Development of Novel CO2 Reforming Process and its Simulation Model

Shuhei Wakamatsu[*1], Fuyuki Yagi[1], Tomoyuki Mikuriya [1],*
Ryuichirou Kajiyama [1], Mitsunori Shimura[1], Yoshifumi Suehiro[2]

[1] Chiyoda Corporation, Kawasaki, Kanagawa, 210-0855, Japan

[2] Oil&Gas Technology Research & Development, Japan Oil, Gas and Metals National Corporation, Mihama, Chiba, 261-0025, Japan

Introduction

Gas To Liquid (GTL) processes have recently been praised as effective technologies for the utilization of natural gas fields on medium or small scales which are not available for LNG. The capital cost of synthesis gas production section in GTL processes has been accounted for around 60% of the total capital cost[1), 2)]. Therefore the development of more compact synthesis gas production processes with high energy efficiency is desired.

We have been developing new CO_2/H_2O reforming catalyst and process through Japan Oil, Gas and Metals National Corporation (JOGMEC) GTL National project since 1999. The new process by using a tubular reformer which does not need an expensive oxygen plant can directly generate the stoichiometrically balanced synthesis gases which have no excess of H_2 and CO as suitable feed gases for Fisher-Tropsch(FT) synthesis, methanol and dimethyl ether and so forth. This proprietary catalyst with a high resistance to carbon deposition can produce synthesis gases by lower CO_2/Carbon and H_2O/Carbon molar ratio in the feed gas composition with low energy consumption.

The simulator to predict the temperature profile and gas compositions in the catalyst bed has also been developed for the design of the tubular reformer.

The pilot plant tests of this process were successfully carried out at Yufutsu gas field in Japan, and high economics were shown on the feasibility study.

Experimental

Catalyst: The commercial size ring catalysts of 16mm outer diameter, 8mm inner diameter and 16mm length were prepared by loading of novel metals (Rh, Ru and Pt etc.) on basic metal oxide supports. An average side crashing strength of the catalysts was 500N/piece. Catalyst surface property, Lewis acidity and basicity, was designed precisely to exhibit high activity and decoking nature.

Pilot test : For the pilot plant operations, about 120L of commercial size catalysts were charged in mono-tube reformer which has 12.0m length and 11.0cm inner diameter, and were reduced at around 800ºC under atmospheric pressure before starting the reaction tests. Synthesis gas with H_2/CO=2 was generated directly by CO_2 and H_2O reforming of natural gas. Feed H_2O/CO_2/Carbon ratio was 1.15-1.64/0.40-0.60/1, and reaction conditions were at 865-890ºC, 1.5-1.9MPaG and GHSV=3000 1/HR. The total content of higher hydrocarbons in natural gas, for example ethane and propane, was around 13% and total sulfur content was around 1ppm.

Simulator : The concept of the simulator is shown in Fig. 1.

