A Study on a Steam Reformer for Methanol*

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The purpose of this study is to provide thermal and chemical design standards for a steam reforming reactor of methanol, for recovering the waste heat of a gas turbine and an automobile engine. For this purpose, this study included both experiments on chemical reaction, and simulations for the reactor. As a result, it was found that there is a law of similarity between the chemical reactions and heat transfer. Also, the simulation would be applicable to investigations concerning the characteristic behavior of an actual reactor system, from which the standards of an applicable design for a steam reformer were derived.

Key Words : Steam Reforming, Methanol, Recovering of Waste Heat, Gas Turbine, Alcohol Fuel

1. Introduction

Methanol fuel, which has attracted special interest as an alternative fuel to oil, is so reactive that steam reforming or decomposing is possible at temperatures below 300°C. Since these reactions are endothermic, the heat value of methanol after the reforming or decomposing process, increases by about 15 or 20%. Thus, it has often been pointed out that applying these chemical processes for the recovery of waste heat in a gas turbine will result in a higher thermal efficiency, exceeding 50% (LHV) being feasible. Although in the design of a reformer for recovering the waste heat of a gas turbine there are some important factors; such as flow rate of the exhaust gas, waste heat, temperature of the gas, heat resisting

temperature of the catalyst, and especially heat transfer between the gas and the reactor tube etc., design standards have not taken such factors into consideration yet.

Accordingly, the purpose of this study is to provide design standards for a steam reformer by taking such factors into account. These standards should be obtained by experimental procedures, but it is very difficult to perform such large scale experiments so as to be applicable to an actual system. Therefore, in this study, the characteristics of reaction in a reformer, and the various quantities needed for design were investigated by performing numerical simulations. In addition, experiments were performed to obtain the reaction velocity of reforming, and to examine the validity of the simulation results.

Nomenclature :

A : Coefficient of catalyst ability
 C : Concentration, mol/m³
 c_p : Average specific heat at constant pressure, J/(kg · K)
 D_e : Effective diffusivity, m²/h
 F : Flow rate of sample, mol/h
 G : Mass flux, kg/(m²·h)

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- $\bar{G}$: Flow rate of fuel (methanol), $\text{kg}/(\text{m}^2 \cdot \text{h})$
 $-\Delta H$: Reaction heat, J/mol
 h_w : Coefficient of heat transfer, $\text{J}/(\text{m}^2 \cdot \text{h} \cdot \text{K})$
 k : Coefficient of reaction velocity
 k_e : Effective heat conductivity, $\text{J}/(\text{m} \cdot \text{h} \cdot \text{K})$
 L : Distance in axial direction, m
 L_o : Length of reactor tube whose reaction rate reaches 99%, m
 M_{av} : Average molecular weight, kg/mol
 Nu : Nusselt number
 $\dot{Q}$: Amount of heat transfer, $\text{J}/(\text{m}^2 \cdot \text{h})$
 Q : Amount of nondimensional heat transfer
 r : Velocity of reaction, $\text{mol}/(\text{g} \cdot \text{cat} \cdot \text{h})$
 R : Distance in radial direction, m
 R_w : Radius of tube, mm
 Re : Reynolds number
 t : Temperature, $^\circ\text{C}$
 t_w : Wall temperature of reactor tube $^\circ\text{C}$
 u : Velocity of reactant, m/h
 W : Amount of catalyst, g
 X : Reaction rate
 Y_0 : Molar ratio at inlet of reaction tube
 P_b : Volumetric density of catalyst = amount of catalyst/volume of catalyst bed, kg/m^3

2. Apparatus and Procedure

In this study, a formula for the reaction velocity of steam reforming was first determined by experiments using the apparatus shown in Fig. 1. Second, reaction rate and heat transfer were estimated by solving the equation of simulation for steam reforming in which the formula of the reaction velocity obtained was used. In addition, using the apparatus shown in Fig. 2, the reaction rate and the heat transfer

Fig. 1 Apparatus for determining the velocity of reaction

were measured and the results were used to examine the validity of the simulation.

As shown in Fig. 1, the reactor tube employed has an inside diameter of 22 mm and a length of 400 mm. The catalyst was mixed with 5 mm diameter glass ball ($d=5$ mm), and was then charged to the central part of the reactor, which was 100 mm in length. There were 5 to 10 catalysts ranging in weight from 2.48 to 4.98 g. Reaction temperature was measured by 3 thermocouples (CA), 2 of which were located at the inlet and the outlet in the central axis of the tube. The other one was set on the outer surface of the tube. The reactor tube was heated by an electric heater, automatically controlled to maintain a constant temperature.

