Korean J. Chem. Eng., **30**(4), 790-795 (2013)
DOI: 10.1007/s11814-012-0210-1

Temperature oscillations in methanol partial oxidation reactor for the production of hydrogen

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(*Received 6 August 2012 • accepted 2 December 2012*)

Abstract−Methanol partial oxidation (POX) is a well-known reforming reaction for the production of hydrogen from methanol. Since POX is relatively fast and highly exothermic, this reforming method will be efficient for the fast start-up and load-following operation. However, POX generates hot spots around catalyst and even oscillations in the reactor temperature. These should be relieved for longer operations of the reactor without catalyst degradations. For this, temperature oscillations in a POX reactor are investigated experimentally. Various patterns of temperature oscillations according to feed flow rates of reactants and reactor temperatures are obtained. The bifurcation phenomena from regular oscillations to chaotic oscillations are found as the methanol flow rate increases. These experimental results can be used for theoretical analyses of oscillations and for designing safe reforming reactors.

Key words: Methanol Partial Oxidation, Temperature Oscillations, Chaotic Oscillations, Hydrogen Production

INTRODUCTION

As concerns about environmental problems such as air pollution and the green house effect are growing, fuel cells being operated with hydrogen without polluting the environment have come into the spotlight [1-3]. However, because of technical difficulties in storage, portability and lack of infrastructure for hydrogen production and distribution, the on-board hydrogen generation has been considered. Methanol reforming is the potential candidate for this on-board system due to its good selectivity for hydrogen and small production of carbon dioxide [3,4]. Particularly, methanol can be converted to hydrogen at relatively low temperature and atmosphere pressure, offering manageable reaction ambient [5].

There are several methanol reforming reactions for production of hydrogen from methanol [6]. One is the steam reforming:

$$CH_3OH(g)+H_2O(g)\rightarrow CO_2(g)+3H_2(g),\ \Delta H^o_{298}=49.4\ \text{kJ/mol} \qquad (1)$$

It produces 3 moles of hydrogen per 1 mole of methanol and a small amount of carbon monoxide as byproduct. Because the reaction is endothermic, how to supply the reaction heat quickly and efficiently is a key factor that determines the efficiency and ability to tract the load of hydrogen. The other is the partial oxidation (POX) of methanol:

$$CH_3OH(g)+0.5O_2(g)\rightarrow CO_2(g)+2H_2(g),\ \Delta H^o_{298}=-192.2\ \text{kJ/mol} \qquad (2)$$

It produces 2 moles of hydrogen per 1 mole of methanol. Because it is exothermic and its reaction rate is fast, the reactor based on this reaction will have excellent load following characteristics inherently. However, the reactor will suffer from hot spots and oscillations in the reactor temperature due to the fast and highly exothermic reaction of methanol oxidation. The above two reactions can be carried out with the same copper-based catalysts. Hence they can be combined for the reaction heat to be zero:

$$\begin{aligned}&CH_3OH(g)+0.125O_2(g)+0.75H_2O(g)\\&\quad\rightarrow CO_2(g)+2.75H_2(g),\ \Delta H^o_{298}=0\end{aligned} \qquad (3)$$

It is called autothermal methanol reforming. It takes advantages of both reactions (1) and (2) and is widely used in practice.

The autothermal steam reforming used most widely shows the characteristics of POX at the inlet part of reactor. It is because the oxidation reaction is faster than the steam reforming reaction and both reactions for the autothermal steam reforming do not usually occur at the same region of reactor [6]. Hence, the autothermal steam reforming reactor can suffer from the same operational difficulties as the POX, unless highly conductive reactors such as honeycomb [7] and micro channel reactors have been used. Here the POX reactor is considered. This will be helpful in designing and operating the POX reactor as well as the autothermal steam reforming reactor safely.