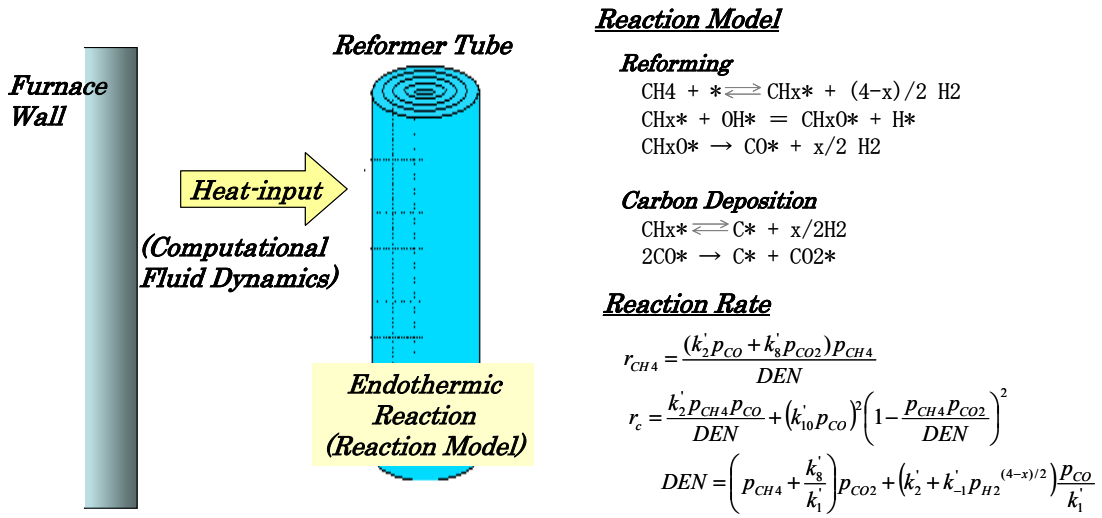

Figure 1. Concept of CO_2 reforming Simulator

The heat–input of the reformer tube from the burners is calculated by computational fluid dynamics, and the endothermic heat-flux is calculated by the simulator. The modeling of reactions for reforming and carbon formation on the catalyst surface is conducted with consideration from the laboratory experimental results and information on literatures[3]. Catalysts life under optional operation conditions can be estimated because the carbon formation rate is taken into the consideration. Representative elementary reactions are shown. The reaction rate of CH_4 and the carbon formation reaction rate are expressed by the rate constant on elementary reactions and the partial gas pressures.

Results and Discussion

Fig.2 shows the relation between volume of feed gases and compositions of those to obtain constant amount of synthesis gases with H_2/CO molar ratio of 2.0.

The volume of synthesis gases was estimated by the equilibrium calculation of steam reforming and water-gas shift reactions at 850°C and 2.1MPa. At the point of nearby feed molar ratio of $CH_4:CO_2:H_2O$=1.0:0.4:1.0, volume of feed gas is minimized and it is predicted that preferable operations with lower energy consumption can be accomplished. But on CO_2/H_2O reforming with ordinary reforming catalysts, the selection of these

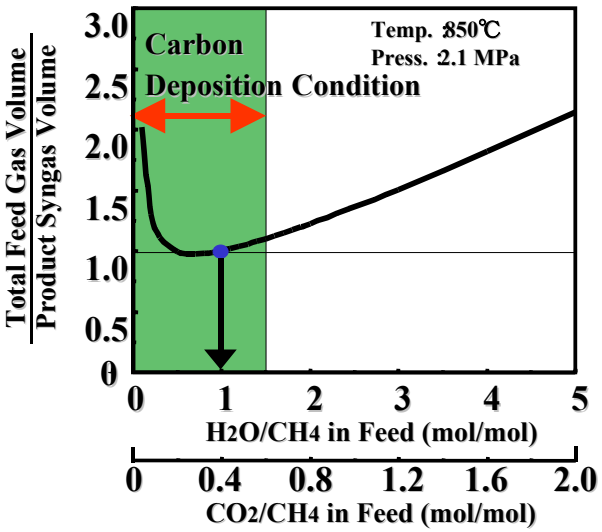

Figure 2. Optimal CO_2/CH_4 and H_2O/CH_4 Molar Ratio in Feed Gas to Produce Syngas (H_2/CO=2.0) for FT Synthesis

operating conditions is prohibited by higher potential for carbon formation, and particular technologies for decoking will be required [4),5)].

The results of the pilot plant operation are shown in Fig. 3. In this figure, the conversions of natural gas are presented by comparison with the percentage of the equilibrium values at the same reaction conditions.

