Experimental study on a methanol auto-thermal reforming for compact reformer

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Abstract
Performance of self-sustaining methanol auto-thermal reforming (ATR) was investigated experimentally in order to elucidate a reforming reaction mechanism and a condition required for high purity H₂ production for compact reformer. The reformer consists of vaporizing and reforming sections in a single unit. The exothermic oxidation and endothermic steam reforming (STR) take place simultaneously in the reforming section. The reforming section is surrounded by the vaporizing section and then the heat for vaporization is supplied from the reforming section. Two types of exothermic oxidation reaction were investigated as the heat source for STR; one is a partial oxidation (POX) and the other is a total oxidation (TOX). CuO/ZnO/Al₂O₃ catalyst and Pt/Al₂O₃ catalyst were used for STR and POX, respectively. While, only CuO/ZnO/Al₂O₃ catalyst was needed for TOX because TOX took place when fuel and oxygen were supplied to the CuO/ZnO/Al₂O₃ catalyst. Experiments were investigated in the range of oxygen/carbon ratio (O/C ratio) 0.1-1.5, steam/carbon ratio (S/C ratio) 1.0-3.0 and N₂ mole ratio 79-50% in oxidizer. The results showed that the H₂ formation reached maximum at around O/C=0.4 in both STR/POX and STR/TOX cases in the present study. When O/C ratio is decreased from 0.4, heat formation by the oxidation reactions decreases and is insufficient to reform residual CH₃OH by STR. As a result, H₂ formation and the methanol conversion ratio decrease. When O/C ratio is increased from 0.4, the H₂ formation decreases, because methanol is consumed with the excess O₂ by TOX and CH₃OH for STR decreases. After all, O/C=0.4 gives an appropriate balance of heat supply and methanol for H₂ production. These results elucidate that the reaction rate of oxidation reactions, POX and TOX, is much faster than that of STR. In other words, methanol is first consumed by the oxidation reaction and the residual methanol is used for STR. For S/C ratio, H₂ formation is decreased in the higher S/C ratio. N₂ mole ratio in oxidizer has few influence over the reforming gas. The chemical equilibrium calculations support the experimental results.

Key words: Methanol, Steam reforming, Partial oxidation, Total oxidation, Auto-thermal reforming, Hydrogen, Oxygen/Carbon ratio, Steam/Carbon ratio

1. Introduction
A compact reformer is a suitable method for supplying H₂ to Polymer Electrolyte Fuel Cell (PEFC) because it has some advantages in terms of cost, safety, and hydrogen density (Geissler, et al., 2001) compared with other hydrogen supplying methods such as highly pressured cylinder and metal hydrides. Various hydrocarbons, such as methanol (Agrell, et al., 2002, Chein, et al., 2011, Chen, et al., 2011, Vadlamudi and Palanki, 2011, Yoon, et al., 2008), ethanol (Khila, et al., 2013, Liguras, Kondarides and Verykios, 2003, Rabenstein and Hacker, 2008), gasoline (Kang, Bae, J. and Bae, G., 2006, Wang, Murata and Inaba, 2005), methane (Zhua, Zhang and King, 2001, Pinto, et al., 2011), and
propane (Wanga, et al., 2010), have been studied as a reforming fuel in literatures. Methanol is supposed to be the most attractive fuel for a reformer for PEFC because it is low C/H ratio, low reforming temperature and commercially available (Saika, et al., 2006). In addition, it is expected that methanol is formed by biomass technology which makes the methanol carbon free in future.

Steam reforming (STR) is widely used for H₂ production from methanol because it produces syngas containing high concentration H₂ and low CO (Israni and Harold, 2011). However, some heating device is needed to carry on reforming because STR is an endothermic reaction. To solve this undesirable issue for compact reformer, auto-thermal reforming (ATR), which is the combination of endothermic STR and exothermic partial oxidation (POX), was proposed in the late 1980s (Jenkins and Shutt, 1989). It reduces a heating device required for STR and the quick start-up is realized (Brown and Gulari, 2004). In addition to the conventional auto-thermal reforming (STR/POX), another type of ATR, a combination of STR and total oxidation (TOX) is reported (Geissler, et al., 2001, Lattner and Harold, 2007). As a consequence, a reactor for these processes does not require external heating once having reached reaction temperature and can offer faster start-up.

