

# Investigation on the application of reformed coke oven gas in direct reduction iron production with a mathematical model

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**Abstract** To investigate the application of reformed coke oven gas (COG) in producing the direct reduction iron (DRI), we simulated a countercurrent gas solid moving bed reactor in which the iron ore pellet was reduced by reformed COG. An ordinary differential equation (ODE) was set based on the unreacted shrinking core model considering both mass and energy balances of the reactor. The concentration and temperature profiles of all species within the reactor were obtained by solving the ODE system. The solid conversion and gas utilization were studied by changing gas flow rate, solid flow rate, reactor length, and the ratio of O/CH<sub>4</sub> to guide the practical application of COG in DRI production. Model results showed that COG was suitable for the DRI production. In order to meet the requirement of the industrial production, the minimum gas flow rate was set as 130,000 Nm<sup>3</sup>/h, and the maximum production was 90 t/h. The reactor length and the mole ratio  $x(\text{O}): x(\text{CH}_4)$  were depended on the actual industrial situations.

**Keywords** Mathematical simulation · Reformed coke oven gas · Gas solid reactor · Direct reduction

## Nomenclature

$A_p$	Pellet external surface area (m <sup>2</sup> )
$C_b$	Gas concentration of the reactants (mol/m <sup>3</sup> )
$C_e$	Equilibrium concentration of the gas (mol/m <sup>3</sup> )
$C_p$	Heat capacity (J/(mol·K))
$d$	Diameter of the iron ore pellet (m)

$D_e$	Effective diffusivity (m <sup>2</sup> /s)
$G_m$	Molar flow (mol/(m <sup>2</sup> ·s))
$\Delta_r G_m$	Standard molar Gibbs free energy
$H$	Reaction enthalpy (J/mol)
$h$	Heat transfer coefficient (pellets/gas) (J/(s·m <sup>2</sup> ·K))
$k_r$	Kinetic constant (m/s)
$K$	Equilibrium constant
$L$	Reactor length considered (m)
$M_w$	Molecular weight (kg/mol)
$n_p$	Number of pellets per unit volume (L/m <sup>3</sup> )
$\hat{R}$	Reaction rate per pellet (mol/s)
$r_0$	Original radius of the pellet (m)
$r$	Radius of the unreacted core (m)
$T$	Temperature (K)
$u_g$	Gas velocity (m/s)
$u_s$	Solid velocity (m/s)
$x$	Gas molar fraction
$Z$	Space variable inside the reactor (m)
$\rho$	The density of the solid pellet (kg/m <sup>3</sup> )
$\eta$	Gas utilization rate
g	Gas
in	Gas inlet
L	Reactor bottom
s	Solid

## 1 Introduction

Coke oven gas (COG), which mainly consists of hydrogen (54 %–59 %), methane (24 %–27 %) and carbon monoxide (5.5 %–7 %), is a byproduct from the metallurgical coke producing process with series of treatment. The emission of COG is up to a level of 300–350 Nm<sup>3</sup> per ton dry coke. As we all know, China is abundant in coal. It was reported that above  $4 \times 10^9$  t cokes were produced in

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China in 2012, which is maximum in the world. The yield of COG amounts to  $1.4 \times 10^{12}$  Nm<sup>3</sup>. However there is a huge surplus of COG, 20 % of which is used as a fuel in the coke ovens. A large amount of the COG has not been properly utilized leading to the serious environmental pollution and resource waste [1–3]. At the same time, the direct reduced iron (DRI) produced in a gas solid reactor cannot be well developed because of the natural gas resources shortage in China. It is a promising technology to reform COG into a synthesis gas, which can be used as metallurgical reduction gas for the production of DRI.

In this paper, the reformed COG is applied to reduce iron ore pellet in a gas solid countercurrent moving bed reactor in the Midrex way. The reactor is fed with iron ore pellets at the top. Reduction reaction takes place as the charge descends in counter-current contact with hot reducing gas, which is generated by catalytic reforming of COG together with a portion of reducing off-gas. Some of these gases mixed with COG are fed to the reformer, and the remainder is burned as a fuel to produce heat in the reformer. Therefore the amount of the recycled gas is of great significance, which determines the consumption of COG per unit weight DRI.