Samples were made by mixing the molar ratios of the water (S) and the methanol (M) $S/M=1, 2$ and 3 . The experiments investigating the reaction velocity were carried out under temperatures ranging from 200 to 300°C . The sample fed by the feed pump was vaporized in a vaporizer set before entering the reactor tube, and was then carried into the reactor by nitrogen gas. An analysis of the reaction products was carried out by gas chromatography after they had passed through a cooler, an ice-trap, and a gas sampler.

The catalyst used was type N 211 produced by the Nikkai Chemical Co. Ltd. The shape was cylindrical, 6 mm in diameter and 5.5 mm in length. It contained $\text{CuO} + \text{ZnO}$. In this experiment, since the catalyst required reduction before use in order to keep its reactivity, the reduction and charging were performed for every test. The reduction was allowed to run for 90 minutes by purging with nitrogen gas at 10 ml/min. Reduction was completed when there was no water in the flowing gas. Finally, the temperature in the reactor was set at the experimental level by purging with nitrogen gas again, and the experiment was begun.

Figure 2 displays an outline of the apparatus used

Fig. 2 Experimental apparatus for steam reforming

for the measurement of heat transfer. The reactor tube was made of stainless steel with an inside diameter of 24 mm and a length of 100 mm. In the central section of this tube whose length was 550 mm, 100 g of catalyst was charged, mixed with glass balls. Thermocouples (CA) were set at 110 mm intervals along the central axis and the outer surface of the tube. The heating of the reactor was carried out by 8 electric heaters (100W) which maintained the wall temperature at 250°C. The amount of heat transfer was calculated by measuring the difference in electric power supplied with reaction from the electric power without reaction, where 'without reaction' corresponds to cases where only nitrogen gas was used. Also, the reduction of the catalyst and the reaction path are almost the same as the case shown in Fig. 1.

3. Steam Reforming Methanol

The reaction of reforming is represented as follows:

This is an endothermic reaction with the heat of reaction, -58.1 kJ/mol at 250°C, as is well known. But this reaction may produce by-products such as methan, dimethylether, carbon, etc. which are not suitable for the recovery of waste heat because they are exothermic. Therefore, the analyses of these by-products were performed using a thermal conductivity detector for which the fillers used were APS, fulsin for water, aldehydes, alcohol; and active carbon for hydrogen, nitrogen, carbon monoxide and methane, respectively. Table 1 shows the reaction products at a temperature of 260°C. It is shown that CO is the only by-product above 0.5% and the others, such as methane, were not detected. Furthermore, it should be noted that CO has never exceeded 1% independently of S/M .

4. Formula of Reaction Velocity

The reforming reactor examined is an integral type, so the formula for reaction velocity is assumed as follows:

$$r = k \cdot C_{\text{CH}_3\text{OH}}^m \cdot C_{\text{H}_2\text{O}}^n \quad (2)$$

where k is the constant of reaction velocity; C is the molar concentration and m , n represent its dependence.

Table 1 Reaction products (%)

S/M	1	2	3
H ₂	75.0~75.4	75.2~75.9	74.2~75.7
CO ₂	23.7~24.4	23.5~24.0	23.5~24.8
CO	0.6~1.0	0.5~0.9	0.7~1.0

Therefore, the formula for reaction velocity, r , was arrived at by determining k , m and n experimentally. Thus, the formula obtained sufficed for performing the simulation, as described later.

Figure 3 shows the results obtained from experiments for determining r . This is the case for a reaction temperature of 260°C, where the ordinate represents the degree of conversion from methanol to hydrogen, X , and the abscissa represents the ratio of the catalyst, W , to the flow rate of the sample, F . As is obvious from Fig. 3, the results plotted gather well on a curve for W/F , independent of S/M . Therefore, for the same values of W/F , less S/M contains more methanol because F is a blend of methanol and water. A series of experiments were performed for five points between 200 and 300°C, from which the formula of r were obtained as eqns. (3) and (4). According to eqns. (3) and (4), this reaction proceeded most suitably at $S/M=1$ because they were dependent on S/M . Thus, the experiments for measuring heat transfer were fulfilled at $S/M=1$.

5. Simulation on the Steam Reforming

5.1 Basic equations

For introducing the governing equations for the reactions and heat transfer in the reactor, the following assumptions are made:

- (1) there is no difference in temperature between the catalyst and the reactants;
- (2) heat conduction and mass diffusion in the axial direction are neglected;
- (3) velocities of gas flow in a tube are uniform in each cross section; and
- (4) physical properties of the reactants hold constant values.

