CFD Modeling of Exhaust Heat Recovery Using Methane Steam Reforming in Steam Reformer of Chemically Recuperated Gas Turbine

Qian Liu, Hongtao Zheng, Lin Cai, Qiang Long, Ren Yang

Abstract

To ensure the maximum exhaust heat recovery in different working conditions in Steam Reformer (SR) of Chemically Recuperated Gas Turbine (CRGT), this paper studied the influence of steam to carbon ratio (S/C), reformer inlet temperature, and total mass flow rate in catalytic bed on the reactant conversion, product selectivity, heat recovery rate and fuel calorific value increasing rate by numerical simulation. It's noted that the working parameters are given based on the chemically recuperated test bench. The model considered catalytic bed as porous media region using Fluent, including fluid flow, heat transfer and chemical reactions on reformer. Chemical reaction rates were implemented in C language and were used as a User-Defined Function (UDF) in Fluent. As a result, in single stage SR, namely the insulating tubular reactor, the reactant temperature and concentration continually decline along the axial position, especially in the inlet decline significantly. The higher inlet temperature is better for reactant conversion and heat recovery rate. When steam mass flow is fixed, the higher S/C is, the lower heat recovery rate is. In a certain total mass flow rate, the length L of reaction zone has no significant influence on the reactant conversion, product selectivity, heat recovery rate and the fuel calorific value increasing rate. When the length L is fixed, as total mass flow rate increases, methane conversion and fuel calorific value increasing rate reduce, while, heat recovery rate increases. The proposed research confirms optimal fuel mass flow and S/C in reformer under certain working conditions, and provides the basis for operation and regulation of Chemically Recuperated Test Bench.

Keywords: Steam Reformer; Exhaust Heat Recovery; Reaction Kinetics; Numerical Simulation

1. Introduction

Chemically Recuperated Gas Turbine (CRGT) can be used as the engine for ship owing to higher thermal efficiency and lower NOx emission. The Steam Reformer (SR) as the kernel component can take advantage of exhaust from gas turbine by the strong endothermic fuel steam reforming reaction. High-efficiency heat recovery is the key benefit of SR. To pack the catalyst conveniently and reduce the volume of SR as small as possible, SR is separated with the superheater and heat exchanger, seen in Figure 1. First, superheated vapor steam from superheater mixed with fuel enter into SR. Second, strong endothermic reactions occur in SR so that the cracked gas temperature is lower. Then to ensure the combustion stability, the cracked gas flows through heat exchanger and last flows into the combustion chamber. In this paper, single stage SR model schematic diagram is shown in Figure 2. The length of every part for SR is L.

In term of the design of SR, scholars carried out some research on SR by means of simulation. Assuming that steam reforming reactions in equilibrium conversion process, they established mathematical model for SR, studied the impact factors for its performance, and put forward some ideas about its structure design [1-3]. However, they only considered thermodynamic effects, without taking into account the influence of chemical kinetic, which was not enough accurate for SR structure design.

Methane steam reforming technology (MSR) was developed in the nineteen thirties. Its industrial application for hydrogen production is relatively mature. In order to improve the hydrogen yield and
purity, scholars have carried out a large number of experimental researches on catalyst, reactor design and reaction process [4-6]. Taking into account the experiment expense, numerical simulation has been widely used in the field of combustion [7], fluid mechanism [8], and chemical industrial and so on. Scholars have carried out in-depth researches on methane steam reforming by means of numerical simulation. They have established steady and dynamic mathematical model of methane steam reforming for hydrogen production, and investigate the effects of operating pressure, inlet temperature, S/C, gas hourly space velocity (GHSV) on CH4 conversion, H2 yield and H2 purity by the intrinsic kinetics equations[9,10]. Since the main purpose is to increase the yield of hydrogen, they all considered the conditions that the external wall heat flux was added on the flow. While in the chemically recuperated test bench the reaction parts are in the insulation space, it is necessary to study methane steam reforming in adiabatic condition.