In the past decades, some mathematical models have been presented to study the DRI in gas solid reactor. The first model was set up by Amundson et al. [4–6], in which a linear function was used in the solid temperature change in order to approximate the reaction rate and find analytical solution. However, its application was limited to a large scale. Parisi and Laborde [7] developed a model based on one-dimensional unreacted shrinking core model neglecting the pellet porosity, in which the mass and heat transfer through the gas film surrounding the solid pellet were also negligible. Sasan and Hassan [8] studied the countercurrent moving bed reactor using the tree-stage shrinking core model, in which the porosity of iron was taken into account as well. Nouri et al. [9] analyzed a nonisothermal, steady state and heterogeneous model. The pellet model was based on a grain model with product layer resistance. Xu et al. [10–12] simulated the shaft furnace with a three-stage shrinking core model considering the heat losses. The DRI is produced with the natural gas [4–12], but the main aim of this paper is to investigate the DRI production with reformed COG in a similar simulation way.

It has become a subject of current interest to use the COG as reducing gas in DRI production in China. The paper about this topic was first reported by Ma et al. [13] In their paper, the heated COG was injected into the shaft furnace without reform. Cao et al. [14] had also studied the HYL-ZR process by using the unreformed COG. However this way could not be well developed since the high grade iron could not be used in the production. Zhao et al. [15] discussed the COG consumption for DRI production in the gas solid shaft furnace.

Based on the thermodynamic calculations, they found that the heating process was the decisive part in DRI production process with COG. In addition, the COG reforming process from the aspects of thermodynamic and kinetic had been investigated [16–19]. In this paper, the COG used in DRI production was reformed different from Refs. [13, 14], and the COG reforming process using the shaft model results which was more reliable was also investigated different from Refs. [16–19].

The performance of using reformed COG in the DRI production with similar operating conditions of Midrex plant was investigated for the first time in this paper. A mathematical model based on the first order unreacted shrinking core model was set up by simulating the gas–solid reactor. The mass and energy balance of the reactor can simultaneously lead to a set of ordinary differential equations (ODE). After solving the ODE, we can obtain the performance of the reactor under different operating conditions.

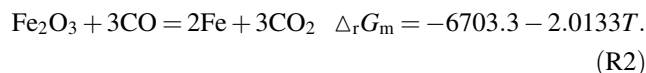
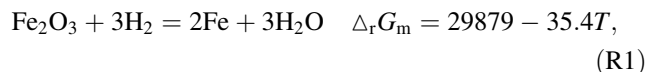
## 2 Mathematical model

### 2.1 Assumptions

A nonporous hematite pellet reduced by the reformed COG is studied. The overall approximations considered for this model are as follows:

- (i) The pellet model is based on unreacted shrinking core model that was used by several authors [7–12].
- (ii) The pellet is assumed to be isothermal, constant radius, geometrically spherical grain.
- (iii) The reduction is supposed to be noncatalytic, reversible and first order reaction.
- (iv) Only ideal gas mixture is taken into account.
- (v) It is considered to be steady state operation.
- (vi) For both gas and solid phase steam, it is plug flow.
- (vii) The carbon deposition is ignored.
- (viii) The heat loss is considering as 10 %.

The considered chemical reactions can be simplified to



### 2.2 Mass and energy balance equations

Based on the mass and energy balance of the gas and solid phases and the above approximations (i)–(vi), the following equations are set up:

$$\text{Gas phase} \\ u_g \frac{dC_{\text{H}_2}}{dZ} = n_p \hat{R}_{\text{H}_2}, \quad (1)$$

$$u_g \frac{dC_{CO}}{dZ} = n_p \hat{R}_{CO}, \quad (2)$$

$$C_{Pg} G_{mg} \frac{dT_g}{dZ} = \frac{0.1 C_{Pg} G_{mg}}{L} + 4\pi r_0^2 n_p h (T_g - T_s). \quad (3)$$