There have been many reports for oscillations in nonlinear chemical processes [8] including oxidations of reactants such as CO, H_2 and NH_3 [9] and homogeneous azeotropic distillation systems [10]. Ionescu at al. [11] detected thermal oscillations during methanol oxidation on palladium catalysts. They found that the oxygen flow rate plays an important role in the presence of thermal oscillations, and the oscillation amplitude was observed up to 160 °C at particular reaction condition. In addition, other experimental conditions such as reaction temperature, reactant concentration and catalysts contribute the oscillatory characteristics. Werner et al. [12] tried to explain the reason that the thermal oscillations happen in a methanol oxidation with copper-based catalyst by analyzing the reaction mechanism in more details. They suggested several reaction intermediates and catalyst sites. Lin et al. [13] proposed several reaction pathways in the POX of methanol and suggested the best possible one. Raimondi [14] verified that copper in the catalyst is oxidized at a low temperature region where most copper exists as Cu(I), whereas oxidized Cu_2O can go through reduction by methanol efficiently at a high temperature region on which they confirmed existence of

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Cu(0) dominantly. At a much lower temperature region with the presence of water, the copper is oxidized to Cu(II), making productivity of H_2 to be inactive. Those facts provide evidence that there are some competitive reactions according to temperatures, leading to thermal oscillations in the POX. However, the thermal oscillation in POX is still not understood well and is being studied.

Most of the above thermal oscillations in the POX reaction are based on small ideal reactors. Jung at al. [4] discovered thermal oscillations in a practical plug flow POX reactor. The reactor is made of aluminum tube and the catalyst is coated on the tube. For this practical reactor, there may be additional factors contributing thermal oscillations. For this, thermal oscillations in a practical plug flow POX reactor are revisited and various experimental results collected.

EXPERIMENTAL

1. Catalyst and Reactors

The copper-zinc-magnesium-aluminum catalyst with urea was employed for the POX reaction. The components of the catalyst are the same as the well-known commercial catalyst, Synetic 33-5. The catalyst is mixed with urea to be gel and coated on the inside-wall of aluminum tube, which is used for the plug flow reactor (PFR). The urea in the catalyst reacts with both Al_2O_3 and aluminum. That enables the catalyst to be bound to the surface of aluminum tube. The procedure for preparing the gelated catalyst with the urea (urea CZMA) and to coat to the PFR is as follows [4]:

Step 1. Prepare $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, and dissolve them, whose composition is the same as in Table 1 in the 500 mL de-ionized water.

Step 2. Dissolve the 60.05 g urea in another 500 mL de-ionized water. Mix it with the above solution, resulting in 1 L solution.

Step 3. Heat the 1 L solution and maintain its temperature to be 100 °C with stirring for 10 hours.

Step 4. With increasing the temperature to 150 °C with stirring the solution continuously, evaporate the solvent (water) until the solution starts to become gel.

Step 5. Prepare the aluminum tube (diameter: 1/4 in., thickness: 0.5 mm, length: 10 cm). For cleaning of the tube, dip it into 5 vol% sulfuric acid for an hour and rinse it with the de-ionized water. Dry it in the 80 °C oven for more than an hour.

Step 6. Plaster the gelated catalyst on the inside-wall of the aluminum tube until its weight deposited on the wall is 0.1 g.

Step 7. Put the tube covered with the gelated catalyst into a furnace. Dry it for 10 hours by increasing the furnace temperature from room temperature to 180 °C at the rate of 5 °C/min.

Step 8. Calcinate the tube for 3 hours with heating up from 180 °C to 450 °C by the same rate as above.

Fig. 1 shows the SEM image of the catalyst coated on the inside-wall of the aluminum tube [4]. We can see that metal hydroxides of catalyst are combined with the layer of Al_2O_3.

Table 1. Components of catalyst [18]

Component	Mass (g)
$Cu(NO_3)_2 \cdot 3H_2O$	93.52
$Zn(NO_3)_2 \cdot 6H_2O$	42.21
$Mg(NO_3)_2 \cdot 6H_2O$	6.12
$Al(NO_3)_3 \cdot 9H_2O$	8.85

