

PROCESS SIMULATION OF AN INTEGRATED COKE DRY QUENCHING COMBINED GASIFICATION

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Abstract

In this paper, an integrated coke dry quenching combined gasification system using coke oven gas and steam to quench the incandescent coke is proposed. The distinct advantages of the system include energy conservation, pollution reduction, coke quality improvement and full use of resources. Based on the minimization of the Gibbs free energy, the flow rate and composition of the syngas are predicted. At the same time, the effects of the coke oven gas flow rate and the steam consumption on the flow rate and composition of the syngas as well as exergy efficiency is analyzed by using PRO/II simulator. Finally, the effects of the coke oven gas flow rate and the steam consumption remarkably on flow rate and composition of the syngas and exergy efficiency are investigated.

Keywords: Integrated coke dry quenching combined Gasification; Syngas; Exergy; PRO/II.

1. Introduction

The coke dry quenching (CDQ) technique was introduced in Switzerland by the Sulzer brothers in the 1920s. A few decades later, an improved conception of the CDQ process for continuous operation was produced by the Giprokoks Institute in Russia. In the CDQ process [1], the incandescent coke is refrigerated by a circulating gas mainly composed of nitrogen, enter a boiler to produce superheated steam. Therefore, not only can the CDQ technology save energy, but it can also protect the environment and further improve the quality of coke [2].

Due to the concern of environment protection and energy crisis, it is important to develop a new CDQ technology which can protect the environment and save energy [3]. To evaluate the efficiency of a thermal system, energy analysis is often used, while exergy analysis, a way to indicate the possibilities for thermodynamical improvement and optimize the thermal system, has been another important tool in the past few decades. Prins [4] using energy and exergy analysis to study the system of the oxidation and gasification found that up to 75% of the chemical exergy contained in solid carbon can be preserved in the chemical exergy of carbon monoxide and hydrogen at optimum gasification temperatures the ranges of which are 1100-1200 K (under normal pressure) and 1200-1300 K (under 10 bar pressure). Errera, etc. [5] performed a thermodynamic analysis -- first and second laws analysis for a CDQ process and concluded the importance of complete thermodynamic analysis.

Along with the rapid development of computer technology, simulation software has been widely applied in coal and biomass gasification and syngas production. For example, Han [6] studied the production process of synthesizing dimethyl ether from coal-based syngas on Aspen Plus platform. The simulation results agreed well with data obtained in laboratory experiment. Lee [7] studied a coal gasification system for the production of hydrogen using the PRO/II simulator with a good result.

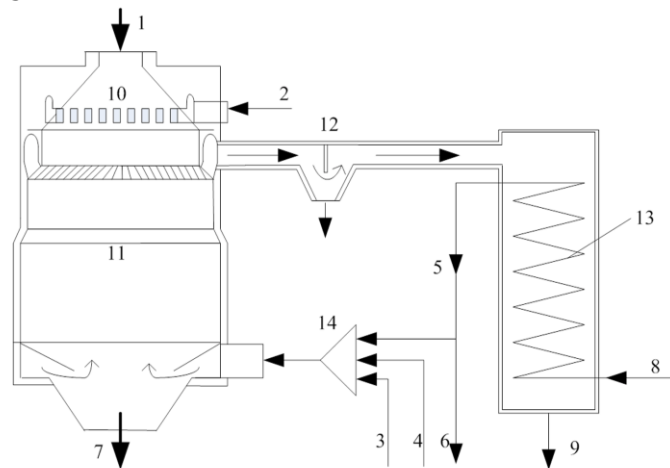
In this paper, an integrated coke dry quenching combined gasification (ICDQCG) system is proposed, which uses the steam generated in boiler and COG(coke oven gas) produced in the coke oven to quench the incandescent coke, thus making full use of resources and providing raw materials for the production of methanol, methane and other products. This paper discusses the principle of the ICDQCG system, the effects of COG and consumed steam on the production of syngas, both in the perspective of amount and composition and

system exergy efficiency using PRO/II simulator.

2. The integrated coke dry quenching combined gasification (ICDQCG) system

2.1. Process description

Fig. 1 is a schematic diagram of the ICDQCG system. In the ICDQCG system, the ICDQCG chamber, the essential part of the system, can be divided into two functional zones: preheating zone 10 and cooling zone 11. The incandescent coke is charged into the top of ICDQCG furnace and preheated by heat released from reaction of coke oven gas and air in preheating zone 10. The preheated coke then moves downwards to the cooling zone 11, where the major reactions (1) ~ (6) [8, 9] take place and the syngas begins to generate. The generated syngas leaves the ICDQCG system through annular passage 12 located at the top of the cooling zone 11 for the boiler 13 where the thermal energy of the syngas is transferred to steam 5.



