

# Effect of oxygen distribution for hot spot and carbon deposition minimization in a methane autothermal reforming reactor

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**Key Words :** Autothermal reforming, Oxygen distribution, Carbon deposition, Hot spot

## Abstract

In autothermal reforming reaction, oxygen to carbon ratio (OCR) and steam to carbon ratio (SCR) are significant factors, which control temperature and carbon deposition into the reactor. The OCR is more sensitive than the SCR to affect the temperature distribution and reforming efficiency. In conventional operation, hydrocarbon fuel, steam, and oxygen was homogeneously mixed and injected into the reactor in order to get hydrogen-rich gas. The temperature was abruptly raised due to fast oxidation reaction in the former part of the reactor. Deactivation of packed catalysts can be accelerated there. In the present study, therefore, the effect of the oxygen distribution is introduced and investigated to suppress the carbon deposition and to maintain the reactor in the mild operating temperature (e.g., 700~800°C). In order to investigate the effect numerically, the following models are adopted; heterogeneous reaction model and two-medium model for heat balance.

### Nomenclature

$a$  : Interstitial heat/mass transfer surface area ( $\text{m}^2/\text{m}^3$ )  
 $C_p$  : Heat capacity ( $\text{kJ}/\text{kmol K}$ )  
 $F$  : Heat/mass flux ( $\text{kJ}/\text{m}^2\text{s}$ ,  $\text{kg}/\text{m}^2\text{s}$ )  
GHSV : Gas hourly space velocity ( $\text{h}^{-1}$ )  
; Gas volume flow rate divided by catalyst volume at 0°C, 1atm  
 $h$  : Heat/mass transfer coefficient ( $\text{W}/\text{m}^2\text{K}$ ,  $\text{m}/\text{s}$ )  
 $M$  : Molecular weight ( $\text{kg}/\text{kmol}$ )  
OCR : Oxygen to carbon ratio (mole/mole)  
 $R$  : Rate of reaction ( $\text{kmol}/\text{kg}_{\text{cat}}\text{s}$ )  
SCR : Steam to carbon ratio (mole/mole)  
 $T$  : Temperature (K)  
 $Y$  : mass fraction  
 $\Delta H$  : Heat of reaction ( $\text{kJ}/\text{kmol}$ )

### Subscript

cat : Catalyst  
d : Mass transfer  
eff : Effective  
f : Fluid

$i$  : Species  $i$   
s : Solid  
t : Heat transfer

### Greek letters

$\varepsilon$  : Porosity  
 $\rho$  : Density ( $\text{kg}/\text{m}^3$ )  
 $\eta$  : Effectiveness factor

## 1. Introduction

Fuel cells are strongly attractive due to eco-friendly energy conversion device and high efficiency, compared with conventional energy sources<sup>(1)</sup>. In order to use fuel cell, hydrogen should be stably supplied at anode. Therefore, the production of the hydrogen is also an important issue. There are some methods to get hydrogen; electrolysis, reforming from hydrocarbon fuels (e.g., Methane, n-Butane, Diesel, etc). As a bridge-technology, the fuel reforming technology has been widely studied using various reforming reactions such as partial oxidation (POX), steam reforming (SR), and autothermal reforming (ATR). ATR has some merits due to thermally neutral, and the feasibility of compactness compared with SR<sup>(2)</sup>. Based on the previous studies,

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OCR is a more sensitive factor to manage the temperature of the reactor than SCR. Higher OCR condition leads big axial temperature gradient and lower hydrogen yield whereas too low OCR makes the reactor be inactivated. Theoretically the band of possible OCR exists and it should be selected to operate the reactor more effectively<sup>(3-5)</sup>. When the catalysts are exposed into the hot environment during the operating, they can be easily deactivated due to thermal depletion. Therefore, it is very important to maintain appropriate temperature, which sufficiently activates the reactions to get hydrogen-rich gas. Conventionally hydrocarbon fuels, steam and oxygen are injected with between GHSV of 10,000 and 20,000. However, sudden temperature increase is shown in the former part of the reactor in the conventional type reactor. Peak temperature can be over 1,000 °C with high gas flow rate following rapid catalyst deactivation. Therefore in this paper, the effect of oxygen distribution to control the internal temperature will be introduced and extensively investigated