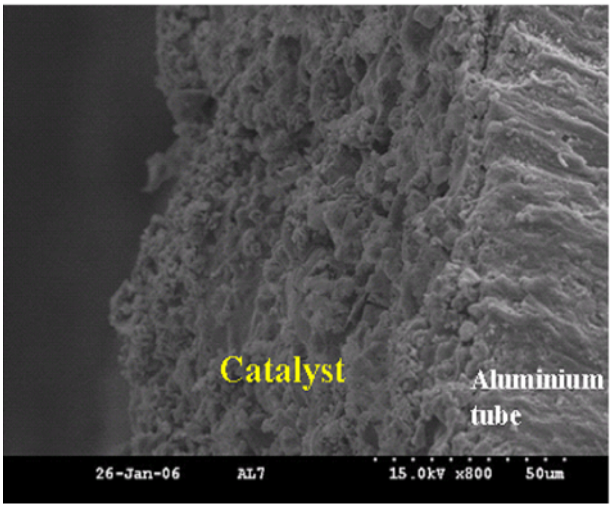


Fig. 1. A SEM image of the urea CZMA coated on the inside-wall of aluminum tube (this image was provided by [4]).

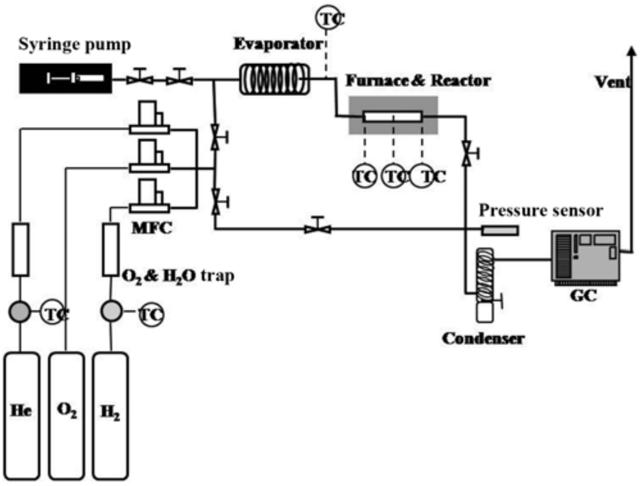


Fig. 2. Schematic diagram of the experimental apparatus for the POX reaction experiment [18].

2. Apparatus

Fig. 2 shows the outline of the overall system for POX experiments [18]. The mass flow controllers (MFC) are used to maintain the oxygen and helium gas flow rates, and the syringe pump pushes the liquid methanol with a fixed volumetric rate. The liquid methanol is vaporized by the evaporator and mixed with the other gases of oxygen and helium. All pipe lines are stainless steel with diameter of 1/8 inch and their temperatures are kept 150 °C with heating lines. The mixed gases go to the PFR in the furnace. Condensable components from the outlet of PFR such as water and unreacted methanol are condensed and trapped in the condenser and are removed. Then non-condensable components are analyzed by the gas chromatography (GC, Agilent 7890A). To measure the mixed gas temperatures in the reactor, three K-type thermocouples are installed at places where inlet, middle and outlet of the reactor. In addition, to observe the pressure in the reactor, a pressure sensor is equipped on the outlet of the PFR. The data of temperatures and pressures are acquired at 10 samples per second using the data acquisition system (National Instruments; NI-9211 and NI-9256).