The assumed reactor is a porous cylinder with a uniform distribution of catalyst, exchanging heat from the outside of the tube. Considering the conserva-

Fig. 3 Relation between X and W/F

tion of energy and mass under the above assumptions, the basic equations for the steady state are given as eqns. (5) and (6). In these equations, 't' is the reaction temperature, 'X' the reaction rate and 'r' the reaction velocity given by eqn. (3). Furthermore, k_e and h_w were given from the theoretical equations presented by Yagi, Kunii and Suzuki et al⁽⁶⁾⁽⁷⁾ and also $D_e=0.4536 \text{ m}^2/\text{h}$. Thus, the basic equations were solved numerically under the boundary conditions of eqns. (7)~(9), where the wall temperature, T_w , is assumed to be kept uniform at 250°C ; $S/M=1$; and $G=10-5500 \text{ kg}/(\text{m}^2\text{h})$.

$$-\frac{\partial t}{\partial L} + \frac{k_e}{G \cdot c_p} \left(\frac{\partial^2 t}{\partial R^2} + \frac{1}{R} \frac{\partial t}{\partial R} \right) + \frac{r \cdot P_b \cdot (-\Delta H)}{G \cdot C_p} = 0 \quad (5)$$

$$-\frac{\partial x}{\partial L} + \frac{D_e}{u} \left(\frac{\partial^2 x}{\partial R^2} + \frac{1}{R} \frac{\partial x}{\partial R} \right) + \frac{r \cdot P_b \cdot M_{av}}{G \cdot r_0} = 0 \quad (6)$$

$$L=0: t=t_0(R), \quad x=x_0(R) \quad (7)$$

$$R=0: \partial t/\partial R = \partial x/\partial R = 0 \quad (8)$$

$$R=R_w: -k_e(\partial t/\partial R) = h_w(t - t_w) \quad (9)$$

$$\partial x/\partial R = 0$$

The porous cylinder described above assumed to have

Fig. 4 Relation between X and L/L_0

Fig. 5 Relation between X and L/L_0 (Effects of R_w)

the catalyst uniformly distributed, differs from the actual conditions employed; but previous studies⁽⁸⁾⁽⁹⁾ have reported that there are no effects resulting the differing conditions.

5.2 Reaction rate

Figure 4 displays the reaction rate obtained where $S/M=1$ with $G=77.4-154.8 \text{ kg}/(\text{m}^2\text{h})$ at 250°C , comparing the results of both the experiment and simulation. In the figure X and L/L_0 are the ordinate and the abscissa, respectively, where L_0 is the distance required to reach the reaction rate of $X=0.99$. As is obvious in Fig. 4, the results due to simulation agree closely with the experimental ones. It should be especially noted that there are no effects due to the differences of mass flux, G .

Figures 5 and 6 show the results obtained for the cases in which the diameter of reaction tubes and the density of catalyst were varied, respectively. Both figures also suggest that the steam reforming is almost independent of differences in the diameter of the tube or in the density of the catalyst. Regarding variations of the temperature and the reaction rate in the radial direction, they are so small as to be consid-

Fig. 6 Relation between X and L/L_0 (Effects of P_b)

Fig. 7 Relation between Q and L/L_0

ered almost negligible excepting those temperatures at the entrance region of the tube. Therefore, they were omitted from this paper.

5.3 Characteristics of heat transfer

Figure 7 shows the characteristics of heat transfer derived from the simulation shown in Fig. 4. The ordinate is the amount of local heat transfer, $\dot{Q}$, along the wall of the tube. The trend of $\dot{Q}$ is to decrease rapidly as L/L_0 increases. Most of the heat required for the reaction is centered in the front half of the tube. Figure 8 displays the nondimensional amount of heat transfer Q derived by integrating $\dot{Q}$ along L/L_0 as follows;

$$Q = \frac{2}{(-\Delta H \cdot G)} \int_0^{L/L_0} \dot{Q} d(L/L_0) \quad (10)$$

Fig. 8 shows the behavior of the amount of heat accumulated along L/L_0 , whose profile corresponds with X in Fig. 4. Also, it is found that the experimental results shown are in agreement with those of the simulations, where the effects of the mass flux, G , could be neglected in the same manner as in Fig. 4.

Fig. 8 Nondimensional amount of heat transfer

Fig. 9 Nusselt number

These results suggest the existence of a law of similarity for wide ranges of this reaction. Therefore, even experimental results obtained using a small apparatus would be useful for clarifying the characteristics of reaction or heat transfer for actual large systems.