seen in Figure 1, steam is produced from flash chamber under certain pressure, and then enters into superheater. Superheater is an ordinary heat exchanger, in which including heat flux emitted by the flue gas, the conductive heat flux of metal wall and the heat flux absorbed by the steam. When the three heat fluxes are equal, heat transferred reaches equilibrium. When enthalpy of flue gas side is constant, due to little change of heat transfer coefficient in the steam side, as steam flow rate increases, the steam temperature decreases; on contrary, with steam flow rate decreasing, the steam temperature increases. Limited by other factors, there is not monotonous proportional relationship between the steam temperature and steam mass flow, and the specific values obtained by overall water system simulation. When the steam is generated in a certain amount, different fuel injection quantity is put into different S/C for SR. It’s necessary to mention that those are actual work processes. In order to study the impact
of a variable on reforming process, other variables need to remain unchanged.

Consequently, to provide the basis for control system of chemically recuperated test bench, it’s necessary to determine the effect of inlet temperature, S/C and total mass flow rate on fuel caloric value increasing rate and heat recovery rate. The length L is going to be optimized to maximize the methane conversion, meantime, and minimize the SR dimensions. It’s better to ensure effective exhaust heat utilization and improve the utilization rate of exhaust heat.

The steam reforming kinetics adopted in this paper was developed by Xu and Froment[11] over a Ni/MgAl2O4 catalyst, a classic study quoted by other scholars [9,12-13]. In this paper, firstly, the mathematical model is validated by comparing the results with experimental data and theoretical equilibrium predictions by CHEMKIN. The experiment was carried out in a reactor with wall temperature of 673K and pressure of 0.1MPa. Secondly, from the point of design and optimal of SR structure, the influence of steam to carbon ratio (S/C), inlet temperature, contact time and total mass flow rate on reactants conversion and products yields is studied by using mathematical model of the steam reforming of methane in conditions of 1.0 MPa and adiabatic. In addition, to judge utilization rate of exhaust heat in SR, the influence on heat recovery rate and fuel caloric value increasing rate is also demonstrated. The proposed research is going to confirm optimal fuel mass flow rate and S/C in reformer under certain working conditions, and provide the basis for operation and regulation of chemically recuperated test bench.

2. Experimental process description

Experimental apparatus and process are illustrated in Figure 3. The feed gas was composed of methane and steam, where steam is generated by steam boiler. The flow rate of methane and water were separately controlled with mass flow controller (Brooks 5850E) and tranquil flow pump (Beijing Xingda Co., 2PB00C). The feed gas flew into reactor after homogeneous mixing. An illustration of the utilized reactor is displayed in Figure 4. The reactor was heated by a ceramic heating pipe and maintained the constant wall temperature through the temperature controller. Qualitative and quantitative analysis of plasma products were carried out on-line with gas chromatograph. Before flowing into gas chromatograph, the products were cooled by cold-trap and dried by allochroic silicagel. The concentration of hydrocarbons and synthesis gas were determined by GC-FID (2m DB-1+ 25 m HP-Al/S Column), GC-TCD (Haysep Q Column +Molecular Sieve 5A Column), respectively. The experiments were carried out at different S/C. The inlet temperature was fixed at 673K and the operating pressure was atmospheric in all cases.

During the experiment, to ensure that the temperature in the catalytic bed reached the set value, reactor was heated by the ceramic heater for two hours before starting the experiment. Temperature transmitters and controllers were used for temperature measurement. Due to thermal inertia, the measured values were deviated from the set point of about 5°C, seen from the controller display.

3. Mathematic modeling of SR

The numerical simulations for the steam reformer were performed using Fluent, considering fluid flow, heat transfer and chemical reactions on reformer. Simultaneous analysis of governing equations and chemical reaction equations is carried out in a multiphysical simulation. Chemical reaction rates are implemented in C language and are used as a User-Defined Function (UDF) in Fluent.