1.incandescent coke; 2. air and coke oven gas; 3. coke oven gas; 4,5,6. steam;7. extinguished coke; 8.water; 9. syngas; 10. preheat zone; 11.cooling zone;12. annular passage;13. the boiler;14. tuyere.

Figure 1. Schematic diagram of the ICDQCG system

2.2. Principle of Process

Besides the heat absorbed physically in traditional CDQ process, heat released from chemical endothermic reactions also exist in the ICDQCG system. In ICDQCG system, the major reaction equations are as follows [8]:



The reaction (1) ~ (5) are strong endothermic reactions, while the reaction equation (6) is micro-exothermic. Because of the introduction of chemical reactions, cooling rate of the new system is much faster than the traditional system which merely has physical absorption of heat.

2.3. Model building

In modeling the ICDQCG system, a model is developed using PRO/II to estimate the effects of the major parameters of the process. The ICDQCG system includes a multiphase reaction involving coke, coke oven gas and high temperature steam. Under these conditions, the reactions in the ICDQCG furnace at thermodynamic quasi-equilibrium conditions. So

the calculation can be realized through material balance and energy balance. The ICDQCG system mainly includes a simple HX model, a conversion reactor and a Gibbs reactor that simulates a chemical reactor by solving the heat and material balance equations based on the principle of minimizing the Gibbs free energy of the components. Since the Gibbs reactor cannot handle coke, the coke has to be fed into conversion reactor being converted into a stream composed of components having equivalent element to coke at the same enthalpy level. The flow diagram of the process using PRO/II is depicted in Fig. 2. The ICDQCG furnace is a typical high temperature system in fully consistent with the application scope of the SRKM equation of state, so it is employed to predict coke oven gas and syngas. The modeling of the process is based on the following simplification:

- (1) Pressure drop, gas leak, hot loss do not exist in the ICDQCG furnace.
- (2) The ICDQCG furnace runs in a stable way, with all the parameters being constant over time.
- (3) The coke oven gas and steam fully contact with the coke.
- (4) All the reactions are fast and easy to reach chemical equilibrium under normal pressure.

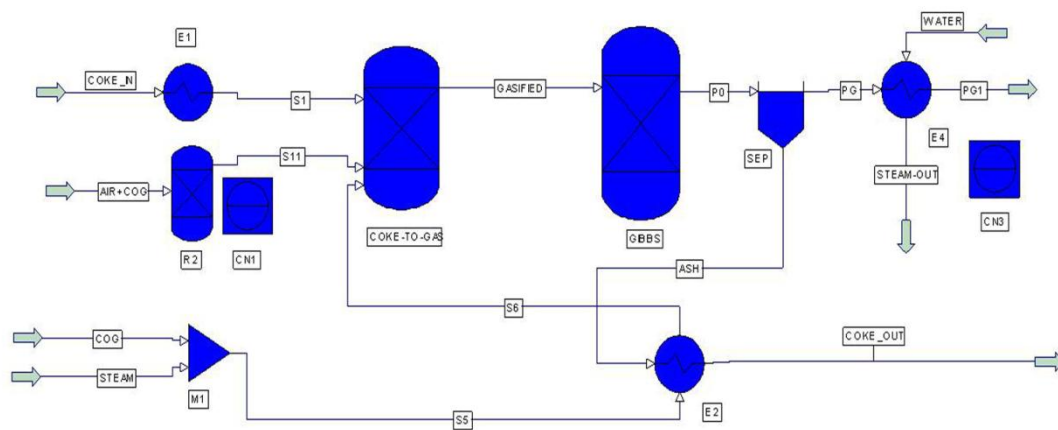


Figure 2. The flow chart of the ICDQCG system established through PRO/II

3. Thermodynamic analysis

3.1. Thermodynamic properties of coke

The physical and chemical properties of coke have been fully developed after years of research. Mathematically, the estimation of the coal calorific value is an accurate analysis falling into two types [10]: the "ultimate analysis" and the "proximate analysis". The former deals with the amount of primary elements-carbon, hydrogen, nitrogen, oxygen (differential), sulfur, etc., while the latter with the amount of moisture, volatile matter, fixed carbon (differential), ash, etc. The coke composition related to the two methods is shown in Table. 1.