Carbon monoxide, produced in reforming process, is harmful to electrodes of PEFC and decrease efficiency of energy system. For this reason, CO remover using preferential oxidation of CO is installed after a reformer to introduced reformed gas into PEFC with CO concentration < 10 ppm (Katsuki, 2005). Besides the CO remover using the chemical reaction, a methanol steam reformer with Pd/Ag membrane was proposed as a method of hydrogen purification. Faizal et al.(2012) elucidated the importance of transport phenomena near the membrane for relatively low flow rate of reformed gas and proposed a quantitative estimation method of H₂ purification flow rate from reformed gas. It showed that the Pd/Ag membrane is useful for compact reformer to produce high purity hydrogen with very low CO concentration, which fulfills the PEFC requirement.

The performance of STR using various Cu-based catalysts was reported (Agrell, et al., 2002, Honga and ReN2008, Sá, et al., 2010, Turco, et al., 2004). Above all, the commercially available catalyst of CuO/ZnO/Al₂O₃ is widely used because of moderate reforming temperature and low concentration of CO in the products (Agrell, et al., 2002). As POX catalyst, Pt/Al₂O₃ was investigated by many researchers and Pt–Alumina catalysts are proposed as active methanol decomposition catalysts (Brown and Gulari, 2004, Cao and HohN2009). As for TOX, no catalyst is necessary because of high equilibrium constant (Wang, et al., 2008) and it is reported that TOX can start when fuel and oxygen are supplied into Cu catalyst (Lattner and Harold, 2007).

In most studies about ATR, reformer consisting of separated reactors for exothermic oxidative reaction and endothermic STR were investigated. In this case, the heat transfer through a wall between reactors is needed, which makes the reformer size larger. Chen et al. investigated a low-CO methanol processor for the online supply of hydrogen to a proton exchange membrane fuel cell (PEMFC) composed of a steam reformer and a catalytic combustor (Chen, et al., 2011). While the steam reformer was successfully heated by an attached catalytic combustor without any additional electrical power supply, it takes more than 15 minutes to raise the temperature in the steam reformer enough for STR activation and stabilize after starting the combustor due to buffering effect by a wall between them.

When the exothermic and endothermic reactions occur in the same place, the heat formed by the exothermic reaction can be used for the endothermic reaction without heat transfer through the wall. As a result, downsizing of the reformer and the less heat loss are expected in addition to quick start-up and a good response to temperature change. The heat transport between STR and oxidation reactions and the performance for H₂ production in various shapes of reactor were investigated using a simulation method (Ma, et al., 1996). In addition, mathematical analysis of different reactor schemes for the auto-thermal reforming from methanol has been done in order to elucidate the most preferred stand-alone reactor (Karim, et al., 2005). However, few experimental studies about the performance of ATR reactor in which the exothermic and endothermic reactions take place in the same place have been done and the optimum condition has not been proposed yet.

In this study, the performance of a compact methanol reformer in which the exothermic and endothermic reactions take place in the same place was investigated experimentally to elucidate a reaction mechanism of methanol auto-thermal reforming and an appropriate condition for high purity H₂ production. The chemical equilibrium calculations were carried out to verify the results of experiments.
2. Experimental and Calculation Method

2.1 Reaction Formula of Auto-thermal Reforming

The overall reaction of methanol steam reforming (STR) is modeled as Equation (1). It indicates that the STR is endothermic. This overall reaction can be divided into two reactions consisting of methanol decomposition (MD) and water-gas shift (WGS) reaction, as shown in Eqs. (2) and (3) respectively. Eq. (2) is the main pathway to produce H₂. At the same time, CO is produced as a by-product in appreciable amounts. More H₂ is formed and CO is reduced through Eq. (3).