The flow was calculated using the standard \( k-\varepsilon \) turbulence with standard wall functions. The catalytic zone was considered as porous media which were needed to modify the conduction flux and the transient terms in standard energy transport equation and add a momentum source term to the standard fluid flow equations. The properties of catalytic zone are seen in Table 2, which are taken to be the same as experiment. In turbulent flows, packed beds are modeled using both permeability and an inertial loss coefficient.

Regarding the solution accuracy and CPU time, a 2D axis-symmetric model was employed. Considering grid density in zones should increase with species concentration gradients, the grids in reactor entrance were refined. In addition, a very fine mesh was applied near wall in order to resolve the high reaction rate. A view of the model including the boundary conditions and surface meshes are pictured in Figure 5, respectively for validated model (a) and calculated model (b). The analyzed
calculation area in validated model is meshed with hybrid mesh, including triangular mesh in free flow region and quadrilateral mesh in porous media flow region using Gambit. The analyzed calculation area in calculated model is meshed with quadrilateral mesh. Grid-dependent learning is accomplished for the validated model (a) and calculated model (b), and at last the number of cells employed is as following, seen in Table 1. In all cases, the numerical computations were considered to be converged when the scaled residuals of the different variables were lower than $10^{-6}$ for all variables. Mass-flow-inlet and pressure-outlet boundary conditions were used for reactor inlet and outlet, respectively.

Table 1. Meshes

<table>
<thead>
<tr>
<th>Model</th>
<th>Validated model</th>
<th>Calculated model-Length L(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>66422</td>
<td>20600 26880 34632 48000 51200</td>
</tr>
</tbody>
</table>

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<tr>
<td>Cells</td>
<td>66422</td>
<td>20600 26880 34632 48000 51200</td>
</tr>
</tbody>
</table>

Figure 3. Schematic diagram of experimental setup

Figure 4. Schematic diagram of experimental setup

Figure 5. Boundary conditions and the employed meshes
Table 2. Catalytic zone properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst particle diameter $d_p$ (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Porosity (cm$^3$/cm$^3$)</td>
<td>0.445</td>
</tr>
<tr>
<td>Catalyst solid density (kg/m$^3$)</td>
<td>1728</td>
</tr>
<tr>
<td>Bed heat capacity (J/kg K)</td>
<td>871</td>
</tr>
<tr>
<td>Solid thermal conductivity (W/m K)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 3. Reaction Equations

<table>
<thead>
<tr>
<th>Designation</th>
<th>Equations</th>
<th>$\Delta H_{\text{rev}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$</td>
<td>206</td>
</tr>
<tr>
<td>Water Gas Shift</td>
<td>$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$</td>
<td>-41</td>
</tr>
<tr>
<td>Direct Steam Reforming</td>
<td>$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$</td>
<td>165</td>
</tr>
</tbody>
</table>

3.1 Kinetic models

The dominant SMR catalytic chemical reactions are listed in Table 3. The reaction rates of SMR on Ni catalyst are adopted in this study. The combined kinetic model of the steam reforming reactions contains the reaction equilibrium constants, the Arrhenius kinetic parameters, and the Van’t Hoff adsorption parameters, see in Table 4. The corresponding rate equations for SMR reactions $r_i$ [mol (g catmol) h$^{-1}$] are expressed as[11]:

$$r_i = \frac{k_i}{p_i^{1.5}} \left[ p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}} - p_{\text{H}_2} \cdot p_{\text{CO}} \right] K_{\text{eq}_i}$$  

$$r_i = \frac{k_i}{p_i^{1.5}} \left[ p_{\text{CO}} \cdot p_{\text{H}_2\text{O}} - p_{\text{H}_2} \cdot p_{\text{CO}_2} \right] K_{\text{eq}_i}$$  

$$r_i = \frac{k_i}{p_i^{1.5}} \left[ p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}} - p_{\text{H}_2} \cdot p_{\text{CO}_2} \right] K_{\text{eq}_i}$$  