## 2. Mathematical model

### 2.1 Assumptions and model simplification

In order to simplify the model, some physical assumptions are introduced. Chemical equilibrium is incorporated although the carbon deposition can be occurred for start-up and/or operation. In this paper, transient behavior is ignored to investigate steady-state performance of the reactor. In addition, oxygen is uniformly supplied into the catalytic bed with small thermal inertia. Therefore, the distributed oxygen can be shortly heated up with main stream temperature. Assumptions are summarized in order to just justify the effect of oxygen distribution as follows:

- Transient behavior is neglected.
- Plug flow is extensively assumed in the porous medium reactor.
- For geometrical simplification, oxygen is uniformly supplied in the main reactor.
- The distributed oxygen is heated up to the main stream temperature as soon as it is exposed in the reactor.
- Axisymmetric coordinates are adopted.
- Hydrogen oxidation reaction is neglected.

### 2.2 Governing equations

In the paper, porous medium approach is adopted to model the physical phenomena. Two-medium model is

incorporated to solve energy balance equation with chemical reactions on the catalytic surface.

#### Bulk gas phase

$$\frac{\partial}{\partial x_j} (\rho_f C_p u_{D,j} T_f + F_{t,f,j}) = h_t a_{sf} (T_s - T_f) \quad (1)$$

where  $F_{t,f}$  denotes heat flux for bulk gas, it can be

$$F_{t,f} = -k_{eff,f} \frac{\partial T_f}{\partial x} \quad (2)$$

#### Solid phase

$$\frac{\partial}{\partial x_j} (F_{t,s,j}) = h_t a_{sf} (T_f - T_s) + (1 - \varepsilon) \rho_{cat} \sum_{j=1}^N (-\Delta H_j) \eta_j R_j \quad (3)$$

where  $F_{t,s}$  denotes heat flux for the solid phase, it can be

$$F_{t,s} = -k_{eff,s} \frac{\partial T_s}{\partial x} \quad (4)$$

#### Bulk gas species

$$\frac{\partial}{\partial x_j} (\rho u_{D,j} Y_f + F_{d,f,j}) = \rho_f h_d a_{d,sf} (Y_s - Y_f) \quad (5)$$

where  $F_{d,f}$  denotes diffusive flux for the bulk gas phase, it can be

$$F_{d,f} = -d_{eff,f} \frac{\partial \rho_f Y_f}{\partial x} \quad (6)$$

#### Solid species

$$\rho_f h_d a_{d,sf} (Y_f - Y_s) + \rho_{cat} r_i M_i = 0 \quad (7)$$

Other constitutive equations can be found in other literatures<sup>(6,7)</sup>.

### 2.3 Chemical reactions

Catalytic reactions mainly occur on the surface of the catalysts. Main reactions considered in this study are shown below.

#### Full combustion



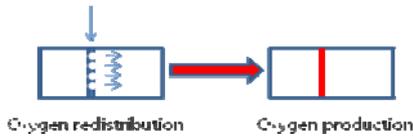
#### Steam reforming



#### Water-gas shift



In order to solve the energy and mass balance equations, detailed kinetic data should be included<sup>(5,6)</sup>. The rate



**Fig.1** Special treatment of oxygen distribution

equations are based on the Langmuir-Hinshelwood theory<sup>(8)</sup>. Pt- Al<sub>2</sub>O<sub>3</sub> catalysts are packed in the reactor with a spherical type. From the preliminary experiments, the developed code is extensively validated comparing with reformat gases and temperature distribution<sup>(3)</sup>.

#### 2.4 Boundary conditions and special treatment

In order to solve the above equations, boundary conditions are necessary to be specified. In this problem, Dirichlet and Neumann conditions are applied. The ATR reactor is normally operating in a furnace integrated with fuel cells.

