Development of 10-kWe preferential oxidation system for fuel cell vehicles

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Abstract

A preferential oxidation (PROX) reactor for a 10-kWe polymer electrolyte membrane fuel cell (PEMFC) system is developed. Pt-Ru/Al$_2$O$_3$ catalyst powder, with a size of 300–600 μm is applied for the PROX reaction. To minimize pressure drop and to avoid hot spots in the catalyst bed, the reactor is designed as a dual-staged, multi-tube system. The performance of the 10-kWe PROX unit is evaluated by feeding simulated gasoline reformate which contains 1.2 wt.% carbon monoxide (CO). The CO concentration of the treated reformate is lower than 20 ppm in the steady-state and is under 30 ppm at 65% load change. Hydrogen loss in the steady-state is about 1.5% and the pressure drop across the reactor is 4 psi. Start-up characteristics of the 10-kWe PROX system are also investigated. It takes 3 min to reduce the CO concentration to below 20 ppm. Several controllable factors are found to shorten the start-up time. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Fuel cell; Preferential oxidation reaction; Platinum-ruthenium catalyst; Carbon monoxide

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) can be operated with either pure hydrogen or reformate gas which contains a certain amount of impurities. In transportation applications, the use of pure hydrogen is known to be the best, in the sense that the fuel cell engine can be made compact and its dynamic characteristics are close to those of conventional-internal-combustion engines [1]. The problem is, however, that a hydrogen infrastructure does not exist at present and the practical storage of hydrogen on-board still requires many technical improvements. Therefore, an on-board reforming system has been considered as the near-term solution for vehicles powered by fuel cells [2]. An on-board reformer consists of two sub-systems. One is the cracking unit, which generates the H$_2$-rich reformate gas from the conventionally available hydrocarbon fuels. The other sub-system is the clean-up unit which removes CO from the reformate gas. CO is the main culprit in reducing the performance of PEMFC; it must be reduced to below 20

to 100 ppm given the anode material and the operation method of the PEMFC [3,4]. In general, reduction in the CO content is achieved either by a water-gas shift (WGS) reaction or by a PROX. The former reaction is the easier to control, since WGS ($\Delta H = -41.1$ kJ/mol CO) is a much weaker exothermic reaction than PROX ($\Delta H = -283$ kJ/mol CO). On the other hand, the volume of catalyst required to oxidize a certain amount of CO is less for PROX, since the rate of the PROX reaction is faster than that of the WGS reaction. Moreover, there is a limit in thermodynamic conversion in a shift reaction, so that a CO concentration which is sufficiently low for acceptability by the PEMFC system can never be achieved. In general, for the reforming system of the PEMFC, the CO clean-up sub-unit has to be an appropriate combination of WGS and PROX considering the controllability and total volume of the system. It is known that a CO concentration of 1–2 wt.% after the WGS reaction and before the PROX reaction is optimum in terms of the overall performance of the system.

Several different types of PROX catalysts have been reported during the past decade. Among them, Pt [5], Au [5,6], Ru [7] and Pt alloys [8] have been known to have high activity for CO oxidation in the hydrogen-rich reformate gas. The temperature range in which both activity and selectivity are satisfied is so narrow that the catalysts may not allow even a slight disturbance of the system. Fuel cells,

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especially those for transportation applications, suffer severe load change as well as frequent start-ups. Hence, the aforementioned types of catalyst cannot be used as the PROX catalyst without a precise and complex control of temperature. Recently, it has been reported [9–11] that Pt-Ru catalyst, which is also used as the anode material of in the direct method fuel cell (DMFC), has high activity and selectivity over a wide range of temperature, Currently, the properties of the catalyst are under evaluation in order to determine the best method of preparation and the optimum alloy composition. In this study, a Pt-Ru/Al$_2$O$_3$ catalyst is made by an incipient wetness method and its performance is evaluated in 1 and 10-kWe PROX systems for vehicle applications.

2. Experimental

2.1. Catalyst preparation and activity test

A mixed solution of platinum and ruthenium precursors was prepared by adding H$_2$PtCl$_6$ and RuCl$_3$ at a certain ration to de-ionized water. The solution was impregnated on γ-alumina of size 300–600 μm. Impregnation was achieved by an incipient wetness method, in which the pore volume of the support material was exactly estimated and only the corresponding amount of precursor mixture was added. In that way, there was no remaining residue which would contribute to an error in the predetermined atomic ratio of Pt:Ru. The resulted paste was dried overnight until it became a powder. Finally, the powder was calcinated in hydrogen for 4 h.