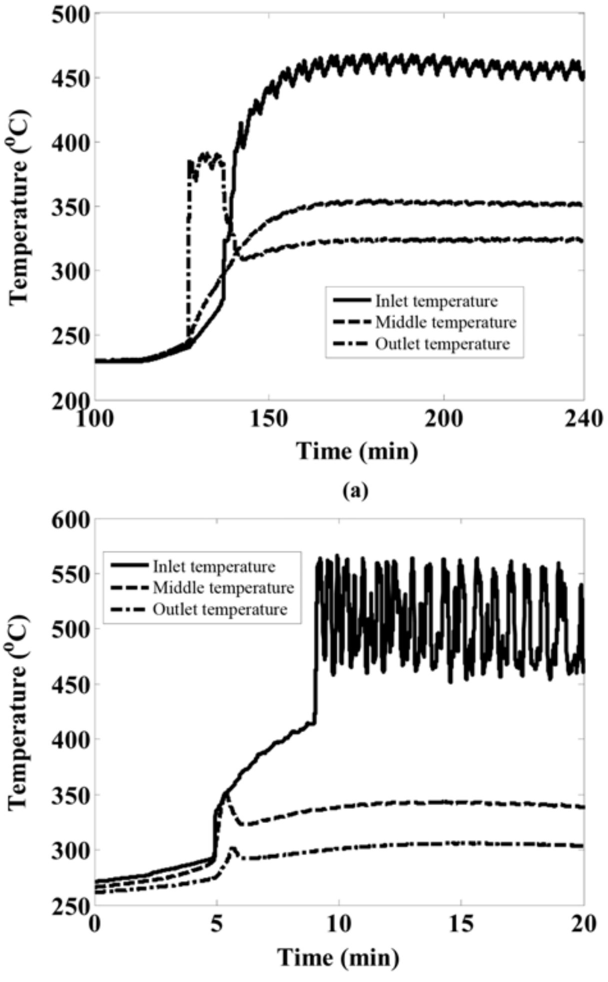
RESULTS AND DISCUSSION

Oscillations in chemical processes are due to various factors such as the reaction itself, diffusion, adsorption and operating conditions. Oscillatory chemical processes can show chaotic behaviors [15,16]. Hence, for safe design and operation of chemical processes, it is needed to understand the causes of oscillations. In the systems point of view, the oscillatory systems can be considered as a feedback loop with fast subsystem and slow subsystem [16,17]. For our PFR where the partial oxidation of methanol occurs, the slow subsystem is evidently the thermal system (dynamical system for temperature changes). Here, experiments are carried out to know what the fast subsystem is.

1. Temperature Oscillations

To start up the reactor, the reactor is heated by the electric furnace whose temperature is controlled at a given temperature and the reactants are fed. During the POX reaction of methanol, temperature profiles are measured at the inlet, middle and outlet of the reactor. Fig. 3 shows typical profiles of the reactor temperatures. When the reactor temperature reaches a certain value (about 260 °C), the reactor temperature jumps abruptly. We call this the ignition point. Then the temperature starts oscillating, especially the inlet temperature. The oscillation in Fig. 3(a) appears somewhat regular. Fig. 3(b) shows the start-up trajectories of reactor temperatures for higher reactant flow rates than those of Fig. 3(a). The ignition point is similar, but the oscillation is rather chaotic.

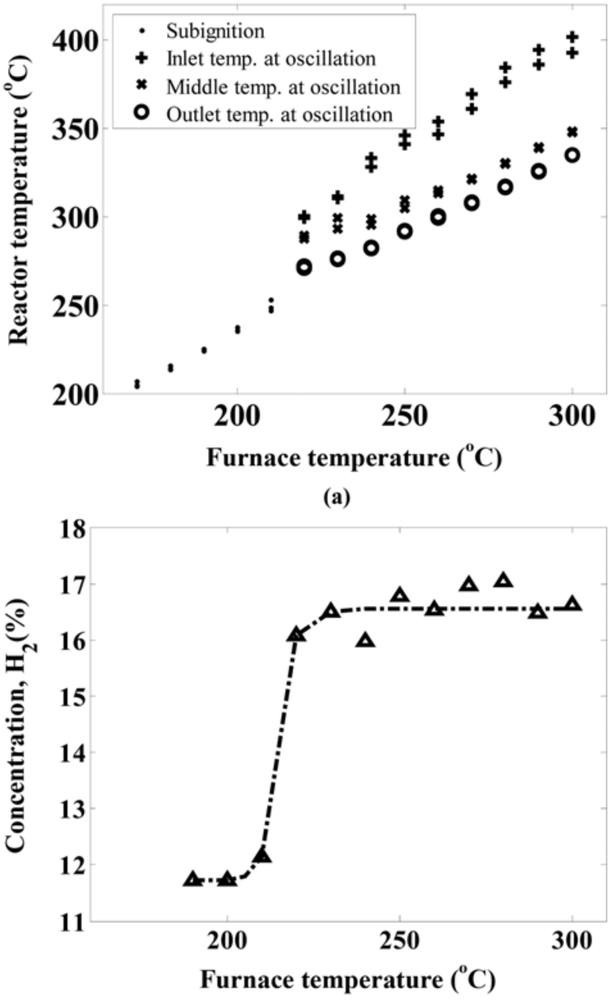
Fig. 4 shows reactor temperatures according to the furnace temperatures and hydrogen generated. Experiments with all amount of feeds maintained constant are carried out for various furnace temperatures and hydrogen yields are analyzed by the GC. Fig. 4(a) shows the temperatures at three spots of the reactor in their steady states or cyclic steady states. In the figure, • indicates that the thermal oscillation does not appear in the reactor, while ○, + and × indicate a pair of the maximum and minimum value of the oscillations, confirming existence of the oscillations at the upper ignition