$$DEN = 1 + K_{\text{CO}} \cdot p_{\text{CO}} + K_{\text{H}_2} \cdot p_{\text{H}_2} + K_{\text{CH}_4} \cdot p_{\text{CH}_4} + K_{\text{H}_2\text{O}} \cdot \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

$$p_i = c_{\text{CO}4} + c_{\text{H}_2\text{O}2} + c_{\text{H}_2} + c_{\text{CO}} + c_{\text{CO}_2} \cdot p$$

where $i$ indicates CH$_4$, CO, CO$_2$, H$_2$, H$_2$O.

Table 4. Parameters of intrinsic rate equations[11]

<table>
<thead>
<tr>
<th>Equilibrium Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{eq}_1} = 1.198 \times 10^7 \cdot \exp\left(\frac{-26830}{T}\right)$ kPa$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic Parameters</th>
<th>$A_i$ [mol (g catmol)$^{-1}$ h$^{-1}$]</th>
<th>$E_i$ [kJ mol$^{-1}$]</th>
<th>Adsorption Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction No.</td>
<td></td>
<td></td>
<td>$B_i$ [MPa$^{-1}$]</td>
</tr>
<tr>
<td>1</td>
<td>1.336e15 MPa$^{-0.5}$</td>
<td>240.1</td>
<td>CO</td>
</tr>
<tr>
<td>2</td>
<td>1.955e7 MPa$^{-1}$</td>
<td>67.13</td>
<td>H$_2$</td>
</tr>
<tr>
<td>3</td>
<td>3.226e14 MPa$^{-0.5}$</td>
<td>243.9</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>CH$_4$</td>
</tr>
<tr>
<td>$k_i = A_i \cdot \exp\left(\frac{-E_i}{RT}\right)$</td>
<td>=reaction 1, 2, 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The unit of the reaction rate in the model is mol (g catmol)$^{-1}$ h$^{-1}$, to make it comply with the unit...
in FLUENT, the following equation is used to transform the unit:

$$R_i = \frac{r_i \cdot \rho}{3600}$$  \hspace{1cm} (6)

Reaction rates for the formation of CO and CO\textsubscript{2} and consumption of CH\textsubscript{4} are as follows:

$$R_{CO2} = R_2 + R_s \quad R_{CH4} = -(R_s + R_i) \quad R_{CO} = R_i - R_s$$  \hspace{1cm} (7)

### 3.2 Validation of the model

In order to verify the goodness of the mathematical model, Figure 6 gives the distribution of methane conversion versus S/C, in which the symbols corresponds to experimental data and solid line corresponds to simulation results. It is evident that the kinetic curve fit quite well experimental data.

![Figure 6. Methane conversion VS. S/C: comparison between experimental data and simulation results; methane flow rate =400mL/min, T =673K.](image)

### 4. Results and discussion

Conversion, selectivity and yield are calculated as follows [4]:

$$X_{CH4} = \frac{y_{CH4,e} - y_{CH4,o}}{y_{CH4,o}} \quad S_{CO} = \frac{x_{CO}}{x_{CO} + x_{CO2}} \quad S_{CO2} = \frac{x_{CO2}}{x_{CO} + x_{CO2}}$$  \hspace{1cm} (8)

In the equations $X_{CH4}$ is the conversion of species CH\textsubscript{4}, $y_i$ the mass fraction and $x_i$ the mole fraction of species i in the product stream.

With 1 mol methane as standard, fuel calorific value increasing rate is calculated as follows:

$$\eta = \frac{Q_{product} - Q_{fuel}}{Q_{fuel}}$$  \hspace{1cm} (9)

In the equations $Q_{product}$ is low heat value of combustion of Synthetic fuel in standard state, $Q_{fuel}$ is low heat value of combustion of feed fuel in standard state.