The catalyst (0.15 g) was loaded into a quartz tube reactor (internal diameter = 4 mm). The catalyst was pretreated in nitrogen at 400 °C to eliminate contaminant gases on the surface, especially hydrogen which might have been adsorbed on the catalyst during calcination. Simulated gasoline reformate was used for the activity test of the catalyst. The composition of the simulated reformate was 36 wt.% H$_2$, 17 wt.% CO$_2$, 28 wt.% N$_2$, 17 wt.% H$_2$O, 1 wt.% CO, and air was added additionally as the oxidant. Each gas was controlled by MFC, while the water content was controlled by a steam generator. The total flow rate was maintained at 100 ml/min (wet basis). The test was performed over the temperature range 100–160 °C at various flow rates of inlet air.

2.2. 1-kWe PROX evaluation

The same amount of catalyst as that used in activity test was applied to a 1-kWe PROX. The reactor was designed so as to minimize pressure drop and to allow efficient heat transfer. A schematic diagram of the 1-kWe PROX system equipped with various performance-evaluating components is given in Fig. 1. The system is designed as two separate stages and inter-stage cooling is applied to control the temperature of the inlet gas between the stages. The volume of the catalyst in each stage is 100 cm^3.

The flow rates of H$_2$, N$_2$, CO$_2$, CO and air were controlled by MFC and the mixed gas passed through a water vapourizer which causes the gas to contain 17 wt.% H$_2$O. The mixed gas, which had the composition of gasoline reformate, was heated to the desired temperature by an electric heater before it entered the first stage. Until the gas reached the desired temperature, it was vented out of the system. When the temperature of the mixed gas is sufficiently high to initiate CO oxidation on the catalyst, the flow was switched to the first stage. Secondary air was added between the first and second stages. The gas mixed with secondary air was cooled to the desired temperature by the inter-stage cooler before it was passed into the second stage. Outlet gas from the second stage was sampled and analyzed to determine the conversion and selectivity.
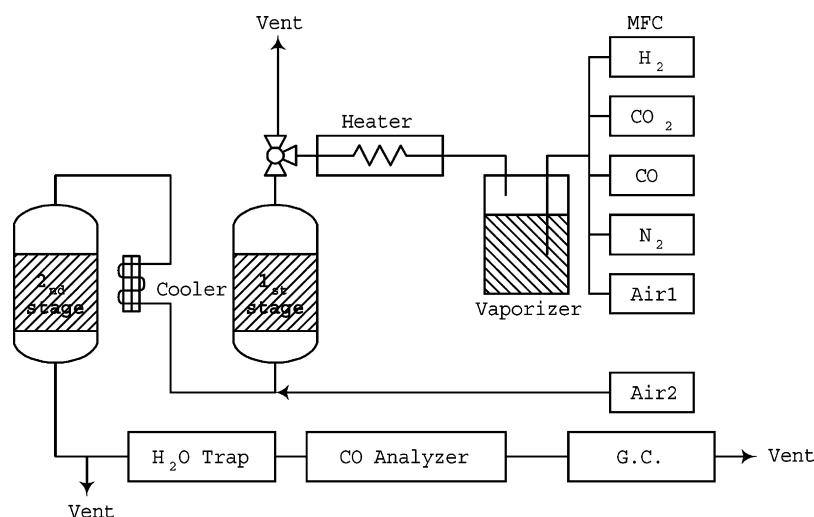

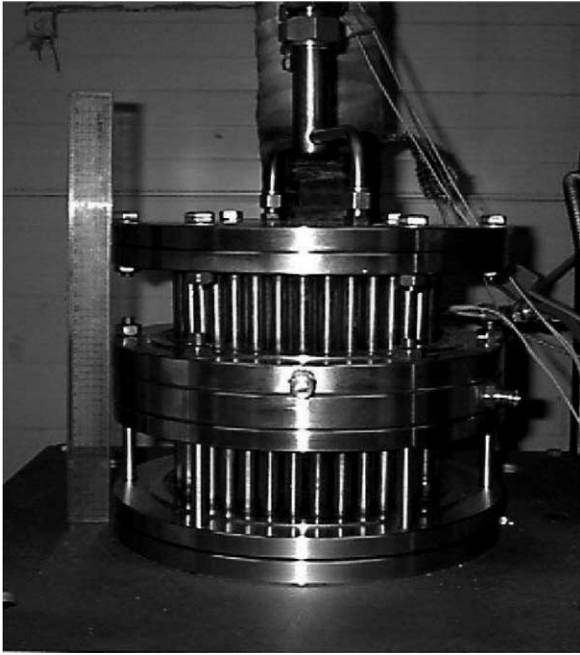Fig. 1. Schematic diagram of PROX evaluation system.

Fig. 2. 10-kWe dual-stage PROX.