Solid phase

$$u_s dC_{Fe_2O_3} = -\frac{1}{3} n_p (\hat{R}_{H_2} + \hat{R}_{CO}), \quad (4)$$

$$C_{Ps} G_{ms} \frac{dT_s}{dZ} = n_p (A_p h (T_g - T_s) - \hat{R}_{H_2} \Delta H_{H_2} - \hat{R}_{CO} \Delta H_{CO}). \quad (5)$$

The boundary conditions are stated as follows:

$$C_{(H_2, Z=L)} = C_{H_2}^0, C_{(CO, Z=L)} = C_{CO}^0,$$

$$C_{(Fe_2O_3, Z=0)} = C_{Fe_2O_3}^0,$$

$$T_{(g, Z=L)} = T_g^{\text{in}}, T_{(s, Z=0)} = T_s^{\text{in}},$$

where  $Z = 0$  means the top of the reactor, and  $Z = L$  means the bottom of the reactor.

### 2.3 Parameter estimation

(i) For each pellet, the relation between the radius of the unreacted core and the concentration of the solid can be expressed as

$$r = \left( r_0^3 - \frac{3(C_{Fe_2O_3}^0 - C_{Fe_2O_3}) M_w}{4\pi n_p \rho} \right)^{1/3}. \quad (6)$$

(ii) The reaction rate equation of each pellet can be given based on the unreacted shrinking core model as follows [20]:

$$R = \frac{4\pi r_0^2 (C_{n,b} - C_{n,e})}{\frac{r_0}{D_n} \left( \frac{r_0}{r} - 1 \right) + \frac{K}{k_{r,n}(1+K)} \left( \frac{r_0}{r} \right)^2}, \quad (7)$$

where  $n$  represents  $H_2$ ,  $CO$  respectively.

(iii) The equilibrium constant is calculated by the following equation:

$$K = \exp\left(-\frac{\Delta_r G_m}{RT}\right). \quad (8)$$

(iv) The kinetic constants of the reaction used in the model are as follows [7]:

$$k_{H_2} = 2.25 \times 10^{-3} \exp(-14700/82.06/T_{H_2}) \text{ m/s}, \quad (9)$$

$$k_{CO} = 6.50 \times 10^{-3} \exp(-28100/82.06/T_{CO}) \text{ m/s}. \quad (10)$$

(v) The effective diffusion coefficients and the heat transfer coefficient are also used from Parisi [7] as follows:

$$D_{H_2} = 1.467 \times 10^{-10} \times T^{1.75} \text{ m}^2/\text{s}, \quad (11)$$

$$D_{CO} = 3.828 \times 10^{-11} \times T^{1.75} \text{ m}^2/\text{s}, \quad (12)$$

$$h = 16.736 \text{ J}/(\text{s} \cdot \text{m}^2 \cdot \text{K}). \quad (13)$$

The values of this differential equation such as enthalpies, specific heats and so on are from Ref. [21]. Therefore, the non-linear differential Eqs. (1)–(5) with the boundary conditions are solved using Runge–Kutta method with Matlab.

## 3 Results and discussion

### 3.1 Model validation

The model was validated by comparing the modeling values with the values of exiting gas composition and solid conversion level of the Midrex plant: Siderca (published by Parisi [7] in 2004). Table 1 summarizes the operating conditions of the plant.

According to the parameters defined by Eqs. (6)–(13) and the operating conditions showed in Table 1, the Eqs. (1)–(5) were numerically solved. The calculated exit gas composition and solid conversion were shown in Table 2 with data directly collected from instruments in the Siderca plant. The model results showed good agreement with the Siderca plant data within the experimental error.

