid chemical reaction combustion with high $Da$ number. The finite rate/vortex dissipation model combines the Arrhenius formula with the eddy dissipation equation. The net reaction rate takes the smaller of the two rates, combining dynamics and turbulence.

The reason for the reaction machine GRI-Mech 3.0 methane detailed chemical reaction mechanism model simplification, the simplified mechanism model includes 14 components and 18 elementary reactions, the reaction is shown in Table 1. The reaction mechanism and thermodynamic file were imported into the solver in the Chemkin format for calculation.

| Reaction Number | Reaction Equation |
|-----------------|-------------------|
| (1)             | $O + H_2 \leftrightarrow H + OH$ |
| (2)             | $H + O_2 \leftrightarrow O + OH$ |
| (3)             | $H + OH + M \leftrightarrow H_2O + M$ |
| (4)             | $OH + H_2 \leftrightarrow H + H_2O$ |
| (5)             | $2OH \leftrightarrow O + H_2O$ |
| (6)             | $O + CH_4 \leftrightarrow OH + CH_3$ |
| (7)             | $H + CH_4 + M \leftrightarrow CH_2 + M$ |
| (8)             | $H + CH_4 \leftrightarrow CH_3 + H_2$ |
| (9)             | $OH + CH_4 \leftrightarrow CH_3 + H_2O$ |
| (10)            | $O + CH_3 \leftrightarrow H + CH_2O$ |
| (11)            | $H + CH_2O + M \leftrightarrow CH_2 + M$ |
| (12)            | $CH_4 + O_2 \leftrightarrow OH + CH_2O$ |
| (13)            | $H + CH_2O \leftrightarrow HCO + H_2$ |
| (14)            | $OH + CH_2O \leftrightarrow HCO + H_2O$ |
| (15)            | $H + HCO \leftrightarrow H + CO$ |
| (16)            | $OH + HCO \leftrightarrow H + CO_2$ |

4. Calculation results

The influence of different furnace pressures on the synthesis synthesis gas of non-catalytic partial oxidation process was investigated by using CFD software. The calculation of the volume parameters of the reforming furnace and the parameters of the coke oven gas were not changed, and the flow field in the furnace was not changed much. Figure 2 shows the distribution of the molar composition of the furnace under the design condition of the reformer (operating pressure is 6 atm), and the volume fraction distribution of $H_2$ conforms to the regional distribution theory of the reformer. Figure 3 is a schematic diagram of the average mole fraction of the $H_2$ outlet and the $H_2/CO$ ratio as a function of pressure (6 atm-30 atm). It can be seen from the figure that during the process of increasing the pressure from 6 atm to 30 atm, the hydrogen content in the synthesis gas of the model is gradually increased, according to the reaction equation, the formation of $H_2$ and CO by $CH_4$, $H_2O$, and $O_2$ is a volume-increased reaction. Theoretically, increasing the pressure should inhibit the conversion of methane, which is contrary to the law in the figure, analysis of the cause shows that the reactor outlet has not reached equilibrium, and the increase in pressure increases the forward reaction rate; the $H_2/CO$ ratio at the outlet is generally around 1.6 and increases slightly with the increase of...
pressure. This ratio is close to the theoretical requirement of methanol and ethylene glycol synthesis, which shows the superiority of the non-catalytic partial oxidation method.

Figure 3. The effect of pressure changes on the export of syngas

In this simulation, the syngas exits directly at the outlet of the reactor, and the reversible reaction does not reach equilibrium. In the industrial reformer, the syngas has a certain residence time in the reformer. When the gas residence time is short, it is closer to the simulation condition. Appropriately increasing the operating pressure is beneficial to the conversion of methane; when the gas residence time is longer, according to the chemical equilibrium principle, increasing the pressure will inhibit the reaction of methane.

5. Conclusion

In this paper, the physical model of a non-catalytic partial oxidation mode coke oven gas reformer is established. The numerical calculation is carried out using CFD software. The calculation results are in line with the basic principle of the gasifier, the H₂ mole fraction at the exit of the furnace is about 0.64, and the H₂/CO ratio is about 1.6. When the syngas stays in the furnace for a short time, the pressure rise is conducive to the conversion of methane, and the H₂/CO ratio will increase slightly with the increase of pressure; when the syngas stays in the furnace for a long time, the predicted increase in pressure will inhibit the conversion of methane.

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