2.3. 10-kWe PROX evaluation

The 10-kWe PROX system is shown in Fig. 2. The same 300–600 μm catalyst was used but the reactor was designed as a two staged, multi-tube system. Each stage consists of 128 parallel tubes with an internal diameter of 0.5 in. The system has an inter-stage cooling plate which is a thin disk fitted between the first and second stages. The catalyst volume is 1.2 l and the actual dimension of the reactor is 20 cm (ϕ) × 20 cm(h). A gas distributor of special design is installed in the inlet part of each stage in order to achieve homogeneous distribution of the reactant gas before it enters the multi-tube bundle. The performance evaluation was done in the same manner as that described for the 1-kWe PROX. The only exception was that the simulated reactant gas does not contain H_2O since the effect of H_2O to the PROX performance was found to be negligible in the previous test with the 1-kWe system. The total flow rate of reactant was 385 l/min. Effluent gas from each stage of the reactor was sampled at the rate of 1 l/min and the sampled gas was dried by passing through a $CaSO_4$ moisture trap. The CO and H_2 concentrations were then analyzed by means of an infrared gas analyzer (California Analytical Instruments) and a HERMOR615 unit (Maihak). The concentrations of CO_2, O_2 and CH_4 were analyzed with a gas chromatograph which was equipped with TCD detectors. The selectivity of CO oxidation was calculated by the following equation:

$$\text{Selectivity} = \left[\frac{\text{moles CO converted to } CO_2}{2(\text{moles total reacted } O_2)}\right] \times 100 \qquad (1)$$

3. Results and discussion

3.1. Catalyst activity

The results of the activity test for the prepared Pt-Ru/Al_2O_3 catalyst are given in Fig. 3. Irrespective of the O_2:CO ratio of the input reactant, the conversion of CO is always above 92% as long as the temperature is maintained at 100–160 °C. As the temperature increases, however, the conversion decreases slightly. This is due to the lower selectivity at higher temperature, which corresponds to increased consumption of oxygen to oxidize H_2 instead of CO. In the PROX reaction, CO and H_2 in the reformate gas react competitively with oxygen. Since the oxygen is the limiting
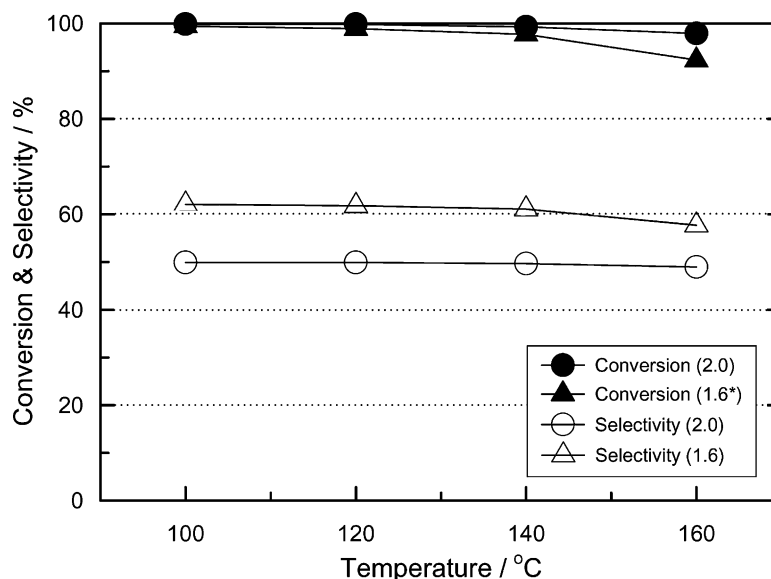

Fig. 3. Conversion and selectivity of Pt-Ru/Al_2O_3 catalyst (numbers in parenthesis are values of O_2:CO stoichiometric ratio).
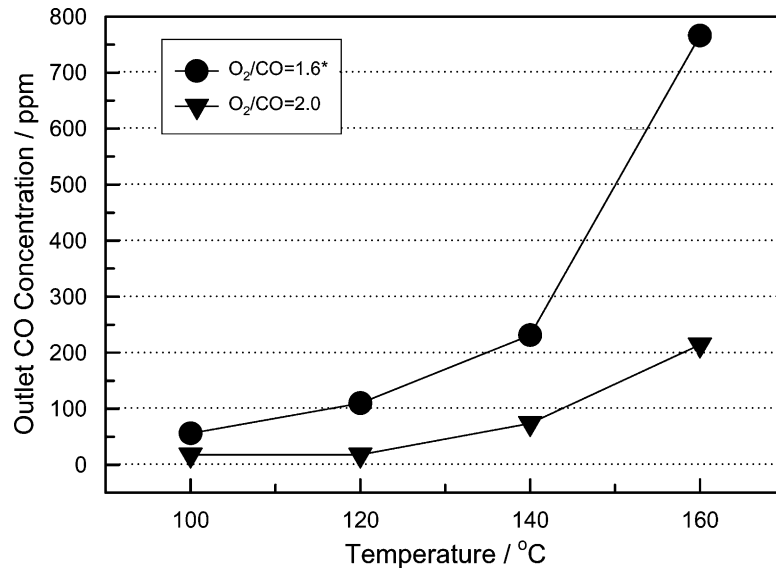
Fig. 4. Outlet CO concentration in activity test of Pt-Ru/Al$_2$O catalyst.