\[
\begin{align*}
\text{Overall steam reforming (STR):} & \quad \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 & \Delta H^0 = 49.8 \text{ kJ/mol} \quad (1) \\
\text{Methanol decomposition (MD):} & \quad \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} & \Delta H^0 = 91.0 \text{ kJ/mol} \quad (2) \\
\text{Water-gas shift (WGS):} & \quad \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 & \Delta H^0 = -41.2 \text{ kJ/mol} \quad (3)
\end{align*}
\]

The heat for the endothermic reaction and evaporation of liquid reactants is supplied from exothermic reactions, Partial oxidation (POX) or Total oxidation (TOX). The overall reaction of POX is indicated by Eq. (4). This overall reaction is divided into two reactions consisting of Methanol decomposition (MD) and Preferential oxidation (PROX) as mentioned in Eqs. (2) and (5), respectively. The Methanol decomposition in Eq. (2) is the same as that of STR. CO is converted to CO₂ with some heat formation by preferential oxidation as mentioned in Eq. (5).

\[
\begin{align*}
\text{Overall partial oxidation (POX):} & \quad \text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO}_2 & \Delta H^0 = -192.0 \text{ kJ/mol} \quad (4) \\
\text{Methanol decomposition (MD):} & \quad \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} & \Delta H^0 = 91.0 \text{ kJ/mol} \quad (2) \\
\text{Preferential oxidation (PROX):} & \quad \text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 & \Delta H^0 = -283.0 \text{ kJ/mol} \quad (5)
\end{align*}
\]

Total oxidation (TOX) is modeled as following equations. Since H₂ is oxidized by the exothermic Hydrogen oxidation reaction in Eq. (7), more heat is formed from the same amount of methanol than POX although less H₂ is formed.

\[
\begin{align*}
\text{Total oxidation (TOX):} & \quad \text{CH}_3\text{OH} + 1.5\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 & \Delta H^0 = -675.6 \text{ kJ/mol} \quad (6) \\
\text{Methanol decomposition (MD):} & \quad \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} & \Delta H^0 = 91.0 \text{ kJ/mol} \quad (2) \\
\text{Hydrogen oxidation (HOX):} & \quad \text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O} & \Delta H^0 = -241.8 \text{ kJ/mol} \quad (7) \\
\text{Preferential oxidation (PROX):} & \quad \text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 & \Delta H^0 = -283.0 \text{ kJ/mol} \quad (5)
\end{align*}
\]

2.2 Experimental Set-up and Procedure

Figure 1 shows a schematic of the cylindrical stainless steel reformer used in this study. It consists of an inner reforming section and outer evaporation section. In the inner reforming section in which catalyst pellets are installed, chemical reactions of STR, POX and TOX mentioned in Section 2.1 occur and then the auto-thermal reforming takes place. Some of the heat is transferred to the outer evaporation section to evaporate methanol and water. K-type thermocouples inserted in inner and outer sections were used to monitor the catalyst bed temperature and evaporator temperature every 1 minute at start-up or 5 minutes in the steady state condition. A commercially available catalyst CuO/ZnO/Al₂O₃ and Pt/Al₂O₃ were used for steam reforming and partial oxidation, respectively. Amounts of STR and POX catalysts were 14.0 g and 3.5 g, respectively. In this regard, GHSV of STR is the range from 10.95 to 16.55 l/(h·g) and GHSV of POX is the range from 27.75 to 57.03 l/(h·g). The reformer was wrapped by a ribbon heater and insulator. The ribbon heater is used to start-up and the insulator reduces the heat loss to the ambient air.

A schematic diagram of experimental set-up is shown in Fig. 2. When the reformer temperature reaches 200 °C which is sufficient for evaporation of methanol and water, methanol and air were started to supply to begin the
oxidation reaction (POX or TOX). The flow rate of methanol, water and air were controlled by each mass flow controllers. When the oxidation reaction (POX or TOX) is started, the catalyst bed temperature increases rapidly. When the catalyst bed temperature reaches 450 °C, water is started to supply to start STR resulting in the decrease in the catalyst bed temperature due to endothermic reaction of STR.