Table 1 Proximate and ultimate analyses of coke

Ultimate analysis Wt%						Proximate analysis Wt%					
C	H	O	N	S	Cl	Ash	MOIS	VM	FM	Ash	
84.72	0.693	0.714	1.163	0.51	—	12.2	0.6	1.9	85.3	12.2	

For solid substances, once the specific heat is specified, it is possible to evaluate almost all the properties needed. An evaluation of the coke specific heat was obtained by linear adjustment of the calorimetric measurements [10], namely:

$$c(T) = a T - 273.15^2 + b T - 273.15 + c \quad (7)$$

Where $a = -3.391 \times 10^{-7} \text{ kJ/kg} \cdot \text{K}^3$, $b = 1.139 \times 10^{-3} \text{ kJ/kg} \cdot \text{K}^2$, $c = 0.766 \text{ kJ/kg} \cdot \text{K}$

Fig. 3 shows that this evaluation method for coke specific heat is in good agreement with the results in literatures [10].

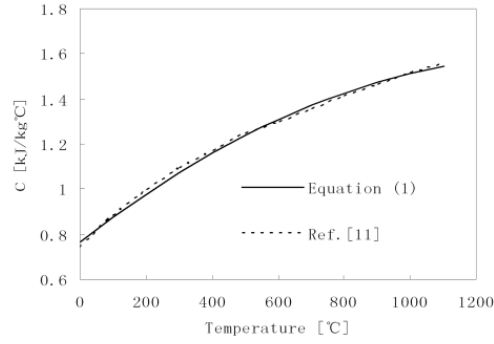


Figure 3. Comparison of the value of the coke specific heat from Eq. (1) with the literature

Since the coke is incompressible, its enthalpy can be approximated by the relation $c(T)=dH/dT$. The reference of enthalpy of the coke ash and moisture at T_0 and P_0 is supposed to be zero [11]. Thus, expression for enthalpy of the ash and moisture is as follows ,

$$H T = a(T - 273.15)^3 + b(T - 273.15)^2 + c(T - 273.15) + 1136 \text{ kJ/kg} \quad (8)$$

Exergy, as a measure of available work potential, is described as $\varepsilon = \varepsilon^{ph} + \varepsilon^o$ where ε^{ph} is related to thermo physical changes (physical exergy) and ε^o to the chemical changes (chemical exergy) of each substance. The physical exergy for the coke can be obtained, namely:

$$\varepsilon^{ph} = (H - H_0) - T_0(S - S_0) \quad (9)$$

Where: H —enthalpy in actual state, kJ/h; H_0 —enthalpy in ambient temperature, kJ/h; T_0 —ambient temperature, K; S —entropy in actual state, kJ/(mol·K); S_0 —entropy in ambient temperature, kJ/(mol·K).

The chemical exergy of coke can be obtained through the literature [12], namely:

$$\begin{aligned} \varepsilon^o = & 34215.87[C] + 21.97[N] + 116702.76[H] + 18260.357[S] \\ & - 13278.593[O] - 298.15 \times 0.71768 \times m_A + 0.6276[O] \\ & \times 32729.8 \times [C] + 141791.11 \times [H] - 17723.842[O] + 16019.49[S] \text{ kJ} \cdot \text{kg}^{-1} \end{aligned} \quad (10)$$

Where $[x]$ is the mass fraction of element x in the coal, m_A is the mass fraction of ash.

3.2. Gibbs free energy

Equilibrium compositions were calculated using the principle of minimization of the Gibbs free energy, which serves to predict the number of moles of each species in gaseous phase. The atom and energy balance serve as restrictions for all possible reactions in the system. The compositions of the six major components in syngas, H_2 , CO , CO_2 , CH_4 , N_2 and H_2O , were calculated using the following equations [13].