reactant, however, the reduction of CO selectivity indicates that the oxidation rate of hydrogen becomes significant at high temperatures. The outlet CO concentration is shown in Fig. 4 as a function of reaction temperature. When the O$_2$:CO ratio is 2.0, the outlet CO concentration is under 20 ppm and the temperature of the reactor is found to be in the range 100–120 °C. The hydrogen consumption is about 2.8% with 0.083 l/kWe of catalyst volume. This result suggests that even a single-staged PROX reactor can achieve an outlet CO concentration of under 20 ppm at steady state as long as the same conditions are maintained throughout the reactor. In a real system, however, it is extremely difficult to maintain the reactor temperature when the hydrogen consumption is so high, even with an extensive temperature control. Hence, the only way to maintain the temperature is

to reduce the hydrogen consumption by decreasing the air supply. This, in turn, reduces the reaction rate and, consequently, the outlet CO concentration in the effluent gas becomes higher. Therefore, it is practically impossible to achieve both low hydrogen consumption and high CO conversion without using a multi-staged reactor system. Accordingly, the required volume of the catalyst for the multi-staged reactor becomes more than 0.083 l/kWe.

3.2. Performance of 1-kWe PROX system

The performance of the single PROX reactor (catalyst volume = 0.1 l/kWe) at various oxygen stoichiometries is shown in Fig. 5. At high oxygen contents, the CO conversion improves but the selectivity deteriorates. This is due to the
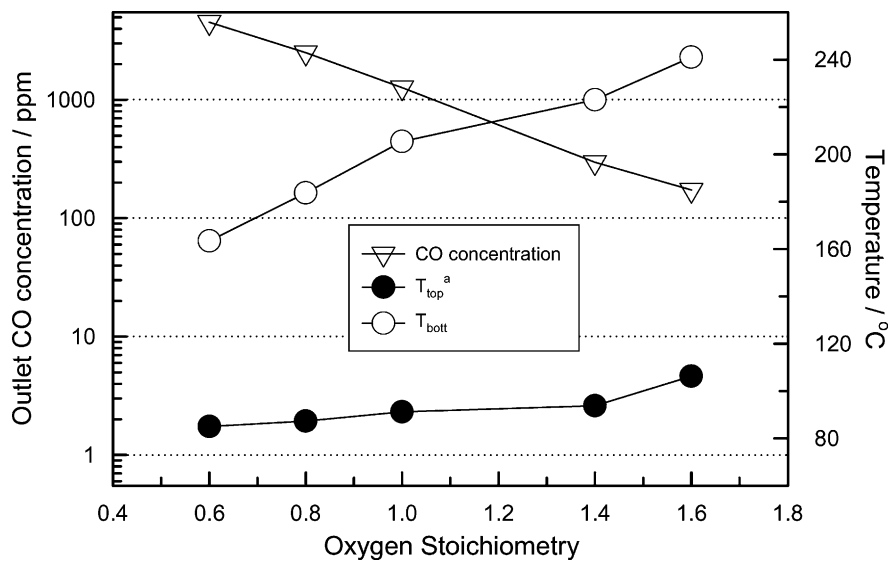

Fig. 5. Outlet CO concentration and temperature of single-staged 1-kWe PROX at different oxygen stoichiometries (T_{top} and T_{bott} are catalyst temperatures at inlet and outlet parts of reactor, respectively).

fact that the excess oxygen starts to induce undesirable hydrogen oxidation which leads to increased temperature in the reactor and, in turn, contributes to lowering of the selectivity. As a result, oxygen which is supposed to be used for CO oxidation is rendered sufficient. If, under these conditions, more oxygen is introduced to complete the CO oxidation, this phenomenon propagates and become even worse. To reduce the hydrogen loss and increase the CO conversion simultaneously, additional stages are required, as mentioned in the previous section. As the number of stage increases, however, control becomes more complex and the cost rises. Therefore, this study has investigated a dual-stage PROX system as the simplest case.