### 3.2 Modeling with the reformed COG data

The model, being used to simulate the reduction zone of the gas solid reactor, was applied to the reformed COG

**Table 1** Operating conditions of Siderca plant

Gas	
Inlet temperature	1,230 K
Gas flow rate	140,000 Nm <sup>3</sup> /h
Inlet gas composition (at the bottom)	
H <sub>2</sub>	52.9 %
CO	34.7 %
H <sub>2</sub> O	5.17 %
CO <sub>2</sub>	2.47 %
CH <sub>4</sub> + N <sub>2</sub>	4.65 %
Solid	
Production (DRI)	100 t/h
Mineral pellet density	3.4 × 10 <sup>3</sup> kg/m <sup>3</sup>
Sponge iron density	3.1 × 10 <sup>3</sup> kg/m <sup>3</sup>
Pellet ratio (r <sub>0</sub> )	0.005 m
n <sub>p</sub>	9.9 × 10 <sup>5</sup> pellets/m <sup>3</sup>
Reactor	
Reaction zone length (Z)	10 m
Diameter	4.88 m

**Table 2** Comparison of the Siderca plant data with model predictions

Off-gas composition (Z = 0)	Siderca plant data/%	Model results/%
H <sub>2</sub>	38 ± 2	38.13
CO	19 ± 1	18.63
H <sub>2</sub> O	20 ± 1	19.94
CO <sub>2</sub>	18.24 ± 1.2	18.54
CH <sub>4</sub> + N <sub>2</sub>	4.65 ± 0.8	4.65
Solid conversion	93.7 ± 1	93.71

**Table 3** Reformed COG data calculated by HSC software (the mole ratio  $x(\text{O})$ :  $x(\text{CH}_4)$  is 1, reforming temperature is 800 °C)

Compound	H <sub>2</sub>	CO	H <sub>2</sub> O	CO <sub>2</sub>	CH <sub>4</sub> + N <sub>2</sub>
Mole fraction/%	70.65	21.46	2.47	0.80	4.62

data. The reformed COG composition was shown in Table 3.

When the same operating conditions in the Siderca plants were used in the COG simulation, the model results were shown in Table 4. As it could be observed, the gas utilization and solid conversion of the COG model results were both lower than those of the nature gas model results. Moreover, the solid conversion of the COG model was too low to meet the production requirement.

Table 5 shows the model results after changing the operating conditions. When the gas flow rate was reduced to 130,000 Nm<sup>3</sup>/h and the solid flow rate was reduced to 90 t/h, the gas utilization and solid conversion of COG model results are acceptable.

**Table 4** Comparison of the nature gas model results with reformed COG model results

Values	Model results of nature gas/%	Model results of reformed COG/%
Gas utilization	32.37	27.17
Solid conversion	93.71	91.03

**Table 5** Model results of the COG model

Off-gas composition (Z = 0)	Model results/%
H <sub>2</sub>	50.69
CO	12.07
H <sub>2</sub> O	22.43
CO <sub>2</sub>	10.19
CH <sub>4</sub> + N <sub>2</sub>	4.62
Gas utilization	30.77
Solid conversion	92.01

The variables along the reaction zone of the simulation are shown in Fig. 1. The reaction rate at the top of the zone is very low due to that the temperature at the solid inlet is too low to make the reaction occur. The reaction rate is the highest at about 2 m from the top of the reactor. This can be explained that the solid temperature and the gas temperature become almost the same at that point. From Fig. 1b we can see that the solid and gas temperature tend to be uniform as the reactor length grows. The difference between the gas and solid temperature is caused by the chemical reaction and heat losses. The solid conversion, depicted in Fig. 1c is only about 92 %. However, the whole reactor length is used efficiently. Figure 1d shows that the molar fraction of the gases (reactive and products) evolve monotonically within the gas solid reactor.