Reformed gas was analyzed by a gas chromatography in the dry base condition. The reformed gas was cooled down and dehydrated before the gas was supplied to the gas chromatography every 20 min after the start of ATR.

The effect of oxygen/carbon ratio (O/C ratio), steam/carbon ratio (S/C ratio) and N₂ ratio in the oxidizer were experimentally investigated. In the case of STR/POX, CuO/ZnO/Al₂O₃ catalyst and Pt/Al₂O₃ catalyst are installed in the reforming section, while only CuO/ZnO/Al₂O₃ catalyst is installed in the STR/TOX case.

Figure 1 Schematic of the methanol reformer

Figure 2 Schematic diagram of experimental set-up
2.3 Chemical Equilibrium Calculation

Chemical equilibrium calculations were carried out using CHEMKIN II as functions of oxygen/carbon ratio (O/C ratio), steam/carbon ratio (S/C ratio) and N₂ mole fraction in the oxidizer. Figure 3 shows mole fraction of initial reactants as a function of O/C ratio. Figs. 3(a), 3(b) and 3(c) show the case of S/C = 1, 2 and 3, respectively. When O/C ratio is increased, mole fraction of O₂ and N₂ increases because O₂ is supplied as an air while mole fraction of other species decreases. Four chemical species, CH₃OH, H₂O, O₂ and N₂ were set as initial reactants. Fig. 3 (d) shows the initial amount of chemical species (H₂O, O₂ and N₂) for one mole CH₃OH. As shown in Fig. 3 (d), O₂ and N₂ linearly increase with an increase in O/C ratio. Fig. 3(d) also shows the case of N₂ mole fraction in the oxidizer of 79 % for air, 70 % and 50%. ※Three horizontal lines of H₂O are seen corresponding to the S/C ratio 1, 2 and 3. Thus, the chemical equilibrium calculation conditions are summarized as follows:

- Adiabatic condition
- Ambient pressure (101.3 kPa)
- Starting temperature: 473.15 K
- O/C ratio: 0.0-1.5
- S/C ratio: 1.0-3.0
- N₂ mole fraction in oxidizer : 79-50%

![Figure 3](image-url)  
Figure 3 Mole fractions in introduced gas and molar ratio to CH₃OH
3. Results and Discussion
3.1 Chemical Equilibrium Calculation

Figure 4 shows the results of chemical equilibrium calculation of the variation in mole amount of chemical species from one mole methanol. It is interesting to note first that no methanol is remained in all cases in the equilibrium condition. The $H_2$ moles for 1mol CH$_3$OH increases with an increase in O/C ratio and reaches a maximum at around O/C=0.3. It decreases with further increase in O/C ratio. When the O/C ratio is beyond 0.3, the equilibrium temperature increase is much significant with increasing O/C ratio compared to that at O/C ratio less than 0.3. $H_2$O once decreases with increasing O/C ratio from 0.0 to around 0.3 and increases with further increase in O/C ratio from 0.3. It indicates that H atoms in $H_2$O are converted to $H_2$ in lower O/C ratio. On the other hand, in higher O/C ratio, H atoms from CH$_3$OH are converted to $H_2$O with higher temperature, which results in more H$_2$O than supplied. All H atoms of reactants are converted to $H_2$ and CO$_2$. A relationship between CO and CO$_2$ formation is similar to that between $H_2$ and $H_2$O except in lower O/C ratio at which CH$_4$ is formed and CO$_2$ is suppressed. CO formation increased and reaches a maximum at around O/C = 0.6 while CO$_2$ formation decreases and increases on contrary to a trend of CO formation, which indicates that the CO is converted to CO$_2$. The increase in S/C ratio does not affect significantly on the composition of reformed gas, especially in lower O/C ratio. In high O/C ratio, the increase in S/C ratio results in the increase in $H_2$ formation and the decrease in equilibrium temperature and CO formation.