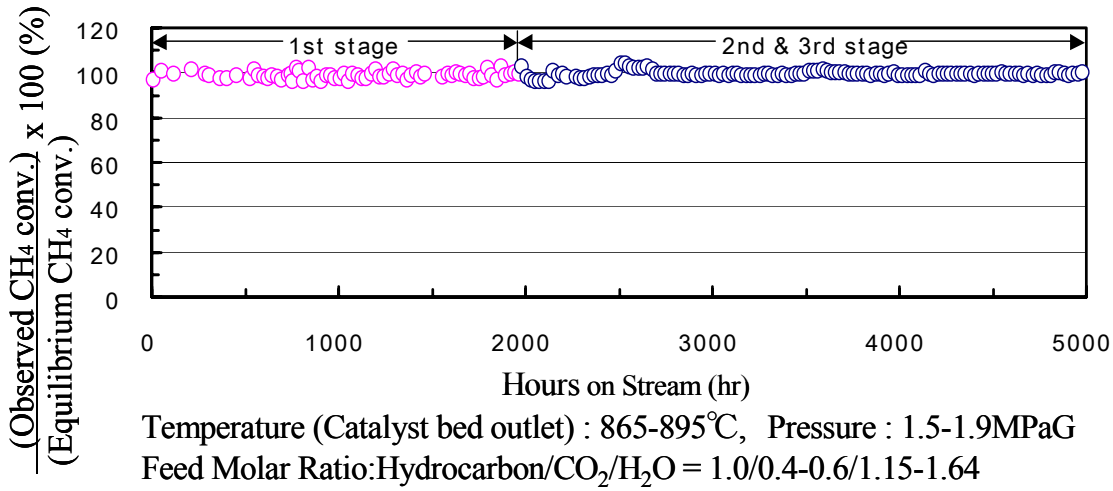

Figure 3. Results of Pilot Plant Tests for CO_2 Reforming

Although catalyst reloading was done after 1st stage operation, some parts of discharged catalysts were recharged at the same position which had been loaded before. So we could investigate total experience of the catalysts. As shown in Fig. 3, the stable operation for more than 5,000 hours has been attained under the target reaction condition. During the operation, little change of the temperature and pressure drop of the catalyst bed was observed. After the total tests, the catalyst was discharged from the reformer and the carbon content of the catalysts was analyzed. The amounts of the carbon deposition on the catalysts which have been loaded during the total test were less than 0.1wt%. From the results, the carbon-free operation has been demonstrated.

Typical fitting results to determine kinetics parameters are shown in Fig. 4. This figure stands each gas compositions with the reaction times. The plots represent the observed value, and corresponding curves present the calculation results. As shown in this figure, calculation results fitted with observed value well, and kinetics parameters in reaction model could be obtained.

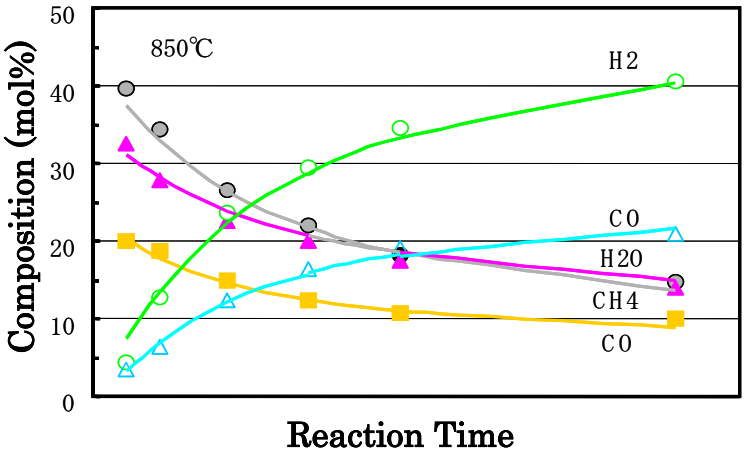

Figure 4. Results of parameter fitting

Through the analysis of the pilot plant test results by the simulator incorporated that reaction model, it was confirmed that it could be effectively used for the CO_2 reformer design.

The feasibility studies of the new GTL process for the utilization of those gas fields have been done. In the Southeast Asia, a lot of gas fields of those sizes containing a certain amount of CO_2 are found. In those natural gas fields, the CO_2 reforming process will be successfully applied to the synthesis gas production as feed for FT synthesis. The basic assumptions of the feasibility studies are as follows, Gas Field Size ; 1.75TCF, Plant Capacity; 15000BPSD (Stand Alone/Grass Roots), Natural Gas Composition; $CH_4/C_2H_6/C_3H_8/C_4^+/N_2/CO_2$ = 77.5/1.0/0.3/0.3/0.8/20.1 (vol%). It is estimated that the plant cost is 560 million US$, and the product oil price COE (Crude Oil Equivalent price) is around 18 US$/bbl.

Acknowledgements

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