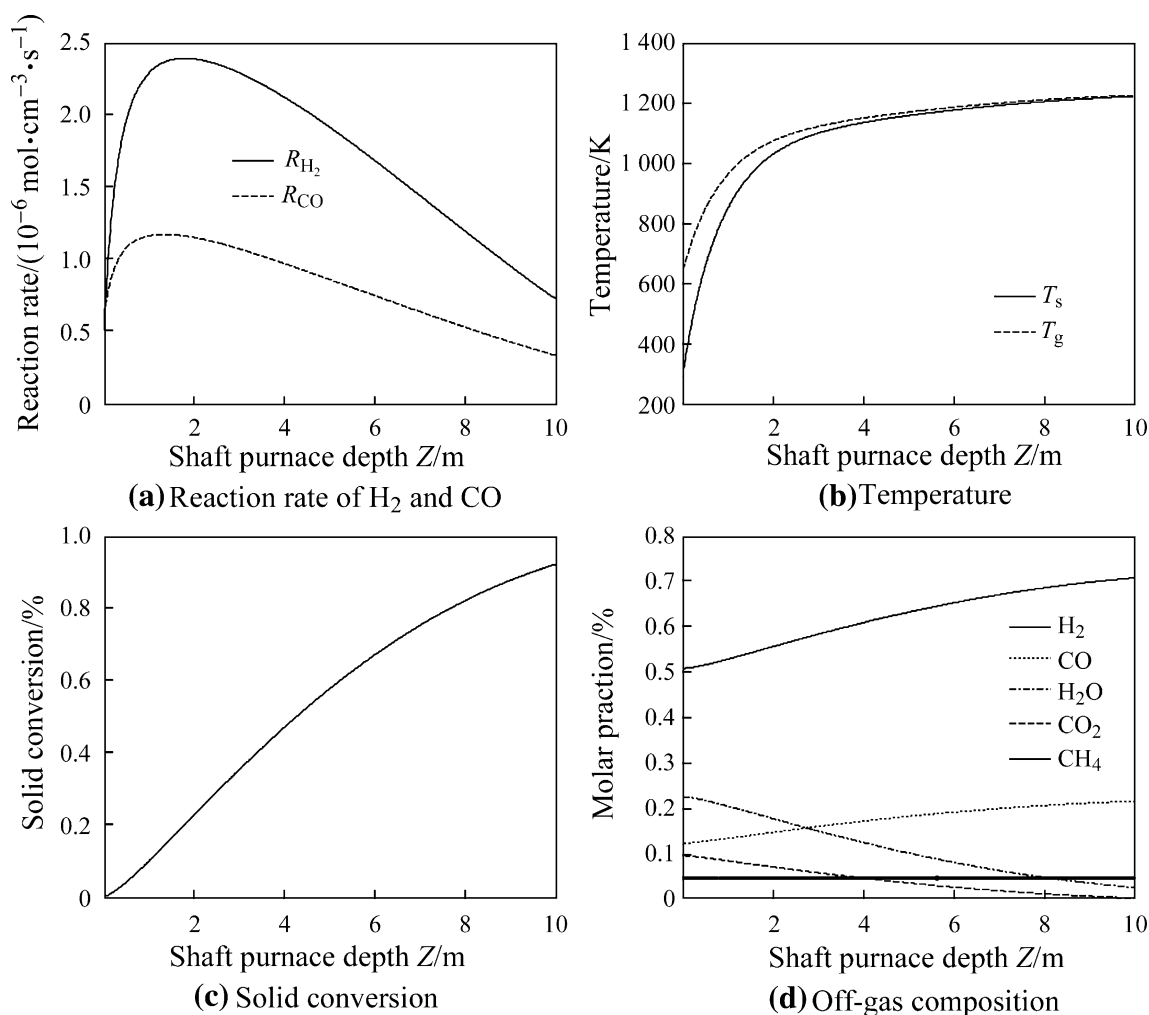
### 3.3 Modeling of the different operating conditions

Different operating conditions are considered to simulate the gas solid reactor, in which the iron ore pellet is reduced by reformed COG. One condition is changed while the other operating conditions remain invariant. The gas utilization rate is calculated by the following expression [22]:

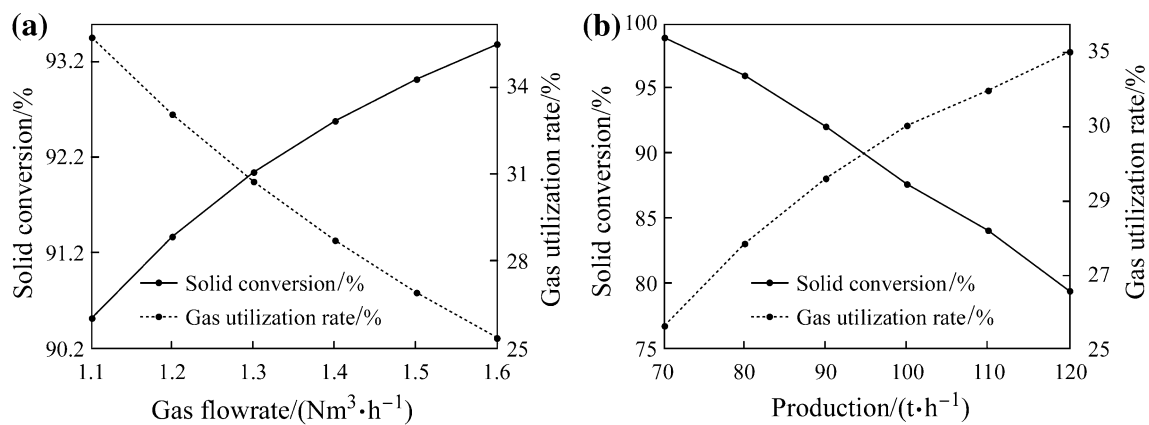
$$\eta = \frac{x_{\text{CO}_2} + x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} + x_{\text{H}_2\text{O}} + x_{\text{CO}} + x_{\text{H}_2}} \quad (14)$$

Figure 2 shows the effect of gas and solid flow rate on solid conversion and gas utilization rate. It can be seen from Fig. 2a that the gas flow rate increase with the conversion rate of the iron ore pellet, on the contrary, decrease with the gas utilization rate. It may be explained that the iron ore pellet is reduced more completely by the surplus reducing gas. However the reducing gas is wasted. When the gas flow rate is 130,000 Nm<sup>3</sup>/h, the solid conversion can reach 92 % that is required by the steel mill. If the gas flow rate is 10,000 Nm<sup>3</sup>/h, it will get about 0.5 % increase of the solid conversion and about 2 % decrease of the gas utilization. The simulations results varying with the production are shown in Fig. 2b. It can be observed that if there is an increase of the production, the solid conversion will decrease and the gas utilization will increase because of the increasing residence time of pellets in the reactor. The conversion level would be lower than 92 % when production is up to 90 t/h. When the production is increased by 10 t/h, the solid conversion will be decreased by about 3.5 % and the gas utilization will be increased by 2 %.

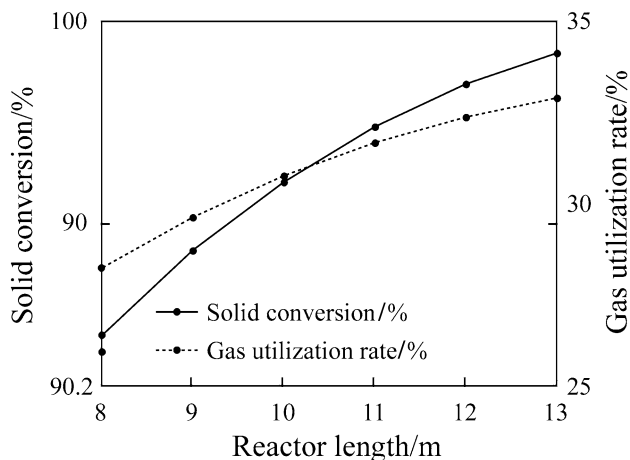
The effect of the reactor length was sketched in Fig. 3. The residence time of pellets in the reactor increases with the increase of the reactor length. Both of the solid conversion and the gas utilization rate are increased. When the reactor length reaches 10 m, the model results of the solid conversion and the gas utilization can meet the industrial



**Fig. 1** Simulation profiles of the variables along the reaction zone



**Fig. 2** Effect of gas flow rate **a** and solid flow rate **b** on solid conversion and gas utilization rate



**Fig. 3** Effect of reactor length on solid conversion and gas utilization rate

production requirement. The increase of 1 m of the reactor length leads to the 2 % growth of the solid conversion and 1 % growth of the gas utilization.