Effect of N$_2$ amount in the reactant is shown in Figure 5. When the amount of N$_2$ in oxidizer is decreased, the temperature increases though amounts of the other chemical species don’t vary clearly. This indicates that the effect of N$_2$ appears through the heat capacity of N$_2$. In fact the equilibrium temperature at constant pressure of N$_2$ varies from 1827 to 2327 °C when the mole fraction of N$_2$ in the oxidizer varies from 0.79 to 0.50.

Figure 4 Formations of each chemical species for 1 mole CH$_3$OH on S/C ratio
3.2 Experimental results

3.2.1 Temperature variation

Figure 6 shows the temperature variation at the catalyst bed in the STR/POX case and S/C=1.0. The reformer was preheated and when the catalyst temperature reaches 200 ºC, fuel and air were supplied to the reformer. The heating by the ribbon heater was stopped when the supply of fuel and air is started. The temperature increases steeply just after the fuel and air was supplied because the POX reaction started. When the temperature increase was recognized, water supply was started immediately to start the endothermic STR reaction, which results in the rapid decrease in the temperature. After the rapid decrease in temperature, the temperature varies gradually toward the steady state condition. Figure 6 also shows that the steady and self-sustaining reforming could be achieved without heat supply by the ribbon heater except O/C=0.1. When O/C=0.1, the temperature gradually decreased and the temperature at the evaporation section decreases less than 65ºC, which is the methanol boiling point. As a result, no methanol gas was supplied into the catalyst section and then the POX was terminated. Temperature at the steady state condition increased with an increase in O/C ratio. The similar trend was observed for the STR/TOX cases.

Figure 7 shows experimental results of average catalyst bed temperature at the steady state condition along with the adiabatic temperature from chemical equilibrium calculation in condition with S/C=1.0. The result of the chemical equilibrium calculation shows that the higher adiabatic temperature was obtained for higher O/C ratio. If O/C ratio is increased keeping methanol mole flow rate constant, the catalyst bed temperature increases monotonically and exceeds an appropriate range of catalyst. The catalyst bed temperature, on the other hand, decreases when the methanol mole flow rate is decreased in experiments because it is determined as a balance between total heat formation by exothermic oxidation reaction and the heat loss. Then, the methanol mole flow rate decreased from 2.00 to 0.75 mole/h with an increase in O/C ratio not to exceed the appropriate temperature range of catalyst. As a result, the catalyst bed temperature was able to keep less than 600 ºC in all range of O/C ratio. When O/C ≦ 0.6, significant difference is observed between STR/POX and STR/TOX, while the difference decreases gradually when O/C ratio is increased. When O/C ≦ 0.6, the methanol mole flow rate is as high as 2.0 mol/h and then the total heat releases of POX and TOX
are relatively large compared to the heat loss and then the difference between POX and TOX can be seen clearly. In other words, the catalyst bed temperature in the STR/TOX case is higher than that in the STR/POX case due to more heat release of TOX. When O/C ratio is increased from O/C=0.6, the methanol mole flow rate is decreased from 2.0 mol/h to 0.75 mol/h and then the total heat release decreases and the effect of heat loss gradually plays a significant role. As a result, the difference between POX and TOX becomes unclear.

When O/C ratio is increased, the catalyst bed temperature increases in each methanol mole flow rate with an increase in chemical equilibrium temperature. It also shows that H$_2$ and CO decrease and H$_2$O and CO$_2$ increase in Figure 4, which means that the oxidation progresses with an increase in O/C ratio. These results suggest that the methanol is first used for oxidation

![Figure 6 Catalyst bed temperature transition for STR/POX, S/C=1.0](image)

![Figure 7 Average of catalyst bed temperature in steady state for each O/C ratio (S/C=1.0)](image)

3.2.2 Reformed gas variation

Figure 8 shows experimental results of methanol conversion ratio and H$_2$ formation from one mole methanol as a function of O/C ratio along with results of equilibrium calculation and estimation.

The estimation was performed under following assumptions; either POX or TOX consumes methanol first for corresponding O$_2$ amount and then residual methanol is reformed to H$_2$ by STR. In this case, all heat necessary for endothermic STR reaction is assumed to be supplied automatically without regard to POX and TOX. As a result, all residual STR can reform methanol to H$_2$ and 3 moles of H$_2$ is formed following Eq. (1) even when O/C=0, which indicates no exothermic reaction, POX or TOX, occurs.