(a)

(b)

Fig. 3. Typical profiles of the reactor temperatures (feeding condition: (a) O_2: 25 mL/min, CH_3OH: 15 mL/min, He: 60 mL/min, (b) O_2: 50 mL/min, CH_3OH: 100 mL/min, He: 100 mL/min).



(a)

(b)

Fig. 4. Reactor temperatures (a) and hydrogen concentrations (b) at the steady state or the cyclic steady state for various furnace temperatures (feeding condition: O_2: 25 mL/min, CH_3OH: 15 mL/min, He: 60 mL/min).

point. Three reactor temperatures below the ignition point are nearly the same and increase slowly as the furnace temperature increases. There are no oscillations in reactor temperature. When reactor temperature reaches the ignition point, the reactor temperature at the inlet part of reactor jumps and oscillates. In the oscillation region, the temperature in the inlet part is much higher than in others, suggesting most partial oxidations occur in front of the reactor. The hydrogen production also jumps at this ignition point as shown in Fig. 4(b). Oscillations in the reactor temperatures are not favored in the viewpoint of reactor operations. The temperature peaks will degrade the catalyst activities and large temperature swings will cause the crack of pipe and leakage of gases. However, the reactor should be operated in this temperature oscillation region for the higher yields of hydrogen in the POX system. Hence, it is important to understand the oscillatory behaviors of the POX reactor for its safe and efficient operations.

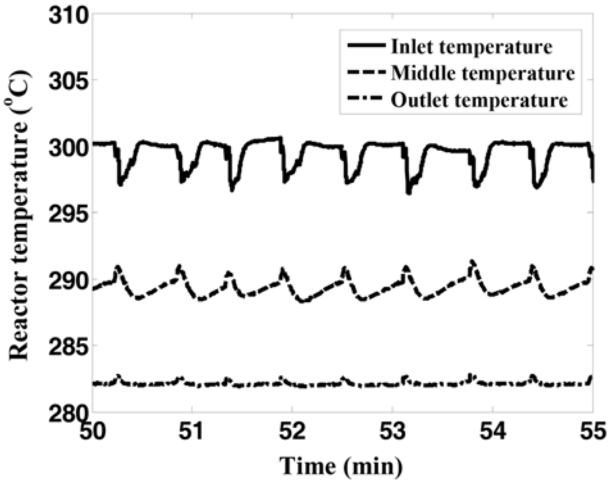


Fig. 5. Thermal oscillations showing that the phase of temperature oscillation at the inlet is opposite to that at the middle (feeding condition: O_2: 25 mL/min, CH_3OH: 15 mL/min, He: 60 mL/min, Furnace temp.: 220 °C).

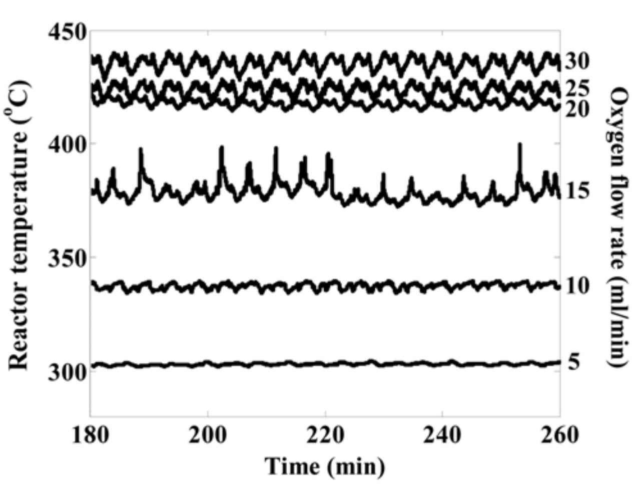


Fig. 6. Patterns of thermal oscillations at the inlet of reactor as the oxygen flow rate changes. (feeding condition: O_2: 5-30 ml/min, CH_3OH: 15 ml/min, He: 80-55 ml/min, Furnace temp.: 250 °C).