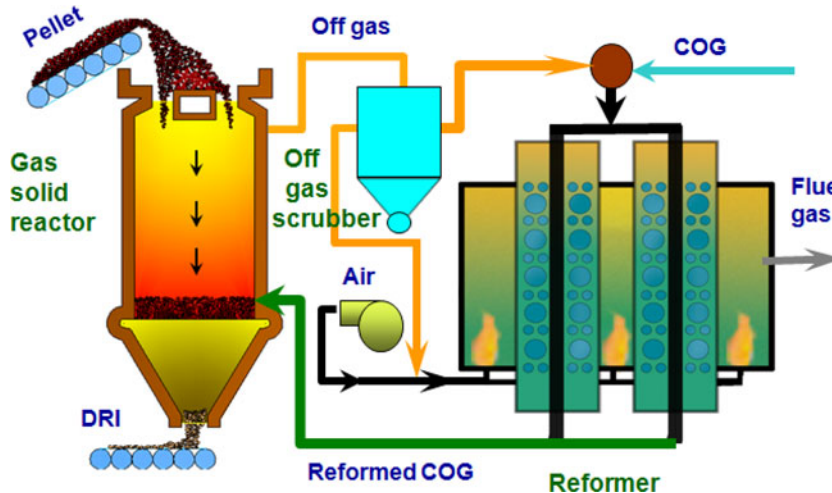
It is proposed that the COG reduction process happens in gas solid reactor. The main components of the process are the gas solid reactor and the gas reformer, as shown in Fig. 4. The iron ore pellet fed on the top of the reactor goes downwards by gravity. Reduction process takes place when the hot reducing gas goes upwards in countercurrent. The iron ore pellet is reduced into DRI, and the gas is oxidized. The oxidized off-gas after scrubbed is partly burned out to heat the reformer up, and partly go back to the reformer as the oxygen source for COG reforming. By doing this, some of H<sub>2</sub> and CO in off-gas can be recycled, and the utilization rate of reducing gas in the system increase greatly. The process can lower carbon dioxide emissions. The recycle ratio is one of the important operation parameters. Table 6

**Table 6** Reformed COG composition calculated by HSC software at different O/CH<sub>4</sub> ratio (reform temperature is 800 °C)

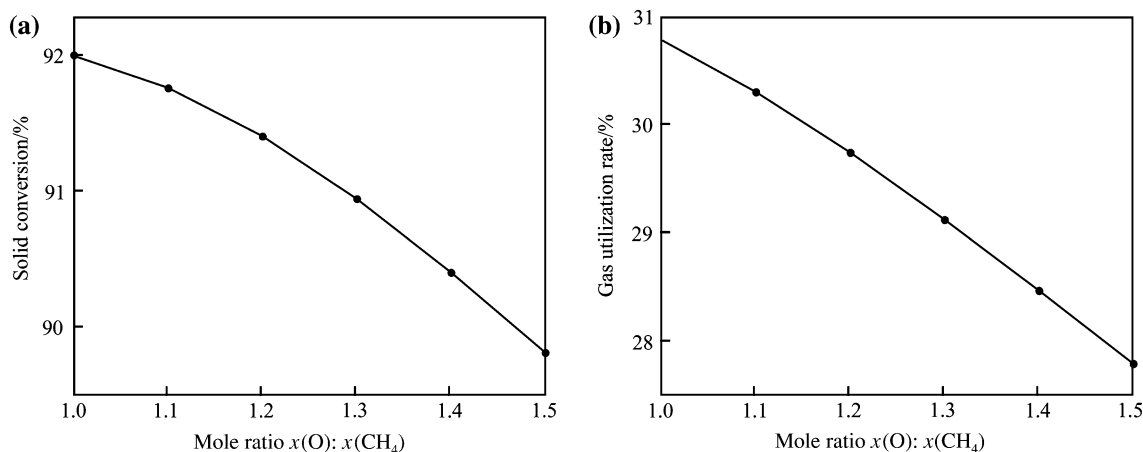
Mole ratio $x(O): x(CH_4)$	H <sub>2</sub> /%	CO/%	H <sub>2</sub> O/%	CO <sub>2</sub> /%	CH <sub>4</sub> /%	N <sub>2</sub> /%
1.0	70.65	21.46	2.47	0.80	1.92	2.69
1.1	69.95	21.52	3.39	1.11	1.37	2.66
1.2	69.00	21.43	4.45	1.46	1.00	2.65
1.3	67.99	21.19	5.58	1.84	0.76	2.64
1.4	66.98	20.82	6.76	2.23	0.58	2.63
1.5	65.69	20.56	8.01	2.64	0.46	2.63

shows the reformed gas composition under different mole ratios  $x(O): x(CH_4)$ .