In the case of STR/POX, the H$_2$ formation from one mole methanol is estimated as follow:

\[ \text{CH}_3\text{OH} = 2.0 \text{ mol/h} \rightarrow 1.5 \text{ mol/h} \rightarrow 1.0 \text{ mol/h} \rightarrow 0.75 \text{ mol/h} \]
where \( C_{\text{H}_2} \) is \( \text{H}_2 \) formation from one mole methanol. Equation (8) means that methanol is consumed by POX first and residual methanol is converted to \( \text{H}_2 \) by STR, which results in the variation in the \( \text{H}_2 \) formation from 3 mole of STR to 2 mole of POX at O/C=0.5. When O/C exceeds 0.5, all methanol is converted to \( \text{H}_2 \) by POX and no methanol is left for STR. As a result, \( \text{H}_2 \) formation is kept constant at 2 mole as mentioned in Eq. (9). The variation in \( \text{H}_2 \) formation by STR/POX is, therefore, shown by broken line in Fig. 8.

In the case of STR/TOX, the \( \text{H}_2 \) formation from 1 mole methanol is estimated as follows:

\[
C_{\text{H}_2} = 3 \text{ mol/s} - 2 \text{ mol/s} \times O/C \quad 0 < O/C < 0.5 \\
C_{\text{H}_2} = 2 \text{ mol/s} \quad 0.5 < O/C < 1.5 \\
\]

Equation 10 means that methanol is consumed by TOX and the residual methanol forms \( \text{H}_2 \) by STR. Since no \( \text{H}_2 \) is formed by TOX as mentioned in Eq. (6), \( \text{H}_2 \) only formed from residual methanol by STR. The variation in \( \text{H}_2 \) formation by STR/TOX is, therefore, shown by dotted line in Fig. 8. \( \text{H}_2 \) formation increases with increasing O/C ratio. When O/C exceeds 0.5, all methanol is converted to \( \text{H}_2 \) and no methanol is left for STR. This corresponds to the difference of catalyst bed temperature of STR/POX and STR/TOX discussed in Sec. 3.2.1. These results indicate that enough heat is supplied for STR by TOX compared to that by POX at the same O/C ratio. When O/C ratio exceeds 0.4, the \( \text{H}_2 \) formation decreases following the estimated straight line of STR/TOX case. It is interesting to note that it is difficult to find dependences of performance of STR/POX and STR/TOX at O/C ≥ 0.5 as shown in Figs. 8 and 9. As shown in Fig. 8, the estimation suggests that the \( \text{H}_2 \) formation at O/C ≥ 0.5 should keep constant at 2 if only the POX is done. \( \text{H}_2 \) formation of both STR/POX and STR/TOX, however, follows the estimation line of STR/TOX. It indicates that even if POX catalyst is installed in the reforming section, it is difficult to keep only POX. As Lattner and Harold (2007) pointed out, TOX can start when fuel and oxygen are supplied into Cu catalyst. In the present study, CuO/ZnO/Al\(_2\)O\(_3\) catalyst for STR is always installed in the reforming section, which results in the start of TOX without regard to the existence of Pt/Al\(_2\)O\(_3\) catalyst for POX. In other words, it may be quite difficult to do POX only when the endothermic reaction and exothermic reaction is done in the same place, using Cu catalyst. These results indicate that the methanol is first consumed by the oxidation reaction, TOX, and the residual methanol is used for STR and produces \( \text{H}_2 \). The \( \text{H}_2 \) formation becomes zero at O/C=1.5 because every methanol is used by TOX reaction. As mentioned in Sec. 3.2.1, the catalyst bed temperature is determined by the balance between heat formation by exothermic reaction and the heat loss. Thus, if the heat insulation of the reformer becomes much better, the peak of \( \text{H}_2 \) formation will shift toward less O/C condition. The result of chemical equilibrium calculation is qualitatively the same in that the \( \text{H}_2 \) formation reaches maximum at around 0.3 as already discussed in Sec. 3.1. The \( \text{H}_2 \) formation in experiments is much more than that of chemical equilibrium calculation and follow the estimation at O/C ≥ 0.5. It means that the catalyst reaction plays a key role for \( \text{H}_2 \) formation at O/C ≥ 0.5.