The Gibbs free energy G^t of the system are given by:

$$G^t = \sum_{j=1}^s G_j^0 n_j + \sum_{j=s+1}^c \sum_{L=1}^P G_{jL} n_{jL} \quad (11)$$

Now is to find the value of n_i that minimize the objective function G^t . The appropriate method is to use the Lagrange multipliers. Elemental and energy balance serve as the constraint:

$$b_k = \sum_{j=1}^s m_{jk} n_j + \sum_{j=s+1}^c \sum_{L=1}^P M_{jk} n_{jL}, \quad k = 1, 2, \dots, E \quad (12)$$

$$\sum_{L=1}^c m_L \Delta H_{f,feed,298}^0 + \sum_{L=1}^c m_L H(T_{feed,L}) = \sum_{i=1}^N n_i \Delta H_{f,prod,298}^0 + \sum_{i=1}^N n_i H_{prod}(T) + Q + \Delta H(T), \quad L = 1, 2, \dots \quad (13)$$

Where

n_j —number of moles of species j , kmol/h; b_k —total number of atoms of the k th element in the reaction mixture; m_{jk} —number of atoms, the j th element in a mole of the k th species; M_{jk} —number of atoms, the j th element in a mole of the k th species; $\Delta H_{f,feed,298}^0$ —enthalpy change of standard enthalpy of formation at 298.15K, kJ/kg; $\Delta H_{f,prod,298}^0$ —enthalpy change of standard enthalpy of formation at 298.15K, kJ/kg; $H(T_{feed,L})$ —enthalpies of each feed at specific temperature, kJ/kg; $H(T_{feed,L})$ —enthalpies of each product at specific temperature, kJ/kg.

3.3. Exergy efficiency

In order to study the effects of the flow rate of COG and the steam consumption on the ICDQCG system, the exergy efficiency is calculated. An exergetic analysis includes mass, energy and exergy balances for all plant components (control volumes) and definition of exergetic efficiency for the ICDQCG system. The exergy efficiency of ICDQCG furnace is defined as follows:

$$\eta = \frac{\varepsilon_{syngas} - \varepsilon_{gasin}}{\varepsilon_{cokein} - \varepsilon_{cokeout}} \quad (14)$$

Where ε_{syngas} —the exergy of the syngas produced, kW; ε_{gasin} —the exergy of the syngas entering ICDQCG furnace, kW; ε_{cokein} —the exergy of the hot coke being fed into the ICDQCG furnace, kW; $\varepsilon_{cokeout}$ —the exergy of the coke exiting the ICDQCG furnace, kW.

$$\eta = \frac{\varepsilon_{steamout} - \varepsilon_{water}}{\varepsilon_{syngasout} - \varepsilon_{syngas}} \quad (15)$$

Where ε_{water} —the exergy of water, kW; $\varepsilon_{steamout}$ —the exergy of steam leaving boiler, kW; $\varepsilon_{syngasout}$ —the exergy of the low temperature syngas, kW.

Exergy efficiency of the ICDQCG system:

$$\eta = \frac{\varepsilon_{steamout} - \varepsilon_{water}}{\varepsilon_{syngasout} - \varepsilon_{syngas}} \quad (16)$$

$$\sum \varepsilon_{gasout} = \varepsilon_{syngas} + \varepsilon_{steamout} \quad (17)$$

Where $\sum \varepsilon_{gasout}$ is the sum of exergy of all kinds of gases leaving the ICDQCG system, kW.

4. Results and discussion

In this ICDQCG system, a steady feed of Coke is 12 kg/min at the temperature of 1323 K. The composition of COG is listed in Table 2 with the major compositions of syngas, H₂, CO and CH₄ presented in the figures.

Table 2 Chemical composition of the coke oven gas

Element	CO	H ₂	CO ₂	CH ₄	C ₂ H ₆	N ₂
Content vol. %	7	60	2	25	2	4

4.1. Effects of the flow rate of COG

In the ICDQCG system, the COG is divided into two streams: one is introduced to the preheating zone 10 located in the upper section of the chamber, and the other to the cooling zone 11 through tuyere 14. The former reacts with air, preheating the hot coke and facilitating reactions. The latter is to cool the hot coke and react with steam to produce syngas. As a general rule, if the flow rate of the hot coke is specified, the flow rate of the COG used for preheating the coke is a constant. Therefore, only the effects of the latter are analyzed in this paper. The effects of the flow rate of COG are presented in Fig. 4,5,6 resp.