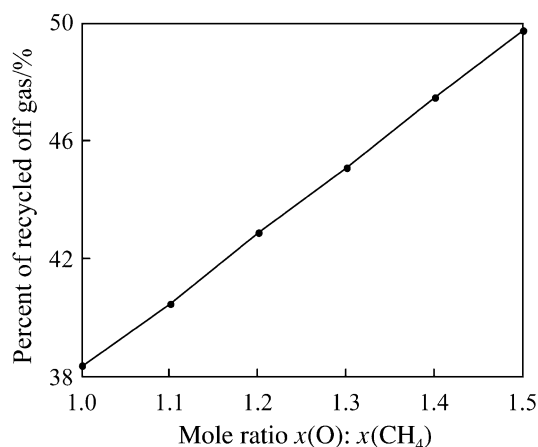
From Table 6, it can be seen that the oxidation gas contents (H<sub>2</sub>O and CO<sub>2</sub>) increase with the increase of mole ratio  $x(O): x(CH_4)$ . It weakens the reducing ability of the inlet gas. However the methane percent is decreased. Figure 5 shows the effect of increasing mole ratio  $x(O): x(CH_4)$  on the solid conversion and gas utilization. As the mole ratio  $x(O): x(CH_4)$  increases, the solid conversion and gas utilization decrease. If the mole ratio  $x(O): x(CH_4)$  grows one step, the solid conversion and the gas utilization will drop about 0.5 %. Therefore, we need to keep the mole ratio  $x(O): x(CH_4)$  as low as possible considering the solid conversion and gas utilization. However, the off-gas recycling ratio increases with the mole ratio  $x(O): x(CH_4)$ , as shown in Fig. 6. When the mole ratio  $x(O): x(CH_4)$  is increased, the oxidation of the mixture of off-gas and fresh COG is increased. One step of the growth of the mole ratio  $x(O): x(CH_4)$  will lead to 2.5 % increase of the recycled off-gas. Therefore, the mole ratio  $x(O): x(CH_4)$  needs to be bigger if we want much more off-gas to recycle.



**Fig. 4** Schematic simplified diagram for the COG reducing process



**Fig. 5** Effect of reform temperature and mole ratio  $x(\text{O}): x(\text{CH}_4)$  on solid conversion **a** and gas utilization **b**



**Fig. 6** Effect of mole ratio  $x(\text{O}): x(\text{CH}_4)$  on the percent of recycled off-gas

#### 4 Conclusions

The results of the model proposed showed that COG could be used in the DRI production. The solid conversion increased with the gas flow rate and reactor length, but decreased with production. The increase of gas utilization could be realized by increasing production and reactor length, decreasing gas flow rate.

Increasing  $10,000 \text{ Nm}^3/\text{h}$  of the gas flow rate would cause about 0.5 % increase of the solid conversion and about 2 % decrease of the gas utilization. The minimum gas flow rate required was  $130,000 \text{ Nm}^3/\text{h}$ . When the production was increased by 10 t/h, the solid conversion would increase by 3.5 % and the gas utilization by 2 %. The maximum production was 90 t/h, which could satisfy the industrial requirement. Every meter increase of reactor length would lead to about 2 % increase of the solid conversion and 1 % increase of the gas utilization.

The solid conversion and gas utilization rate decreased, and off-gas recycling ratio increased with mole ratio  $x(\text{O}): x(\text{CH}_4)$ . If the step of the mole ratio  $x(\text{O}): x(\text{CH}_4)$  was increased to 0.1, the solid conversion would decrease 0.4 %, the gas solid would decrease 0.5 %, and the percent of recycled off-gas would increase 2.5 %. However, an optimization decision with the consideration of more factors in the actual industrial situations must be done.

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