Figure 9 shows CO formation from one mole CH\(_3\)OH. CO formation increases from O/C=0.0 to 0.6 and then decreases with further increase in O/C ratio by the chemical equilibrium calculation. This indicates that CO formation increases with increasing temperature in lean oxidation condition and it decreases when enough oxygen is supplied. The chemical equilibrium calculation shows similar trend. The chemical equilibrium calculation also shows that when O/C ratio is increased, CO decreases while CO\(_2\) increases. It suggests that CO is oxidized and CO shifts to CO\(_2\) with increasing O/C ratio. Also, CO formation steeply decreases with a decreased in methanol flow rate. It is because that when methanol flow rate decreases from 2.0 mol/h to 0.75 mol/h, the total heat release decreases and catalyst bed temperature decreases as discussed in Sec. 3.2.1. As a result, CO formation steeply decreases through the water-gas shift reaction (Eq. (3)) when the methanol flow rate is decreased.

The experimental results show qualitatively the same trend with the chemical equilibrium calculation. Both \( \text{H}_2 \) and
CO is formed by the methanol decomposition reaction mentioned in Eq. 2. Then they increases with an increase in O/C from O/C=0 to 0.6. When O/C exceed around 0.6, enough oxygen is supplied for H₂ oxidation and CO/CO₂ shift reaction. As a result, they decrease.

![Figure 8 H₂ formation form one mole methanol for each O/C ratio](image1)

![Figure 9 CO formation from one mole methanol for each O/C ratio](image2)

### 3.2.3 Effect of S/C ratio

Effect of S/C ratio was investigated in the range of O/C=0.1-0.6 where high H₂ formation is done as discussed in Sec.3.2.2. Results of the chemical equilibrium calculation are shown in Figures 10 and 11. The increase in S/C ratio from S/C=1.0 to 3.0 results in a slight decrease in the adiabatic temperature and the increase in the H₂ moles.

The CO moles decrease in higher S/C ratio remarkably. These results suggest that an increase in H₂O increases H₂ moles and decreases a temperature and CO moles.
Figure 10 Effect of S/C ratio on adiabatic temperature and H\textsubscript{2} formation for equilibrium calculation

Figure 11 Effect of S/C ratio on CO formation for equilibrium calculation

Figures 12 and 13 show experimental results for STR/POX and STR/TOX, respectively and Fig. 14 shows the methanol conversion ratio of both STR/POX and STR/TOX. Different from the chemical equilibrium calculation, the H\textsubscript{2} formation decreases with an increase in S/C. In the case of S/C=3, there is no plot at O/C < 0.3, which means no reforming can be done. In the present reformer, when S/C ratio is increased, the amount of water supplied increases, much energy of vaporization is needed and the excess water vapor (steam) is supplied to the reforming section. These result in a decrease in temperatures at both vaporization section and reforming section. As shown in Figs. 12 and 13, the temperature in vaporization section became less than 65 °C at O/C<0.3 in the case of S/C=3.0. As a result, the heat for STR decreases and the H\textsubscript{2} formation decreases with increasing S/C ratio.

