

APPLICATION OF DETAILED CHEMICAL KINETIC MODEL TO PRACTICAL SYSTEM OF HOT COKE OVEN GAS REFORMING BY NON-CATALYTIC PARTIAL OXIDATION

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Summary

A reforming technology of crude coke oven gas (COG) by non-catalytic partial oxidation has been developed since fiscal 2006. This paper presents experimental results accumulated so far by operating 1/10 scaled pilot equipments that are installed on the platform of full scale coke ovens. Operating the reformer under an optimum condition enabled to double volume flow rate of syngas, and to achieve more than 95 % conversion of hydrocarbons included in the crude COG. Besides the product gas compositions exhibited an optimum range for methanol synthesis. Numerical simulations of the reforming with a detailed chemical kinetic model were also performed toward a better understanding of the chemically reacting flows inside the reformer.

Keywords

Complex reacting flows, Clean coal processing technologies, Hydrogen production.

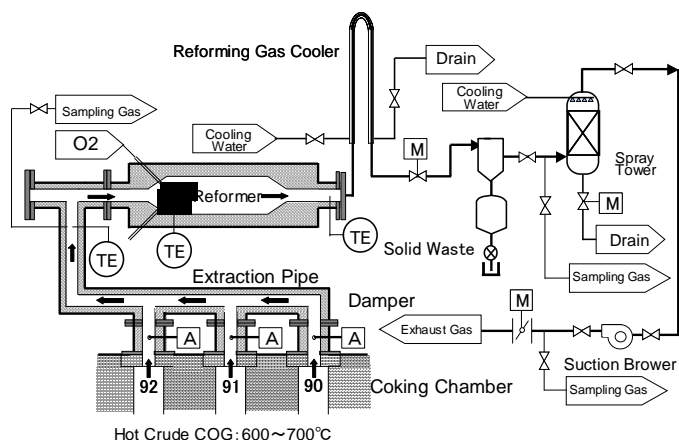
Introduction

In producing metallurgical cokes, coke oven gas (COG) is given off at a level of 300-350 Nm³ per ton of coal. COG consists primarily of hydrogen and methane and also involves carbon monoxide, carbon dioxide, and tar. In the conventional processes, hot COG exhausted from coke ovens is quenched to condense the tar, which is further distilled to obtain a marketable feedstock of aromatic chemicals and pitch cokes. The tar-free COG is refined through a desulfurization facility and used as fuels for coke ovens, fired heaters in ironworks, and power stations. Reforming of crude COG into tar-free H₂/CO-rich syngas taking advantage of sensible heat the COG has been studied¹ toward more effective utilization of COG. For commercialization of a COG reforming technology, experiments of non-catalytic reforming of practical crude COG have been carried out with a 1/10 scaled pilot equipments that has been installed on the platform of full-scale coke ovens. The COG reforming was analyzed numerically with a detailed chemical kinetic model and its applicability to a better understanding of the chemically reacting flows inside the reformer and design of commercial-scale reformers was examined.

COG reforming

The 1/10 scaled pilot equipments were installed on the platform of full-scale coke ovens of Kitakyushu Coking Works of Nippon Coke & Engineering Co., Ltd.. The flow diagram of the pilot equipments is shown in Figure 1. A portion of COG exhausted from the ovens was introduced into the pilot-scale reformer at a prescribed flow rate together with oxygen and then partially oxidized. The

compositions of both inlet and outlet gases were measured



intermittently by means of gas chromatography.

Figure 1 The pilot equipments flow diagram for the COG reforming studies.

Numerical simulations

For a better understanding of the chemical reactions involved in the COG reforming, numerical simulations with a detailed chemical kinetic model were conducted. In Figure 2, the outline of the simulations is schematically represented. The real reactor for the COG reforming was idealized to a tube reactor with a constant inner diameter for one-dimensional plug-flow simulation so that introduced gas experiences the same temperature history

as it does in the real reactor. The mechanism used in this study was proposed by Richter and Howard² and consisted of ~ 2000 reactions, including ~ 260 chemical species from the smallest species of hydrogen radical to the largest molecule of coronene. The calculations were performed the PLUG code in the DETCHEM program package (DETCHEM^{PLUG}).³ The input parameters for calculations were obtained from the reforming tests in 2008 such as inlet velocity, molar composition of crude COG, pressure, gas temperature profiles, and so on. The tar included in the crude COG was assumed to be the mixture of approximately 30 polycyclic aromatic hydrocarbons by referring the literature⁴. The detailed description of the numerical simulation can be found elsewhere^{5,6}.

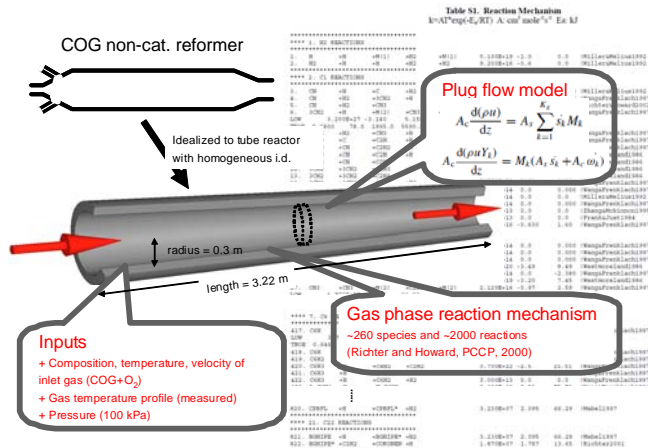


Figure 2 Numerical simulation of the chemically reacting flow in the COG reformer by the combination of a detailed chemical kinetic model and a plug flow reactor model.