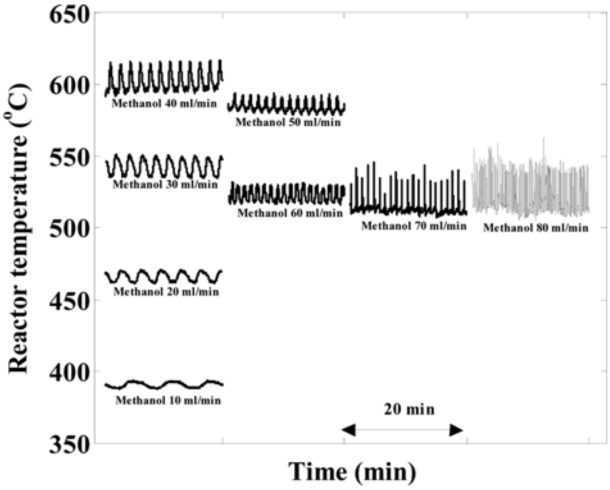
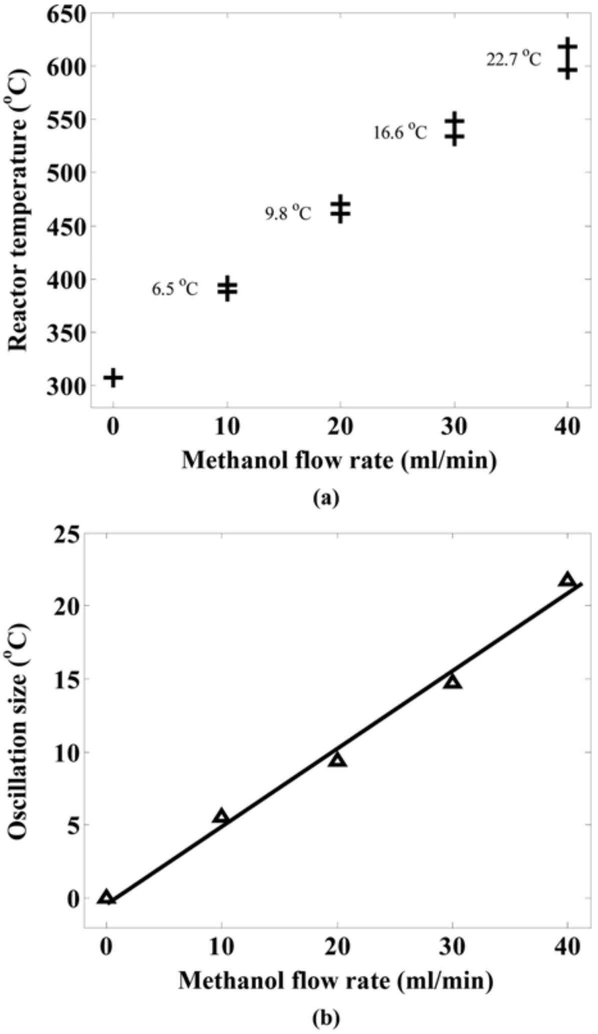


Fig. 7. Patterns of thermal oscillations at the inlet of reactor as the methanol flow rate changes. (feeding condition: O_2: 50 ml/min, CH_3OH: 10-40 ml/min, He: 120 ml/min, Furnace temp.: 300 °C).



(a)

(b)

Fig. 8. Average reactor temperatures and oscillation magnitudes as the methanol flow rate changes (feeding condition: O_2: 50 ml/min, CH_3OH: 0-40 ml/min, He: 120 ml/min, Furnace temp.: 300 °C).