To estimate performance of SR for exhaust heat recovery, heat recovery rate is defined as follows:

$$\kappa = \text{Heat recovery per kilograms} \times \text{total mass flow rate of methane and steam}$$  \hspace{1cm} (10)
4.1 The effects of inlet temperature and length L on methane conversion and products selectivity

Methane concentration distribution versus inlet temperature is shown in Figure 7. The operating conditions are a thermal insulated wall, S/C of 4.0, a mixture of steam and methane flow rate of 0.002665kg/s, and an inlet temperature range from 673K to 873K. The length of reactor is 0.100m. Because of adiabatic wall and strong endothermic reaction of methane steam reforming, methane concentration decreases gradually along the tubular reactor axis. The higher inlet temperature there is for the reactant, the greater the concentration gradient there is near the inlet.

![Figure 7. Methane mass fraction distribution VS. inlet temperature](image)

The operating conditions used in Figure 8 are a thermal insulated wall, S/C of 4.0, a mixture of steam and methane flow rate of 0.002665kg/s, the length L of 0.050m, 0.070m, 0.100m, 0.150m, 0.200m, for different length L the contact time arrange from 509.8 kgcat s/kmol to 2039.2 kgcat s/kmol, and an inlet temperature range from 673K to 873K. The contact time is the ratio of quantity of catalyst to total mole flow rate.

Typical methane conversions versus inlet temperature for different contact time are shown in Figure 8. The positive effect of temperature on methane conversion has been found. The fuel conversion increases with the high inlet temperature. Equilibrium data are also presented, calculated using CHEMKIN basing on STANIAN program, shown as the dashed line, in given inlet temperature of thermal-insulated-wall reactor. In low temperature, methane conversion is lower than chemical equilibrium throughout the increasing contact time. It is indicated that the lower temperature is the longer equilibration time is. In the temperature of 773K, methane conversion coincides with the chemical equilibrium conversion with contact time increasing. However, in higher temperature, the conversion exceeds equilibrium value slightly. The trend in figure 8 is mainly attributed to the
influence of temperature on reaction rate. When inlet temperature is low, the reaction rate is so slow that the residence time has some significant effect on the conversion rate and that methane conversion rate does not reach the equilibrium conversion rate within the given residence time range; and in the higher temperature, methane conversion in different lengths tends to be consistent, and the conversion exceeds equilibrium value slightly by employed kinetic model. But it’s worth taking a moment to flag the fact that the overall trend with the temperature is consistent and in future work we will modify the kinetic model based on experiment data.

Figure 9 shows selectivity versus inlet temperature at different values of contact time, for both CO2 and CO. The operation conditions are set up in the same with last details. In the temperature range of 673K to 873K most methane converted is totally oxidized to CO2. As inlet temperature increases, CO selectivity increases, while CO2 selectivity is on the contrary. This is attributed to the rate of the WGS reaction, where the exothermic reaction becomes more active with a lower reformer temperature.

From Figure 8 and Figure 9 we should note that, when keeping the total mass flow rate as a fixed variable, with inlet temperature increasing, the influence of length of reaction zone on whether methane conversion or product selectivity presents consistent in trend. That is to say, increasing contact time by the way of improving quantity of catalyst is of little effect on the methane conversion.

4.2 The effects of inlet temperature and length L on heat recovery rate and fuel calorific value increasing rate

![Figure 10. Fuel calorific value increasing rate VS. inlet temperature](image1)

![Figure 11. Heat recovery rate VS. inlet temperature](image2)

Because of the adiabatic system, chemical reaction heat required is all from reactant sensible enthalpy. The whole system can be regarded as a constant pressure system, according to the first law of thermodynamics, system enthalpy change is equal to the thermal effects, i.e., the sensible enthalpy change in the tubular reactor is equal to reaction heat, namely recovery heat. Figure 10 presents calculated fuel calorific value increasing rate versus temperature with different values of contact time. It’s noted that the trend of Figure 10 and 11 are consistent with Figure 8. This is because methane steam reaction is strong endothermic reaction, and the increasing of methane conversion inevitably leads to the improvement of fuel calorific value increasing rate of 1 mole methane. In lower temperature, the longer residence time is, the higher methane conversion is. Therefore at a lower temperature, when time=2039.2, the conversion rate and fuel calorific value increasing rate are slightly higher than the other cases. While at a higher temperature, the contact time has little significant effect on heat recovery, which can be corroborative by Figure7 that changes in concentration reach steady near the inlet.

