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Analyses and the Study of Syngas Production in Dual-Gas Resources Polygeneration

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The dual-gas resources polygeneration system technology not only make full use of the complementary characteristics of carbon-rich in gasification and hydrogen-rich in coke oven gas, but also avoid the CO shift reaction, reduce the CO₂ emission reduction and energy loss. This paper analyses and introduces syngas production in dual-gas resources polygeneration system without water-gas shift processes.

Key Words: Carbon catalyst, CH₄-CO₂ reforming, Reaction mechanism, Mass and heat transfer.

INTRODUCTION

A large scale polygeneration technology based on the coal is recognized as a clean coal technology. It is regarded as the perfect combination of coal power production and coal chemical industry¹. The different polygeneration technology approaches are represented in the world. In 1998, the United States proposed "Vision 21" polygeneration systems which is based on gasification, power generation, hydrogen and liquid fuel. Shell company of Netherlands proposed polygeneration system which is close to the concept of the ecological park. Japan's New Energy Development Organization, also in 1998, put forward EAGLE polygeneration plan of a clean coal gasification, gas-fired power generation and fuel cell power generation, synthetic liquid fuels as the main content. In order to achieve the ultimate goal of "zero discharge" in the whole process and make full use of CH₄ and H₂ in coke oven gas, as well as the CO₂ in coal gasification, Taiyuan University of Technology proposed the dual-gas resources polygeneration system technology (gasified and pyrolyzed gas reforming into synthesis gas) in 2005. The basic research of syngas production from dual-gas resources and without water-gas shift processes are the main research topics. This paper analyses and introduces syngas production in dual-gas resources polygeneration system without water-gas shift processes.

Analyses of syngas production in dual-gas resources polygeneration system without water-gas shift processes: The main components of the raw gas in the ash agglomerating fluidized bed gasification are CO~35 %, H₂ ~ 40 %, CO₂~20 %. In order to achieve the requirements of the high conversion rate while discharge CO₂, the usual method is changing the

ratio of H₂ and CO through shift reaction. While, the coke oven gas mainly composed of CO (5-8 %), H₂ (55-60 %) and CH₄ (23-27 %) is used to produce synthetic gas in the method of vapor reforming. Because the coke oven gas is H₂-rich, the content of H₂ in the synthetic gas is too high and supplemental CO is required for ether production. If the coke oven gas and gasified coal gas are mixed by a certain percentage and the CH₄ in the coke oven gas and the CO₂ in the gasification gas can be reformed as CO and H₂ (CH₄+ CO₂=2CO + 2H₂ ΔH = +261 kJ mol⁻¹), it will be easy to achieve the goals of adjustment of H₂ with replacing transformation process and CO₂ emission reduction. According to this, the process of coke oven gas and gasification gas "Double Air Head" of syngas Production from Coke Oven Gas without water-gas shift processes is formed. The key of this process is to develop a CH₄-CO₂ reforming catalyst which is resistance to carbon deposition and its corresponding process and technology.

We found that in high-temperature carbon catalyst system CH₄ in the coke oven gas and CO₂ in the gasification gas can be reformed to produce synthetic gas. It can adjust the ratio of H₂ and CO in the synthesis gas. However, during this catalytic process, coke oven gas and gasification gas of CH₄, CO₂, CO, H₂ and C forms a complex reaction system. This reaction system is characterized by high temperature, multi-component, multi-impurities (tar and S) and multiple reaction. In this system, there are many effects of unknown factors and issues to be resolved. After analysis, the research group study main issues as followed: (1) carbon catalyst types, specific surface area and pore structure on the catalytic activity; (2) carbon catalytic reaction mechanism and kinetics of the process; (3) the hydrodynamics, mass transfer, heat transfer laws of coke oven

gas and coal gasification gas in a catalyst system. Careful investigation on the essence of this complex high-temperature carbon catalyst system is the key step to develop the process of coke oven gas and gasification gas "Double Air Head" of syngas production from coke oven gas without water-gas shift processes.