For a dual-stage system (catalyst volume 0.2 l/kWe, the amount of air into each stage for the complete oxidation of CO is very important. Also, the combined total amount of air for the reaction has to be kept as low as possible. Any excess in oxygen content is directly proportional to the hydrogen loss. The total amount of air is mostly determined by the amount passed into the first stage, since the major portion of CO is removed during this stage. Hence, minimization of the air flow to the first stage is desired. There is, however, a limit to lowering the air flow into this stage. Below a certain point, the CO content in the inter-stage gas flow becomes so high that the CO level never goes below 10 ppm in the second stage. Therefore, there must be optimum amounts of air in the stages to give the lowest hydrogen loss and, hence, the highest CO selectivity.

Results obtained under selected optimum amounts of inlet air are shown in Fig. 6. The second stage can process as much as 1200 ppm of CO inlet, which is the case when the O_2:CO ratio is 1.0 and 2.0 for the first and second stage, respectively. Although the ratio for the second stage is larger than that for the first stage, the actual amount of air into the

second stage is lower, since the CO content in this stage is much lower. At these ratios, the minimum amount of air is used in the system, which translates to the highest CO selectivity. Therefore, steady performance is determined at the optimum conditions and is found to be sufficient for the PROX system to be applicable to PEMFC operations.

The results of a load transient test with the dual-stage PROX system are given in Fig. 7. The total flow to the system is abruptly decreased from 100 to 35% after 5 min and then returned back to 100% some 10 min later. During the transient change of the total flow, the outlet CO concentration remains under 10 ppm, even though the temperatures of the first and second stage are slightly disturbed. For fuel cell systems to be used in vehicular applications, it is highly important to endure such a sudden load change. The load change translates to a change in the amount of reactant and inevitably results in temperature fluctuations in the PROX system. A complex temperature control network can be used to cope with such a disturbance and rapidly return the system to the normal operating conditions. Of course, such a delicate temperature control adds complexity to the system and increases the cost of the vehicle. In this study, the PROX system shows good performance, both for steady states and for transient conditions, without an extensive temperature control. It is believed that this encouraging behaviour is due to the characteristics of the selected PROX catalyst which has high activity and selectivity over a wide range of reaction temperature.

3.3. Performance of 10-kWe PROX system

The CO reduction capability of both the 10-kWe single-staged reactor (catalyst volume 0.06 l/kWe) and the 10-kWe dual-staged reactor (catalyst volume 0.12 l/kWe) is given in
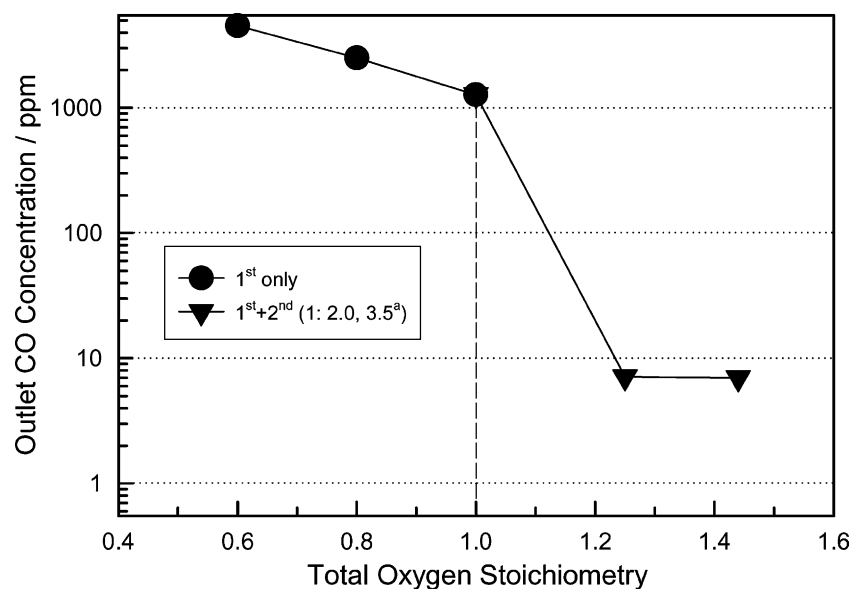