For some experiments, there are considerable temperature oscillations in the middle of the reactor as in Fig. 5. In Fig. 5, there is a noticeable oscillation pattern that the phase of temperature oscillation in the middle of reactor is opposite to that of inlet of reactor. It may provide a clue to determining the oscillation mechanism. A kinetic reason why the reverse oscillations happen in PFR is our future research work.

2. Effects of Oxygen Flow Rates

Fig. 6 shows experimental results of thermal oscillations at the reactor inlet with changing the flow rate of oxygen (the concentration of oxygen). Furnace temperature is set at 220 °C, which is enough to ensure temperature oscillations. Methanol is maintained at 15% throughout experiments. The concentration of oxygen is between 5% and 30%. In these experiments, all of thermal oscillations have similar periods. The average value of reactor temperature increases nearly linearly as the concentration of oxygen increases until 20%. The oxygen concentrations up to 20% will affect the partial oxidation much. When the oxygen concentrations are over 20%, the effect of oxygen is eventually saturated and the methanol concentrations will be the rate determining ones.

3. Effects of Methanol Flow Rates

Fig. 7 shows various temperature oscillations as the methanol flow rate changes. At a relatively low flow rate of methanol, the magnitude and average value of temperature oscillation increase near linearly as the methanol flow rate increases (Fig. 8). Thermal oscillations are regular and their periods decrease exponentially as the methanol flow rate increases (Fig. 9). For large flow rates of methanol more than 80 ml/min, temperature oscillations become irregular. Fig. 10 shows the maximum values of temperatures at every peak of the oscillations. Several points having some range in a line mean that the oscillation patterns are irregular and chaotic. The irregular oscillation continues even when an excessive amount of methanol is fed.

4. Reactor Pressure

The reactor pressure can be one of the causes of oscillations and

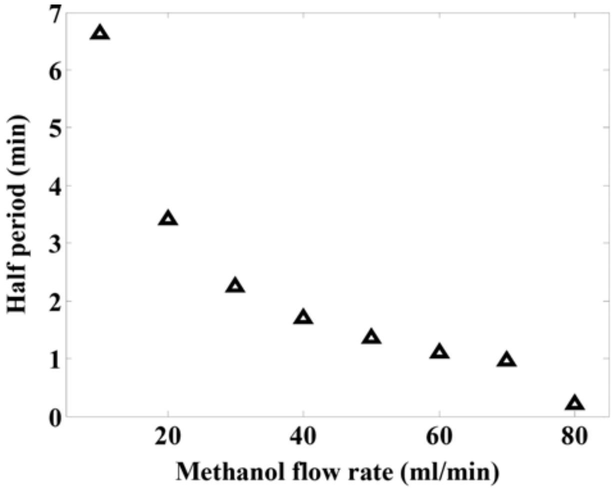


Fig. 9. Half periods of oscillations (feeding condition: O_2: 50 ml/min, CH_3OH: 0-40 ml/min, He: 120 ml/min, Furnace temp.: 300 °C).

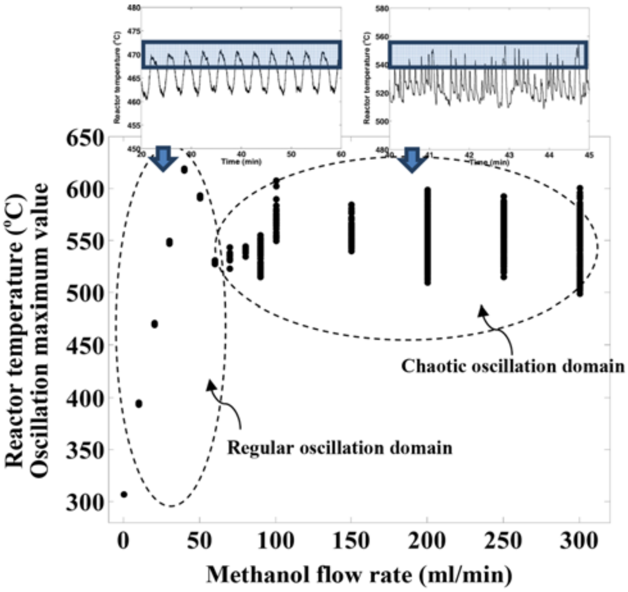


Fig. 10. Regular and irregular oscillation regions (feeding condition: O_2: 50 ml/min, CH_3OH: 0-300 ml/min, He: 120 ml/min, Furnace Temp.: 300 °C).