Carbon catalyst types and specific surface area on the catalytic activity

Effects of different carbon catalysts on the catalytic activity: Fig. 1 shows the effects of different carbon catalysts upon the $\text{CH}_4\text{-CO}_2$ reforming reactions at staying time of 3 s. The figure shows that the different catalysts have pronounced differences in the reforming reaction. The order of catalytic activity of the catalysts used in this study is catalyst III > I > II. The most active catalyst, carbon catalyst III, reaches conversion rate of 55.7 % or higher at 1000 °C. At the same temperature, the conversion rate for catalyst II is only 12.9 % and that for catalyst I is 10.3 %.

Fig. 1. CH_4 conversion over different carbon catalyst

The temperature has an evident influence on catalytic activity. The catalyst III has higher catalytic activity than the reaction temperature at lower 950 °C, however catalytic activity is very weak for catalyst I and II. The graph also shows the negligible difference in performance of catalyst I and II before 1000 °C. However, after temperatures increase above 1050 °C, the effect of catalyst I is much higher than catalyst II. After temperature reaches 1100 °C, there is no discernable difference between carbon catalyst I and III. At 1200 °C, the catalytic activity of three kinds of catalyst turns to the same. This suggests that different carbon materials have an evident influence on $\text{CH}_4\text{-H}_2\text{O}$ reforming reaction at different temperature. The conversion rate curves obtained from catalyzed reactions and uncatalyzed reactions show that at lower temperature range < 900 °C, the difference between catalyzed and uncatalyzed reaction is small. However, the behaviour of catalyst becomes apparent at 1000 °C, the conversion rate reaches 8.6 to 55.7 % in catalyzed reaction, but it is less than 5 % in uncatalyzed

reaction. The evident difference of CH_4 conversion rate between catalyzed and uncatalyzed $\text{CH}_4\text{-H}_2\text{O}$ reforming appears at mid-temperature range of 1030-1150 °C. For example, the conversion rate exhibits > 90 % for catalyzed reaction and only 51.1 % for uncatalyzed reaction.

Characteristics of the carbon catalyst surface area and pore structure: In order to understand the process of reforming reaction, the specific surface area of four different kinds coke was measured (Table-1). Compared with the unused carbon catalyst, the result shows that the surface area and pore volume of carbon catalyst used as CH_4 thermal decomposition and $\text{CH}_4\text{-CO}_2$ reforming are reduced significantly. However, the surface area and pore volume of carbon catalyst used as $\text{CH}_4\text{-H}_2\text{O}$ reforming reaction are increased significantly. The reason of reduction of carbon catalyst surface area and pore volume after CH_4 thermal decomposition is that carbon deposition is formed on the surface and porous of the coke. The enhancement of surface area and pore volume of the carbon catalyst used in $\text{CH}_4\text{-H}_2\text{O}$ are due to $\text{C-H}_2\text{O}$ gasification-reaction, which enlarge hole and increase specific surface area².

Mechanism of carbon catalytic reaction: Studies have shown that the high-temperature carbon materials can catalyze $\text{CH}_4\text{-CO}_2$ reforming reaction in a multi-atmosphere^{3,4}. At the same time, due to high temperatures C with CO_2 or H_2O reaction, C is partial loss. Catalysis of coke was proved as followed: (i) Carbon catalyst surface contain abundant oxygen-containing functional groups, which provide active sites for CH_4 reforming and promote CH_4 conversion. (ii) The difference of oxygen species between metal oxides which the oxygen-containing functional groups of semi-coke is generated during the process of gasification $\text{CO}_2\text{-H}_2\text{O}$ over coke. This is a useful to extend the catalysts of semi-coke.

The essence of $\text{CH}_4\text{-CO}_2$ reforming in the high-temperature carbon system can be divided in two steps^{3,4}: first, the methane decompose into carbon deposition and hydrogen; then the carbon deposition react with carbon dioxide into carbon monoxide. Methane decomposition is a chain reaction, the chain initiation (methane activation) is a crucial step. Oxygen-containing functional groups on the surface of carbon materials are active center, which can reduce the dehydrogenation activation energy of CH_4 . Catalytic activity depends on nucleophilic and pro-electric of oxygen species in the oxygen. Different species of metals make the electric surface charge character of oxygen of its' oxide species inconsistent. And it ultimately results catalytic inconsistent.