Figure 9 displays the Nusselt number obtained from the results of the simulation, in which a solid line indicates the results of the simulation, and a symbol represents those of the experiment. A broken line also shows the Nusselt number without any reaction. R_w indicates the radius of the tube; for our apparatus is $R_w=12$ mm. According to Fig. 9, the results of the case with reaction are 20-30% larger than those without reaction in every R_w . This result means that the heat transfer would be promoted remarkably by the reaction of steam reforming.

5.4 Dimension of reactor

Figure 10 shows the relation between the length of the reactor, L_0 , and the mass flux, G , obtained from the simulation under conditions of a wall temperature of $T_w=250^\circ\text{C}$, $P_b=400$ kg/m³, $S/M=1-2$ and $R_w=12-36$ mm. Figure 10 shows that there is a linear relation between L_0 and G , which is independent of R_w and S/M . Note that G contains the methanol and the distilled water so that L_0 will become shorter as S/M decreases, considering the results shown in Fig. 3. Thus, formulating the relation in Fig. 10 gives the following equation:

$$G = AL_0 \quad (11)$$

where A is a proportional constant, related to the catalyzing ability, in this case, $A=76.39$. For example, if $L=5$ m is substituted into eqn. (11), we obtain $G=382$ kg/(m³h). Therefore, the number of tubes required is derived from eqn. (12), considering S/M and the sectional area of the tube.

Fig. 10 Length of reactor tube

Fig. 11 Length of reactor tube (Cases for various P_b)

$$n = \frac{\bar{G}}{G \cdot \pi R_w^2} \left\{ 1 + \frac{9}{16} \left(\frac{S}{M} \right) \right\} \quad (12)$$

where $\bar{G}$ is the amount of methanol supplied per 1 h. Then, substituting $G=4\,500$ kg/h, $R_w=36$ mm and $S/M=1$ into eqn. (12), the number of tubes becomes $n=4521$.

Figure 11 shows the results for the case in which the volumetric density of the catalyst is varied, but the other conditions remain the same as in Fig. 10. As seen in this figure, it is proved that since a higher P_b gives more G for a same length of tube, L_0 , it would be possible to control the number of tubes by varying P_b .

6. Conclusions

We investigated the thermal and the chemical characteristics of steam reforming required for the design of a reformer applicable to a gas turbine. First, the formula of the reaction velocity for a catalyst of $\text{CuO}+\text{ZnO}$ was determined experimentally. Next, by using this formula of the velocity, simulation equations were solved numerically to clarify the reaction rate and the heat transfer rate. The experiments were

carried out in order to measure them in parallel, and then the standards of design were obtained. The results are as follows.

(1) The formula for the reaction velocity for steam reforming with $\text{CuO}+\text{ZnO}$ catalyst was determined.

(2) The reaction of steam reforming is most favorable at $S/M=1$.

(3) By comparing the results of simulations with those of experiments, the validity of simulation was confirmed.

(4) The characteristics of reaction and heat transfer in a steam reforming reactor were clarified. As a result, there is a law of similarity, and a remarkable analogy between them.

(5) The relation between the length of the reactor, L_0 , and the mass flux, G , was derived, by which the procedure for determining the dimension of the reactor was presented.

References

- (1) Woodley, N. H., Nordman, D. A., Legro, J. R and Davies, D. G., SERI/TR. 11290-1, (1982), p. 1.
- (2) Janes, C. W., Proc. 14th Intersoc. Snergy Convers. Eng. Conf., 2 (1979), p. 1968.
- (3) Finegold, J. G. and Makinon, J. J., SERI/TR., 235-1582 (1982), p. 1.
- (4) Finegold, J. G., Makinon, J. J. and Karpuk, M. E., SERI/TR. 235-1559, (1982), p. 1.
- (5) Nagata, S., Hashimoto, K., Takeda, N., Horiguchi, Y., Suzuki, N. and Akita, T., Kagakukogaku (in Japanese), Vol. 29, No. 8 (1965-8), p. 579.
- (6) Kunii, D. and Suzuki, M., Proc. 3rd Int. Heat Transf. Conf. IV, (1966), p. 344.
- (7) Kunii, D., Chemical Engineering, I (in Japanese), (1962), p. 610, Asakura-shoten.
- (8) Yamazaki, T., Noguchi, Y., Akazuka, T., Iwamura, K. and Ootani, S., Kagaku-kogaku I (in Japanese), Vol. 34, No. 4 (1970-5), p. 407.
- (9) Nagata, S., Hashimoto, K., Taniyama, I. and Nishida, H., Kagakukogaku, (in Japanese), Vol. 26, No. 5 (1970-5), p. 569.