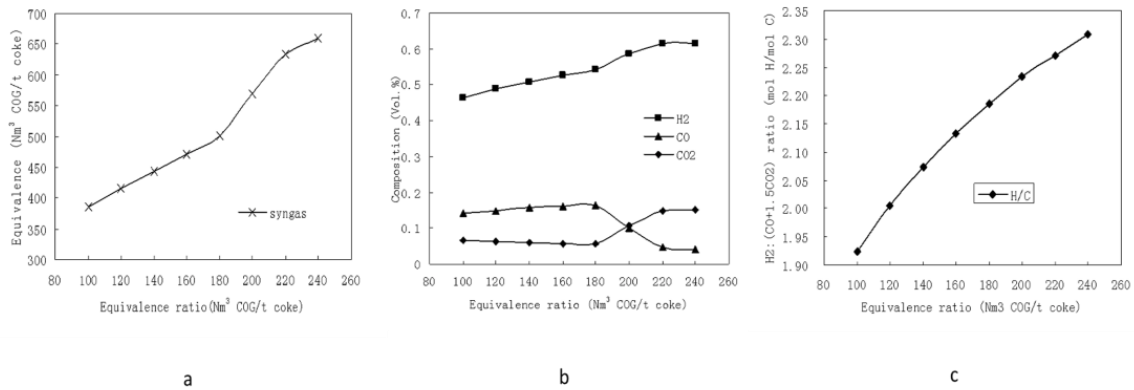


Figure 4. Effects of coke oven gas flow rate on syngas yield, syngas composition and H/C (steam flow rate is 123)

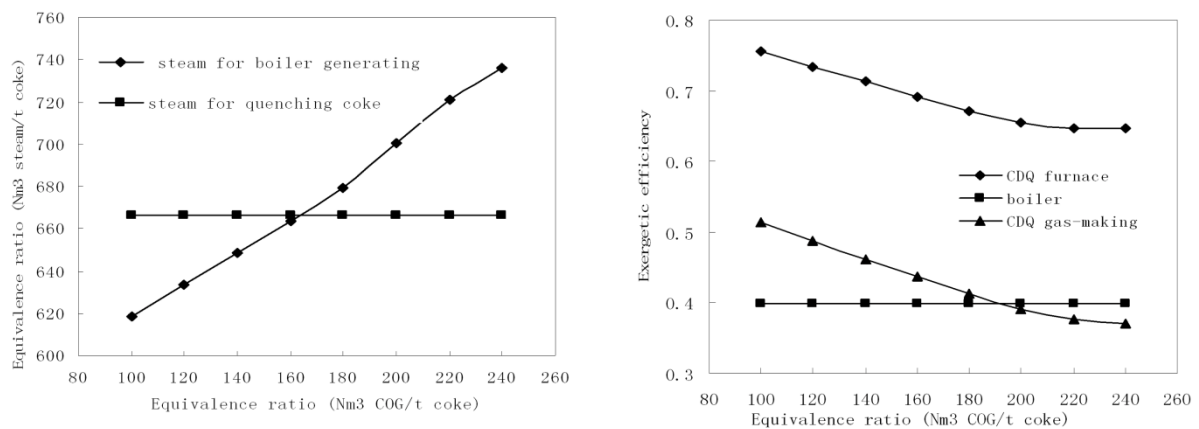


Figure 5. Effects of coke oven gas flow rate on steam yield

Figure 6. Effects of coke oven gas flow rate on exergy efficiency

Fig. 4(a) shows that the flow rate of syngas increases with the increase of the flow rate of COG. This is mainly due to the fact with the sufficient steam, the increase of the COG flow rate continue to move the reactions to the positive direction, increasing the production of the syngas. Fig. 4(b) shows that the concentrations of H₂, CO and CO₂ increase with the flow rate of COG, while the CO₂ concentration decrease until the flow rate of COG reaches nearly 180. There is an inverse tendency of concentrations of CO and CO₂ when the flow rate of COG is between 180 and 220. This is because the reaction (2) is more favorable than the reaction (1). When the flow rate of COG is above 220, the concentrations of H₂, CO and CO₂ have only a slight change. In Fig. 4(c), the H/C ratio [12, 13] which is referred to as the value of H₂/(CO+1.5CO₂) in the following discussion increases proportionally with the COG flow rate.

As shown in Fig. 5, the yield of steam increases proportionally with the COG flow rate. This could be due to the fact that the flow rate of syngas increases with the flow rate of COG. The more heat released by the syngas in the boiler, the more steam generated in the boiler. When the flow rate of COG is above 165, the amount of steam generated in boiler exceeds that of the steam for quenching. And the steam generated could be divided into two streams: one could be directly used to quench the coke and the other to generate electricity.