Through X-ray photoelectron spectra, four oxygen-bearing functional group can be detected on the surface of catalyst⁵⁻⁸: phenolic hydroxyl, carbonyl, carboxyl and lactone. The content of oxygen-bearing functional group in catalyst is shown in Table-2.

It can be found from Table-2, after $\text{CO}_2\text{-CH}_4$ reforming, the content of oxygen-bearing functional group in catalyst de-

TABLE-1
SPECIFIC SURFACE AREA AND PORE SPECIFIC VOLUME ANALYSIS DATA

	Original sample	750 °C CH_4 thermal decomposition sample	850 °C CH_4/CO_2 reforming sample	1000 °C CH_4/CO_2 /steam reforming sample
BET (cm^2/g)	84.19	2.67	2.97	169.60
Pore volume (cm^3/g)	0.05	0.01	0.01	0.11

TABLE-2
CHANGE OF OXYGEN-BEARING FUNCTIONAL GROUP IN CARBON-CATALYST

Item	Content of oxygen-bearing functional group (%)				
	C-C	Phenolic hydroxyl	Carbonyl	Carboxyl	Lactone
Before reaction	56.60	28.66	6.08	6.04	2.62
After reaction	82.14	4.20	9.79	3.67	0.20

clined fiercely, especially the phenolic hydroxyl and lactone, decreases from 28.66 and 2.62 % to 4.2 and 0.2 %, respectively. Based on the phenomenon mentioned above, it can be concluded that the phenolic hydroxyl and lactone play an important role in $\text{CO}_2\text{-CH}_4$ reforming and promote the conversion of CH_4 efficiently. However, with the phenolic hydroxyl and lactone consuming, the conversion of CH_4 drop off. When the phenolic hydroxyl and lactone is consumed completely, the conversion of methane maintains nearly constant.

Mass and heat transfer laws of gas in the catalyst system : When the burning is turbulent diffusion flame, the three-dimensional Cartesian coordinate system K- ϵ equations of general type are as follows^{9,10}:

$$\frac{\partial(\rho k)}{\partial t} + \frac{\partial(\rho k u_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + G_k - \rho \epsilon$$

$$\frac{\partial(\rho \epsilon)}{\partial t} + \frac{\partial(\rho \epsilon u_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\epsilon} \right) \frac{\partial \epsilon}{\partial x_j} \right] + \frac{C_{1\epsilon} \epsilon}{k} G_k - C_{2\epsilon} \rho \frac{\epsilon^2}{k}$$

Component conservation equation is:

$$\frac{\partial(\rho C_s)}{\partial t} + \text{div}(\rho \bar{u} C_s) = \text{div}[D_s \text{grad}(\rho C_s)] + S_s$$

C_s : The volume concentration of S, ρC_s : The mass concentration of the component, D_s : The component diffusion coefficient, S_s : The mass of the component in the reaction per unit time per unit volume.

The mass transfer equation was as followed:

$$N_A = k_G a_m (C_{AG} - C_{AS}) \left(\frac{\text{m}}{\text{s}} \right) \left(\frac{\text{m}^2}{\text{kgcat}} \right) \left(\frac{\text{kmol}}{\text{m}^3} \right)$$

$$= \frac{C_{AG} - C_{AS}}{1/(K_{G a_m})}$$

k_G : The mass transfer coefficient; a_m : The surface area (external surface) of the particles.

Heat transfer equation is:

$$q = h_s a_m (T_s - T_G) = \frac{T_s - T_G}{1/(h_s a_m)}$$

h_s : The heat transfer coefficient; a_m : The particle surface area subscript G: the main particle; subscript S: the particle surface. * $q > 0$, that means that the most heat is absorbed by gas.

According to the heat and mass transfer model, the simulation of heat and mass transfer was investigated, the results were shown in Figs. 2 and 3.

The temperature and gas composition distribution were simulated and optimized by using computational fluid dynamics software, good results were acquired and the testing results of the experimental small reactor were mainly agreement with the simulated results. These simulated results provide the basis for pilot plant design.

Fig. 2. Contour curve and distribution of temperature

Fig. 3. Distribution of gas composition

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