Fig. 6. Outlet CO concentration of dual-staged 1-kWe PROX at different oxygen stoichiometries (numbers in parenthesis are values of O_2:CO ratio for the second stage alone).
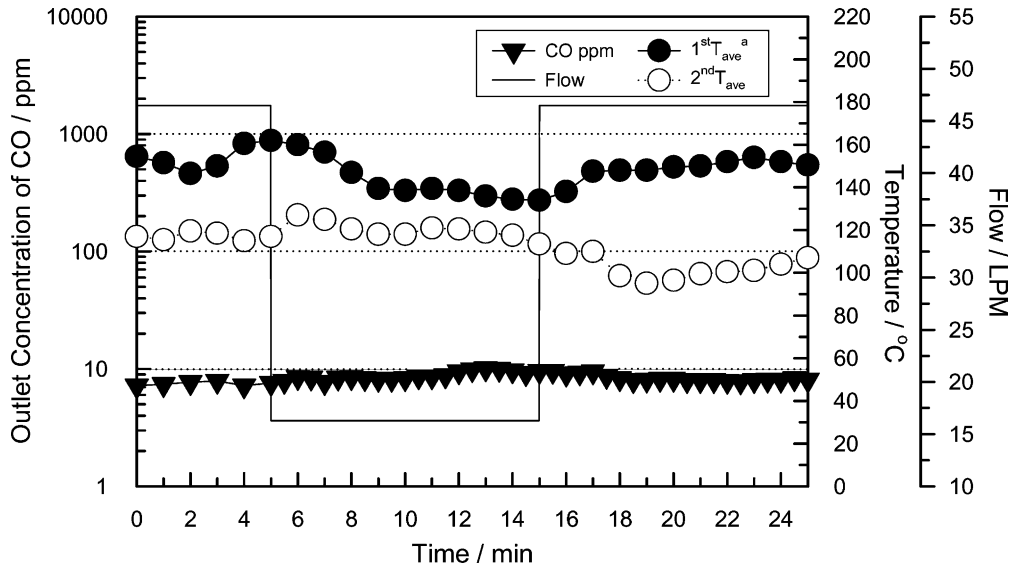
Fig. 7. Steady and load transient performance of dual-staged 1-kWe PROX (T_{ave} is arithmetic mean of catalyst temperature at inlet and outlet parts of each stage).

Fig. 8. The performance test of the single-staged reactor is performed simply by using the first stage from 10-kWe dual-staged reactor. For the single-staged reactor, the outlet CO concentration decreases as the incoming air flow rate increases. Once the air flow rate increases beyond the point at which the stoichiometric O_2:CO ratio is 1.4, however, CO conversion gradually decreases and results in a higher CO concentration at the discharge. This is because the excess air causes oxidation of a significant amount of undesired H_2 which leads to a higher reaction temperature and lower CO selectivity.

The dual-staged reactor system is comprised of two single reactors, inter-stage cooling, and an secondary air inlet to the second stage. The amount of secondary air is controlled so that the outlet CO concentration from the second stage becomes below 20 ppm. The optimum, steady-state operating condition is determined by minimizing the total amount of inlet air while the outlet CO concentration of the second stage is still kept below 20 ppm. When the amount of inlet air to the first stage corresponds to a stoichimetric O_2:CO ratio of 1.0–1.2, the amount of total inlet air is found to be minimum. The air to the second stage at this condition and the corresponding CO concentrations are shown in Fig. 9. At this optimum condition, the outlet CO concentration is under 20 ppm and the hydrogen loss is under 2%.
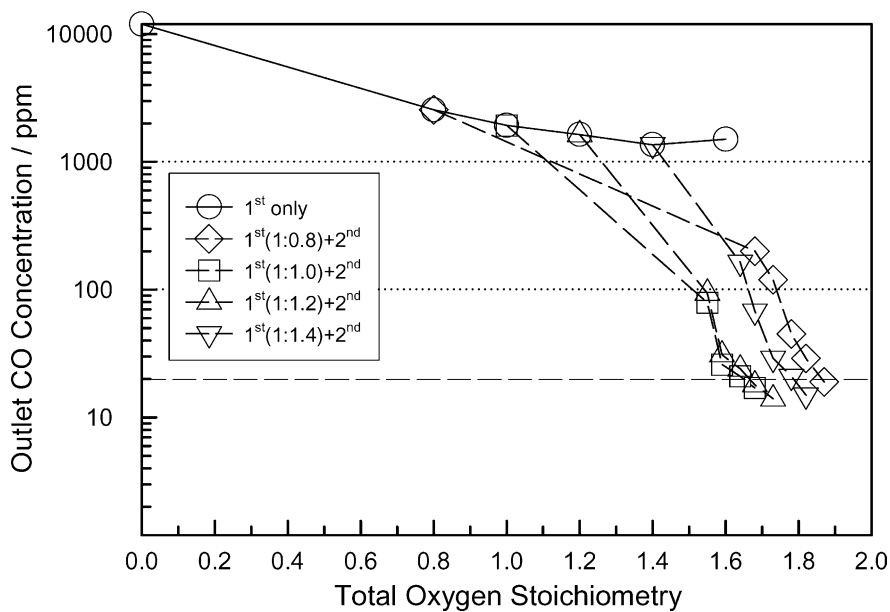