Fig. 6 demonstrates that the exergetic efficiency of the CDQ furnace and the overall ICDQCG system (CDQ gas-making) decreases with the increase of COG flow rate, while the exergetic efficiency of the boiler has only a slight change.

In summary, the flow rate of COG greatly affect the flow rate, composition of the syngas, the steam generated in the boiler and the exergy efficiency of the ICDQCG system. It is necessary to optimize the flow rate of COG for energy saving and syngas purposes.

4.2. Effect of steam consumption

In the ICDQCG system, water is changed into steam after absorbing the heat in the boiler. The steam yielded then is divided into two steams, one enters the ICDQCG furnace from the bottom, reacts with COG to produce syngas, and the other is used to generate electricity or for other purposes. The steam consumption in the following discussion refers to the former. The effects of the steam consumption on the ICDQCG process are presented in Fig.7, 8, 9, 10.

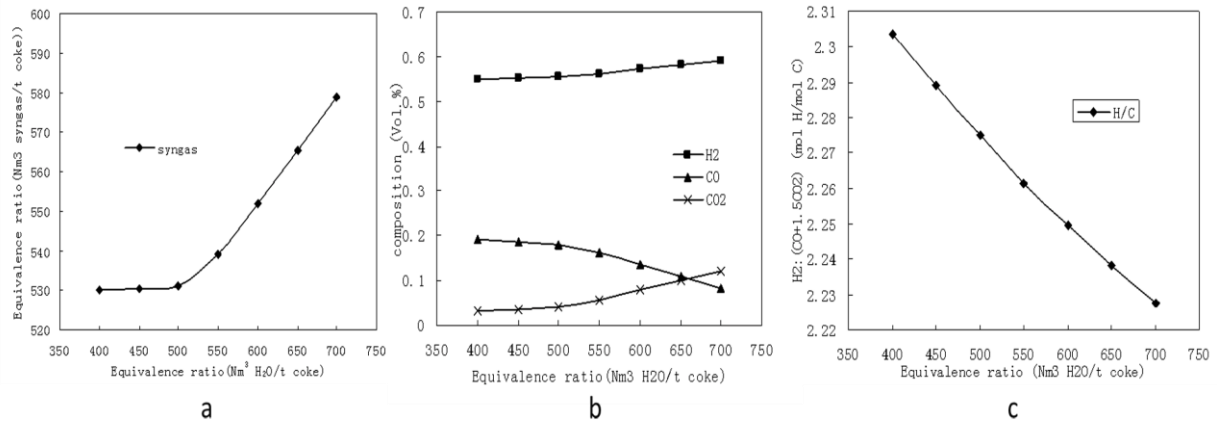


Figure 7. Effects of steam consumption on syngas yield, syngas composition and H/C (COG flow rate is 123)