Therefore, it is rational that the reformer wall is maintained with specified temperatures. As mentioned in section 2.1, the special treatment is introduced to simulate the uniformly distributed oxygen as shown in Fig.1. Assuming that the oxygen is uniformly supplied in the main stream, new oxygen source term is introduced as shown below.

$$S_{\text{Oxygen}} = \zeta_i \dot{m}_{\text{Oxygen}} = \sum_{n=1}^{\text{Number of Cell}} \frac{V_{\text{Cell},n}}{V_{\text{Nozzle}}} \zeta_i \dot{m}_{\text{Oxygen}} \quad (12)$$

### 3. Results and discussion

#### 3.1 Effect of oxygen distribution

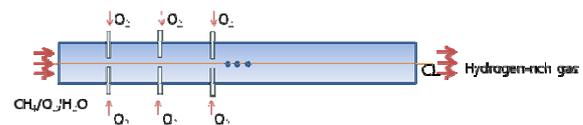
Fig.2 shows the schematic diagram of oxygen distribution system in ATR. In order to investigate the effect of oxygen distribution, the nozzles are embedded in the reactor at the appropriate positions. In this study, as a preliminary simulation, 10% of oxygen is injected in the middle of the reactor. The 90% of oxygen is supplied with other mixture gases. Fig.3 shows bulk gas temperature distribution with two different types. Operating conditions are shown in Table1. In conventional type reactor, methane, oxygen and steam are homogeneously well mixed, and injected into an inlet. As shown in Fig.3, the bulk gas temperature abruptly increases due to fast oxidation reaction followed by the steam reforming reactions resulting in the bulk gas temperature steadily decreases. However, in the newly proposed type reactor, oxygen is distributed in the different position. The strategy has purposes of relatively uniform temperature and high hydrogen production. When oxygen distribution is used, the bulk gas temperature decreases from about 1100 °C to 900 °C

**Table 1** Operating conditions

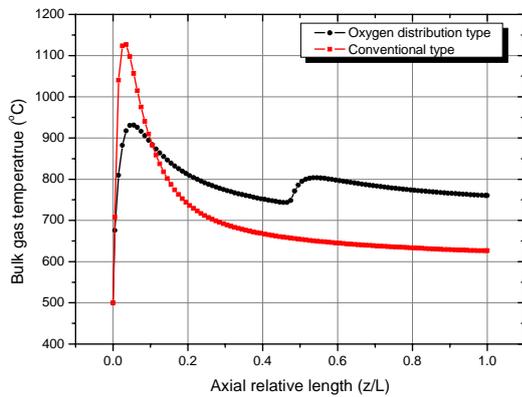
GHSV(h <sup>-1</sup> )	OCR	SCR	Inlet temp.(°C)
5,000	0.5	1.0	500

producing similar hydrogen in Fig.4. When 10% of the oxygen is supplied into the middle of the reactor, the bulk gas temperature is increased to activate the necessary steam reforming reaction. Therefore, hydrogen production in the newly proposed oxygen injection is as high as that in the conventional reactor.

This phenomena result from the higher reaction temperature in the new reactor. In the conventional reactor, POX, SR and WGS are simultaneously occurred, and methane conversion is not 100% because reaction temperature is low to activated continuous steam reforming reaction after strong endothermic reaction. However, in the newly proposed reactor, a part of oxygen at inlet is injected in a different position in order to overcome the problem. The oxygen injection helps the reactor temperature to be high with oxidation reaction. Before the oxygen supply, steam reforming reaction seems to be relatively weaker than the conventional case. However, the total hydrogen is still same or higher than the case. Therefore, oxygen distributed case is helpful to reduce the peak temperature and to get the same or higher hydrogen production. Fig. 5 shows the species distribution with mole fraction base in the reactor. Because the oxygen is supplied at the middle of the reactor, there are some discontinuities in the curve about newly proposed case. Before the secondary oxygen injection, the proposed case has lower hydrogen production compared with the conventional reactor because the sufficient reaction heat is not supplied in the following steam reforming reaction. However, the hydrogen production increases after the secondary oxygen injection because the necessary heat is recovered with the reaction heat, and also too much steam reforming reaction does not take place in the narrow zone. It is advantageous that steam reforming reaction occurs steadily and uniformly maintaining the higher reaction temperature.