Fig. 8. Outlet CO concentration of single and dual-staged 10-kWe PROX at different oxygen stoichiometries (numbers in parenthesis are values of O_2:CO stoichiometric ratio at 1st stage).
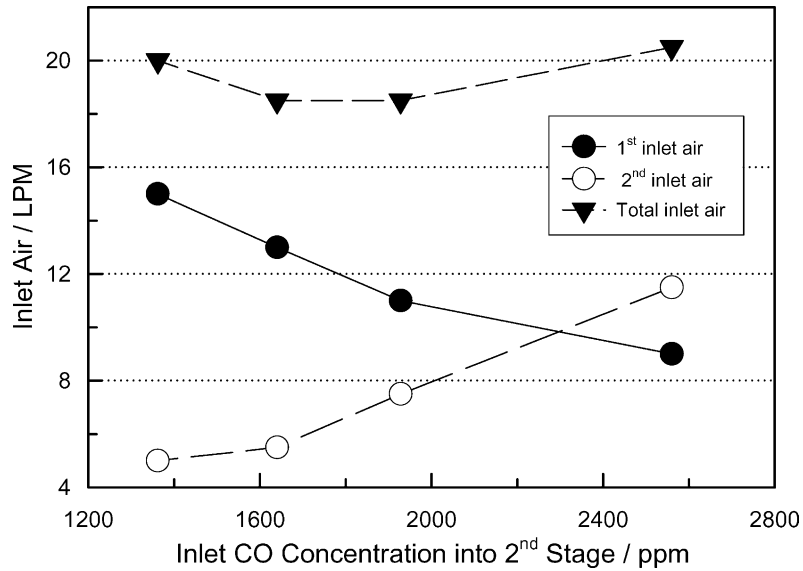
Fig. 9. Total amounts of inlet air into dual-staged 10-kWe PROX for which outlet CO concentration is under 20 ppm, at different inlet CO concentrations into second stage.

The transient performance of the 10-kWe dual-staged PROX system is presented in Fig. 10. The feed flow rate is changed up and down by 65% of the full scale. The temperature is detected on the outer shell of each tube bundle and control of the reaction is based on the detected temperature. This is due to the fact that the temperature of the outer shell is lower than that of the centre part of the tube bundle, and it should be above the ignition temperature of the CO conversion reaction ($\sim 90\,°C$) to guarantee 100% utilization of the whole reactor. The most significant change in outlet CO concentration occurs when the load is increased from 35 to 100%, although it is still below 30 ppm. It does not create a significant problem since it decreases quickly to 20 ppm as the system becomes stable. The short-term rise of

the outlet CO concentration appears to depend on the temperature of the second stage which experiences a lower temperature than the ignition temperature during the load change.

To examine the start-up characteristics, the 10-kWe PROX system was tested manually for various initial conditions. Fast start-up of the system requires a rapid rise in the temperature of the whole catalyst bed above its ignition temperature. During start-up, the most important factors which affect the catalyst temperature are the incoming reactant temperature and the amount of supplied air. With the present system it is found that, for fast start ups, the reactant temperature has to be at least $150\,°C$ and the amount of inlet air should be above the point at which the O_2:CO
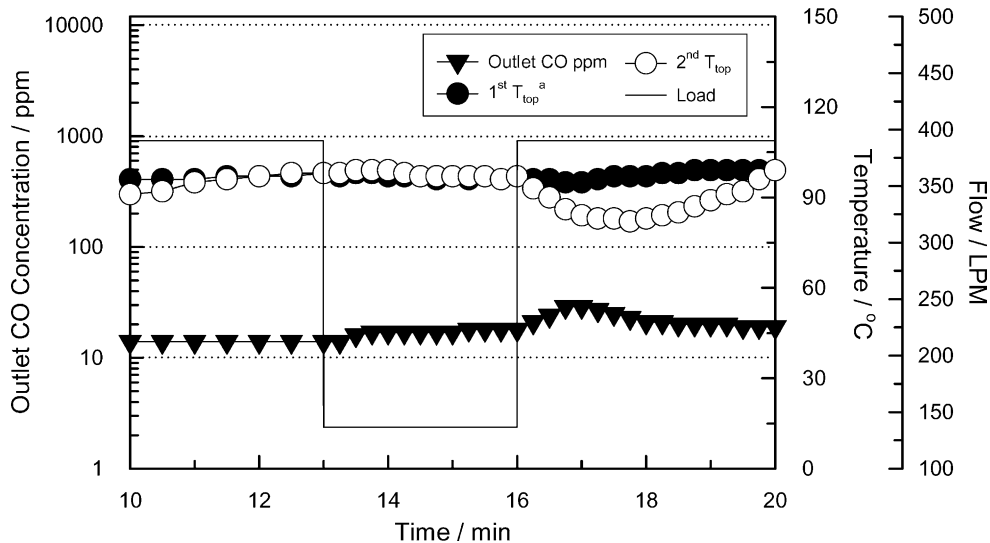