4.3 The effects of S/C on methane conversion and heat recovery rate

When the flow rate and temperature of steam is in a certain amount in the experimental research on the chemically recuperated test bench, in order to clarify the fuel injection quantity, the optimum steam to carbon ratio needs to be determined. The operating conditions used in Figure 12 are a thermal insulated wall, an inlet temperature of 773K, a steam flow rate of 0.0025kg/s, and S/C ranged from 3.0
to 6.0. If the amount of steam is constant, S/C increase will give a proportional decrease in CH4 for high S/C. The dashed line corresponds to equilibrium conversion in different S/C. The tendency of result of the mathematical model is in good agreement with equilibrium conversion. As seen in Figure 13, due to the fuel calorific value increasing rate positively related to methane conversion, with increasing S/C, fuel calorific value increasing rate increases accordingly. On contrary, heat recovery rate presents decreasing tendency. This is because that heat recovery rate is closely correlative to total mass flow rate. So it is evident that smaller S/C is in favor of low-grade waste heat into the chemical energy of the fuel. But taking into account the catalyst carbon deposits, S/C can’t be too small. At last, S/C is elected 4.

![Figure 12. Methane conversion VS. S/C](image1)

![Figure 13. Heat recovery rate(J/s) and fuel calorific value increasing rate VS. S/C](image2)

### 4.4 The effects of total mass flow rate on methane conversion and heat recovery rate

![Figure 14. Methane conversion VS. mass flow rate](image3)

![Figure 15. Heat Recovery Rate(J/s) and Fuel calorific value increasing rate VS. mass flow rate](image4)

The operating conditions used in Figure 14 and 15 are a thermal insulated wall, S/C of 4.0, an inlet temperature of 773K, length L of 0.100m, and total mass flow rate arrange from 0.002665kg/s to 0.007995kg/s. Figure 14 and 15 show the effect of mass flow rate on methane conversions, heat recovery rate and fuel calorific value increasing rate. The methane conversion decreases obviously with the increase of inlet mass flow rate. The fuel calorific value increasing rate matches the tendency of methane conversion. In other words, decreasing contact time by increasing mass flow rate has appreciable impact on methane conversion, which leads finally to the decline of use efficiency of per mole methane. However, an increase in mass flow rate brings in the increase of heat recovery, which represents the ability of a certain catalyst zone for heat recovery is enhanced. From the view of balancing of energy utilization rate and heat recovery rate, an optimized mass flow rate need to be adjusted from time to time based on the working conditions of CRGT.
5. Conclusion

In the insulating tubular reactor, the increment of inlet temperature can efficiently improve reactant conversion and fuel calorific value increasing rate. When steam flow is invariant, to obtain more heat recovery as well as less catalyst carbon deposit, the best steam to carbon ratio is 4. The contact time is directly related to packed quantity of catalyst, i.e. length L and total mass flow rate. When the total mass flow rate is fixed, length L has little effect on methane conversion and heat recovery rate. However, in a certain length L, increasing total mass flow rate can largely decrease fuel calorific value increasing rate, on the contrary, increase heat recovery rate. In the range of 673K to 873K given by design points, the most conversion is 18% and fuel calorific value increasing rate is 2.81% which have a gap with the expectation of 60% and 10% separately. So using non-equilibrium plasma with catalyst synergism for methane steam reforming will be new means to achieve sufficient utilization of dynamic mechanical exhaust heat.

6. References