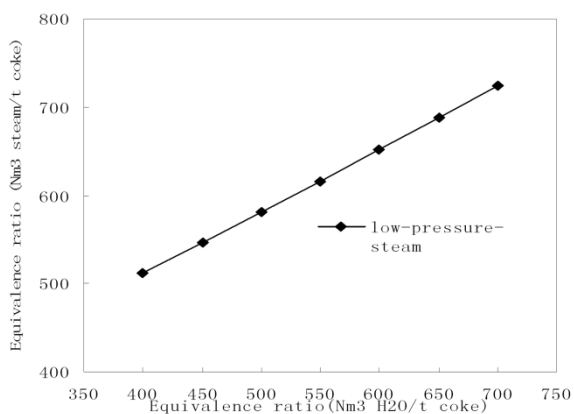


Figure 8. Effects of steam consumption on steam yield

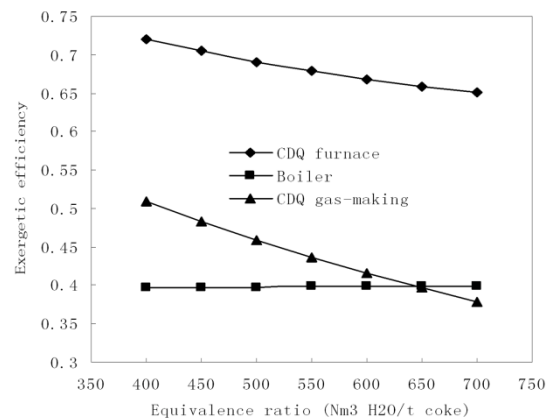


Figure 9. Effects of steam consumption on exergy efficiency

Fig. 7(a) shows that the flow rate of syngas increases with the flow rate of steam. This could be due to the fact that the reaction degree of reaction (1) and reaction (2) are increased with the flow rate of steam. Fig. 7(b) shows that the concentrations of H₂ and CO₂ increase with the flow rate of steam, while the CO concentration decreases. This is because the degree of reaction (2) is carried out more thoroughly than the reaction degree of reaction (1). As presented in Fig. 7(c), the H/C ratio decreases slightly with the increase of the steam flow rate. This is because that the steam is excessive in the reaction of the steam and COG, only exerting a slightly effect on reaction (1) and reaction (2).

As presented in Fig. 8 the yield of steam increases proportionally with the increase of the flow rate of steam. The reason could be that the excess steam leaves the CDQ furnace for the boiler with the syngas, and transfer their thermal energy to the steam in boiler generating more steam. The generated steam could be divided into two parts: one could be directly used to quench the coke, and the other could be used for power generation and other purposes.

Fig. 9 demonstrates that the exergetic efficiency of the CDQ furnace and the entire ICDQCG system decrease with the increase of steam flow rate, while the exergetic efficiency

of the boiler has only a slight change.

From the above analysis, it is useful to study the effect of the flow rate of steam for energy saving and syngas production.

According to the above discussion, the flow rates of COG and steam have a significant effect on the flow rate and composition of the syngas and the flow rate of the steam generated by the boiler and the exergy efficiency of the ICDQCG system, and it is important to find out the optimum inflow rates of COG and steam.

5. Conclusions

In this paper, the ICDQCG system is studied using the minimization of the Gibbs free energy. The results show that the COG flow rate and steam consumption have significant effects on the flow rate and composition of syngas and the exergy efficiency. According to the above discussion, the results are encouraging and helpful to the future's experimental and modeling efforts, which will focus on the chemical kinetics and engineering studies of the ICDQCG system, as well as the economic feasibility.

Symbols

Ash	coke ash	P_0	atmospheric pressure, (Pa)
E	number of elements in the system	P	pressure, (Pa)
FM	fixed carbon	Q	heat, (kJ/kg)
H	enthalpy, (kJ/kg)	S	entropy, (kJ/kg·K)
G	total Gibbs free energy, (kJ/kg)	T	temperature, (K)
m_A	mass fraction of ash in coal	VM	the volatile matter
Mois	moisture	ε	exergy, (kJ/kg)
n_j	number of moles of species j , (kmol/h)	η	exergy efficiency

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References

- [1] Bisio, G. and Rubatto, G.: Energy. 2000, 25, 247.
- [2] Teplistskil, M.G. Gordon, I.Z. and Kudryavaya, N.A. et al.: Coke drying quenching Translated by Lee Zhehao. Metallurgical Industry Press: Beijing, 1981.
- [3] Mori, T. Fujimura, T. and Sato, S.: Trans. ISIJ., 1980, 20(2), 108.
- [4] Prins, M.J. and Ptasiński, K.J.: Energy, 2005, 30(7), 982.
- [5] Errera, M.R. and Milanez, L.F.: Energy Convers. Manage., 2000, 41(2), 109.
- [6] Han, Y.Y. Zhang, H.T. Ying, W.Y. and Fang, D.Y.: Chin. J. Chem. Eng. 2009, 17(1), 108.
- [7] Lee, Y.J. Lee, S.D. Hong, S.I. and Moon, D.J.: Int. J. Hydrogen Energy. 2010, 35(23), 12970.
- [8] Higman, C. and Van Der Burgt, M.: Gasification, 2nd ed.; Gulf Publishing: Burlington, 2008.
- [9] Guo Z.C. Tang H.Q. and Liu J.L.: Fuel, 2005, 84(7-8), 893.
- [10] Pan L.H. and Wei S.B.: CDQ technology. Metallurgical Industry Press: Beijing, 2005.
- [11] Singh, S.P. Weil, S.A. and Babu, S.P.: Energy, 1980, 5(8-9), 905.
- [12] Zhu, M.S.: Exergy analysis of energy system. Tsinghua University Press: Beijing, 1988.
- [13] Jarungthammachote, S. and Dutta, A.: Energy Convers. Manage. 2008, 49(6), 1345.