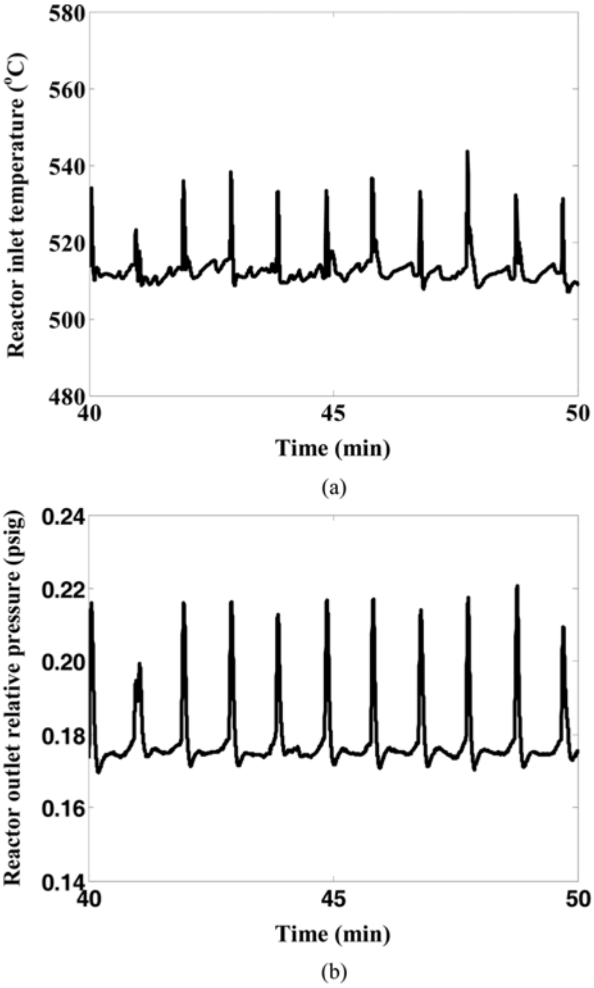


Fig. 11. Patterns of temperatures (a) and pressures (b) (feeding condition: O_2: 50 ml/min, He: 120 ml/min, CH_3OH: 70 ml/min, Furnace Temp.: 300 °C).

it is measured. The POX is a reaction that the total gas volume is expanded. As the reaction proceeds and the reactor temperature increases, the reactor pressure will increase. The increased pressure will hinder flows of reactants to the reactor and this, in turn, may cause oscillation. Fig. 11 shows the reactor temperature and pressure. We can see that the pattern of pressure is the same as the temperature oscillation. Because the magnitude of pressure swing is small, the reactor pressure change may not be the main factor for the oscillation.

CONCLUSION

Thermal oscillations often appear in the partial oxidation (POX) of methanol for the production of hydrogen. The autothermal steam reforming reactor can suffer from these troublesome responses unless it is designed so that heat generated by the partial oxidation part is not dissipated by the steam reforming part well. For the safe design and operation of a POX reactor, thermal oscillations are studied experimentally here. Experimental results can be used to analyze the thermal oscillation mechanism.

The POX reactor temperature increases slowly at first. When it reaches a certain point, it jumps abruptly and starts oscillation. The point can be called as the ignition point. The hydrogen yield also jumps at the ignition point, and hence it is inevitable for the POX reactor to be operated above the ignition point. Various patterns of temperature oscillations according to feed flow rates of reactants and reactor temperatures are obtained. Bifurcation phenomena from regular oscillations to chaotic oscillations are found as the methanol flow rate increases. These experimental results can be used for theoretical analyses of oscillations and for designing safe reforming reactors.

ACKNOWLEDGEMENT

This work (2011-001381) was supported by Mid-career Research Program through NRF grant funded by the MEST.

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