Fig. 10. Steady and load transient performance of dual-staged 10-kWe PROX (T_{top} is catalyst temperatures at inlet parts of each stage).
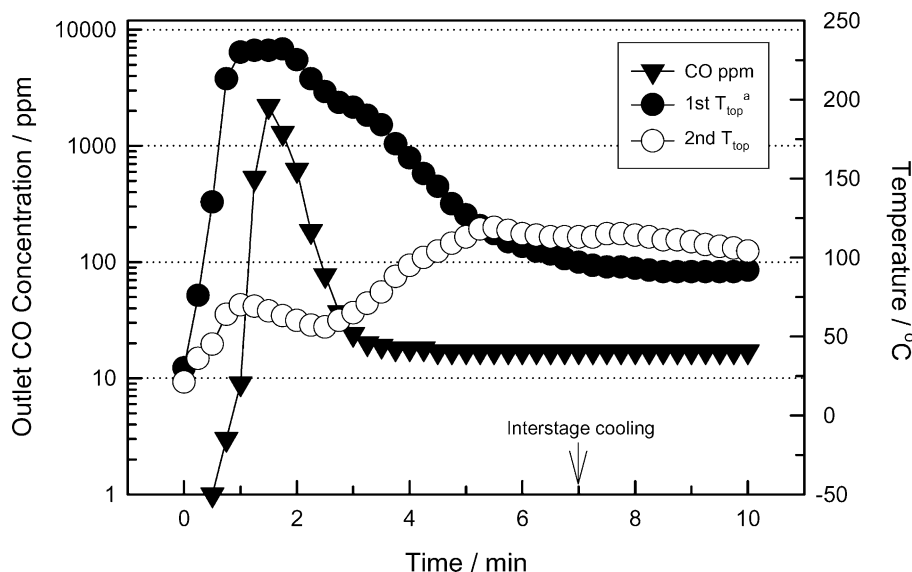
Fig. 11. Start-up characteristics of dual-staged 10-kWe PROX. (T_{top} is catalyst temperature at inlet parts of each stage).

Table 1
PROX performance and specifications

	Reactor type	Stages	Catalyst size (mm)	Catalyst weight (g)	Outlet CO at steady (ppm)	Out CO at 65% load change (ppm)	Start-up time (min)	Catalyst volume (l/kWe)	System volume (l/kWe)
Activity test	Packed bed	Stage 1	0.3–0.6	0.15	<20 ppm (100–120 °C)	–	–	0.083	–
1-kWe	Packed bed	Stage 2 (two bodies)	0.3–0.6	170	<10 ppm (90–180 °C)	<12 ppm	5	0.2	0.26
10-kWe	Packed bed (multi-parallel reactors)	Stage 1 (one body)	0.3–0.6	1000	<20 ppm (90–180 °C)	<30 ppm	3	0.12	0.25

molar ratio is 3.0. Once the system starts, the inlet temperature and inlet air are then controlled down to their optimum values and the temperature of the reactor is maintained in the range 90 to 140 °C. With this start-up procedure, it takes 3 min for the outlet CO concentration to fall below 20 ppm. As shown in Fig. 11, the catalyst temperature of the second stage rises rather more slowly than that of the first stage. This problem appears to be due to the inter-stage cooling of the reactant, even though inter-stage cooling is not necessary at this point. This implies that a further shortening of the start-up time is possible by a simple modification of the operation procedure to circumvent the unnecessary inter-stage cooling of the reactant at start-up.

4. Conclusions

The performance of 1 and 10-kWe PROX are summarized in Table 1. For the 1-kWe PROX the outlet CO concentration is under 10 ppm in both steady state and transient conditions and the hydrogen consumption is 0.7% of the total hydrogen in the reactant. The reactor is a dual-staged, packed bed with a volume of 0.26 l/kWe which is the sum of the volumes of the two reactors and the inter-stage cooling unit. For the 10-kWe PROX, the specific catalyst loading is about half that of the 1-kWe unit. The outlet CO concentration is below 20 ppm at the steady state and below 30 ppm under transient conditions. Hydrogen consumption is 1.8%. The system volume is 0.25 l/kWe which is the sum of the volumes of the catalyst, the void volume between the multi-tubes, and the inter-stage cooling unit. Assuming that the PROX system occupies 20% of the total volume of the fuel processor [12], the fuel processor would be 1.25 l/kWe (or 0.75-kWe/l). This size satisfies the 2004 goal of the partnership for next generator vehicles (PNGV) set in the USA.

To reduce hydrogen consumption and system volume further, a highly dispersed Pt-Ru catalyst, for use in a 25-kWe PROX system, is under development The design of the 10-kWe PROX is based on adiabatic conditions but for the 25-kWe PROX system, both adiabatic and non-adiabatic design will be applied.

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