Results and discussion

Chemical compositions of crude COG and the product gas obtained at selected runs are listed in Table 1. The current reforming with the non-catalytic partial oxidation yields increases in H₂ and CO concentrations. Over 95 % carbon conversions of the hydrocarbons included in the crude COG were also obtained. Beside the reformed gas exhibits an optimum composition for the methanol synthesis, implying non-catalytic reforming method of the COG is one of the promising process to supply material gas to practical methanol plants.

Table 3 Comparison of chemical composition between crude COG and reformed gas

Test run No.	Run08-6-7		Run08-8-8	
	Crude COG	Reformed gas	Crude COG	Reformed gas
Chemical composition (dry)				
(vol.%)				
H ₂	53.7	65.4	56	68
N ₂	5	4.7	1.3	0.5
CH ₄	32	0.8	31.3	0.75
CO	5.7	21.2	6.7	22.7
CO ₂	1.9	7.9	2.5	8
C ₂ H ₄	0.48	0.02	0.77	0.01
C ₂ H ₆	0.11	0	0.12	0
H ₂ S	0.02	0.05	0.09	0.01
C ₆ H ₆	1.17	0	1.24	0
C ₇ H ₈	0.02	0	0.03	0
C ₈ H ₁₀	0	0	0	0
Gas flow rate (Nm ³ /h)	28	43	44	69
Carbon conversion ratio(%)		96		97
Gas amplification ratio *1		2.3		2.2
R-value *2		2		2

*1: Gas amplification ratio = A/B

A: Gas volume of [H₂] + [CO] in reformed gas at standard condition
 B: Gas volume of [H₂] + [CO] in inlet crude COG at standard condition
 *2: R-value is defined as an index by following equations for the optimum gas composition of the product gases for methanol synthesis R-value = E/F/E : Gas volume % of [H₂] - [CO₂] in reformed gas, F : Gas volume % of [CO₂] + [CO] in reformed gas

An example of the outputs from the numerical simulations is shown in Figure 3 in which the major events in chemical reactions are also indicated. After the reactor position at around 0.3 m, the concentration profiles of major species are little changed, indicating the major events in chemical reactions in the COG reforming by partial oxidation are almost completed. Figure 4 demonstrates the predictive capabilities of the current numerical simulations. The comparisons between the test results and the numerical simulations are given for the major gas phase products. The good agreements are found and encourage further potentials of the currently developed numerical simulations with the detailed chemistry in supporting design and optimization of the COG reforming process.

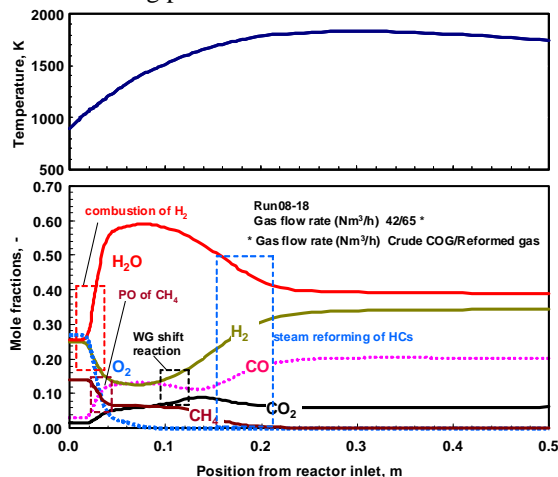


Figure 3 Computed mole fraction profiles of major compounds in the COG reforming.

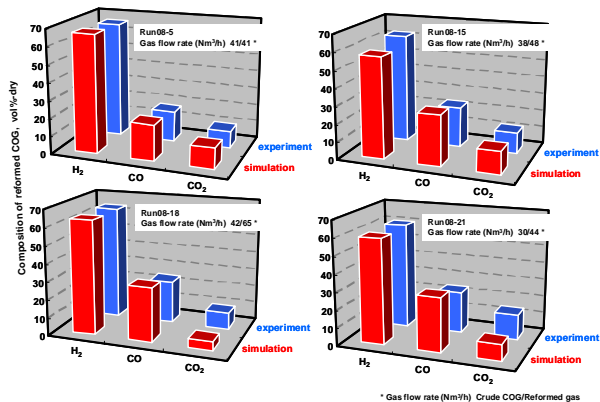


Figure 4 Comparisons between numerically predicted vol % of the reformed gas and experimentally determined compositions of the reformed gas in the selected runs of the reforming tests.

Acknowledgments

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References

1. Onozaki, M., Watanabe, K., Hashimoto, T., Saegusa, H. and Katamaya, Y. *Fuel*, 85, 143-149(2006).
2. Richter, H.; Howard, J. B. *Phys. Chem. Chem. Phys.* 2002, 4 (11), 2038-2055.
3. DETCHEM Software package, www.detchem.com.
4. Kirton, P. J.; Ellis, J.; Crisp, P. T. *Fuel* 1991, 70 (12), 1383-1389.

5. Norinaga, K.; Janardhanan, V. M.; Deutschmann, O. *Int. J. Chem. Kinet.* 2008, 40 (4), 199–208
6. Norinaga, K. and Hayashi, J.i. *Energy Fuels*, in press