**Fig.2** Schematic diagram of oxygen distribution system

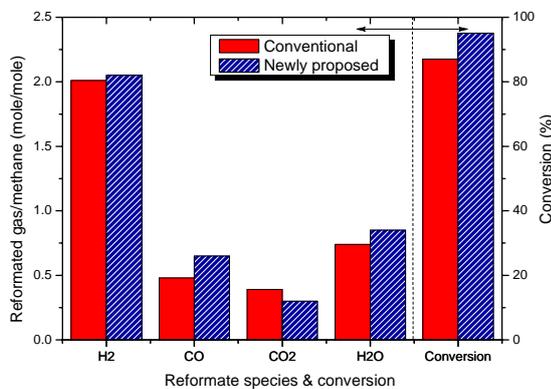


**Fig.3** Bulk gas temperature distribution with different types (OCR=0.5, SCR=1.0, GHSV=5,000h<sup>-1</sup>)

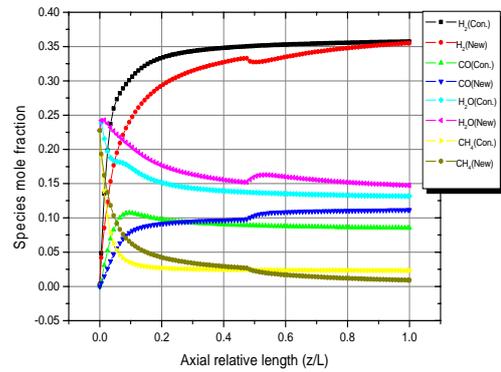
On the other hand, the low reactor temperature affects the carbon formation although the minimized peak temperature is advantageous to other material problems of the packed catalysts. This topic will be discussed in the next section.

### 3.2 Thermodynamic considerations

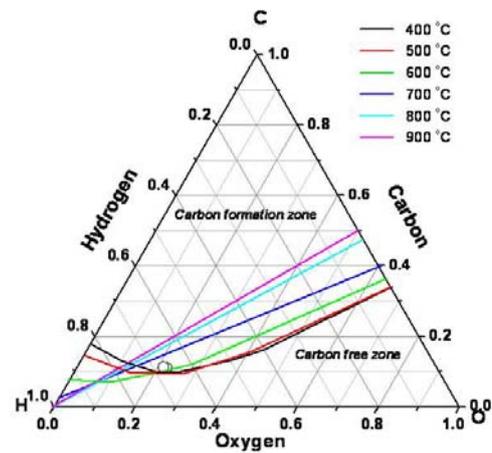
Fig.6 shows ternary diagram of C, H, and O, which determines carbon formation and carbon free zones. The results are based on the thermodynamic theory. In Fig.6, the symbol means that carbon is not formed at the operating conditions. As the chemical reactions occur, the bulk gas temperature is changed. Thereafter it affects the variation of the carbon formation boundary line as shown in Fig.6. Therefore, it is important that the reactor temperature reduces in order to guarantee the catalyst lifetime. However, the lower bound of the temperature is also important to avoid the carbon formation.



**Fig.4** Reformate species production and fuel conversion (OCR=0.5, SCR=1.0, GHSV=5,000h<sup>-1</sup>)



**Fig.5** Reformate species distribution (OCR=0.5, SCR=1.0, GHSV=5,000h<sup>-1</sup>)



**Fig.6** Ternary diagram of C, H and O for carbon formation and free zone

## 4. Conclusion

In this paper, the effect of oxygen distribution is investigated in order to minimize the hot spot and carbon formation. Oxygen distribution is positive to reduce the bulk gas temperature, but too low temperature can deactivate the catalytic reaction and cause the carbon formation.

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