Figure 15 shows the effect of S/C ratio on the CO formation. The CO formation decreases with an increase in S/C ratio. When steam is supplied in CO existing region, the CO to CO\textsubscript{2} shift reaction mentioned in Eq. (11) will take place. It decreases CO moles when S/C ratio is increased.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad (11)
\]
Figure 12 Effect of S/C ratio on $H_2$ formation and the temperature for STR/POX

Figure 13 Effect of S/C ratio on $H_2$ formation and the temperature for STR/TOX

Figure 14 Effect of S/C ratio on methanol conversion

Figure 15 Effect of S/C ratio on CO formation
3.3.4 Effect of $N_2$ mole fraction in oxidizer

Experimental results of the variations in temperature and $H_2$ formation with $N_2$ mole fraction in oxidizer are shown in Figs. 16 and 17. No significant effect of $N_2$ amount in the oxidizer can be detected although the catalyst bed temperature gradually increases in the chemical equilibrium calculation as shown in Figs. 5 due to the effect of heat capacity. The actual temperature is determined not only by the heat capacity of the gas but by the balance of heat formation and heat loss. As a result, catalyst bed temperature does not clearly vary with $N_2$ amount in experiments.

Figures 18 and 19 show time variation in temperature at the catalyst bed and vaporization sections in POX and TOX, when $N_2$ mole fraction in the oxidizer is 79% and 50% at O/C=0.4. It is interesting to note that the temperature variation in TOX at $N_2$ ratio is 50% is unstable. When $N_2$ mole fraction in the oxidizer is decreased, the temperature increases and the reaction zone become thinner and the burning velocity increases. In the case of TOX, no catalyst is used and then TOX is a gaseous reaction. Thus, the TOX reaction zone can be moved unstably in the catalyst chamber. As a result, the temperature at the catalyst bed becomes unstable. On the other hand, the reaction zone of POX is restricted in the catalyst bed zone because the POX is a surface reaction at Pt/Al$\text{O}_3$ catalyst and then the POX reaction is stable without regard to $N_2$ amount. This result suggests that $N_2$ is related to the stability of TOX reaction.

![Figure 16](image1.png)  
Figure 16 Effect of $N_2$ mole fraction on catalyst bed temperature and $H_2$ formation for STR/POX

![Figure 17](image2.png)  
Figure 17 Effect of $N_2$ mole fraction on catalyst bed temperature and $H_2$ formation for STR/TOX
4. Conclusion

The performance of a compact methanol reformer in which the exothermic and endothermic reactions take place at the same place was investigated experimentally in the range of oxygen/carbon (O/C) ratio, 0.1-1.5, steam/carbon (S/C) ratio, 1.0-3.0, and N\textsubscript{2} mole fraction in oxidizer, 79-50\% . The chemical equilibrium calculations were done using CHEMKIN II to verify the experimental results.

At the start-up of reforming, methanol and air should be introduced first in order to start the exothermic oxidation reaction to increase the catalyst bed temperature. When it exceeds more than 400\degree C and the STR is adequately activated, water supply is started. If water is supplied with methanol and air simultaneously from the beginning, STR will not occur due to its lower reaction rate.

The reaction rate of POX and TOX are much faster than that of STR and then methanol is preferentially consumed by O\textsubscript{2}. The heat formation by the oxidation reaction plays an important role in ATR because it supplies the reaction heat to methanol reforming by STR and vaporization of liquid reactants. Excess O\textsubscript{2}, however, consumes much methanol and then H\textsubscript{2} formation decreases. In this study, a maximum H\textsubscript{2} formation was gained around O/C=0.4 in both STR/POX and STR/TOX cases. It can be said that O/C=0.4 is the well-balanced oxygen/carbon ratio having both of sufficient heat
supply and methanol for H₂ production. After the oxidation reactions consumed methanol corresponding to the amount of O₂, H₂ is produced from the residual methanol by STR. For the lower O/C ratio, when O/C ratio is decreased, H₂ formation decreases notwithstanding the residual CH₃OH increases because of a lack of heat formation by exothermic reaction. A main cause of CO formation is the decomposition reaction of CH₃OH and then it increases along with the increase H₂.

The higher steam/carbon ratio is not effective for H₂ formation because the increase in H₂O results in the deactivation of STR in the case of the present compact reformer where the heat is used for not only STR but vaporization of CH₃OH and water. The higher steam/carbon ratio enhances the CO-CO₂ shift reaction which results in a decrease in CO.

The mole fraction of N₂ in oxidizer has no clear effect for the H₂ formation. It is, however, important to the stability of TOX reaction.

References


