On the Catalytic Combustion Behaviors of CH_4 in a MCFC Power Generation System

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Abstract—Catalytic combustion is generally accepted as an environmentally preferred alternative for the generation of heat and power from fossil fuels mainly due to its advantages related to the stable combustion under very lean conditions with low emissions of NOx, CO, and UHC at temperatures lower than those occurred in conventional flame combustion. Despite these advantages, the commercial application of catalytic combustion has been delayed because of complicated reaction processes and the difficulty in developing appropriate catalysts with the required stability and durability. To develop the catalytic combustors, detailed studies on the combustion characteristics of catalytic combustion should be conducted. To the end, in current research, quantitative studies on the combustion characteristics of the catalytic combustors, with a Pd-based catalyst for MCFC power generation systems, relying on numerical simulations have been conducted. In addition, data from experimental studies of variations in outlet temperatures and fuel conversion, taken after operating conditions have been used to validate the present numerical approach. After introducing the governing equations for mass, momentum, and energy equations as well as a description of catalytic combustion kinetics, the effects of the excess air ratio, space velocity, and inlet gas temperature on the catalytic combustion characteristics are extensively investigated. Quantitative comparisons are also conducted with previous experimental data. Finally, some concluding remarks are presented.

Keywords—Catalytic combustion, Methane, BOP, MCFC power generation system, Inlet temperature, Excess air ratio, Space velocity.

I. INTRODUCTION

THE optimum energy carrier for MCFC systems being developed for commercial applications is hydrogen. Of all the potential sources of hydrogen, the most attractive source is natural gas, because it is widely available, clean, and can be converted to hydrogen relatively easily [1].When natural gas is used as a fuel for MCFC systems, the general composition of off-gas from the anode is 36% CO_2, 45% H_2O, 15% H_2, 2% CO, and 2% CH_4 by volume. A combustor is needed to burn out these gases in order to prevent emissions and increase the overall efficiency of the fuel cell systems [2], [3].

In most cases, however, perfect combustion is quite difficult to achieve with a conventional combustor because the anode off-gas includes high concentrations of inert gases, such as H_2O and CO_2. Therefore, a catalytic combustor, which generally operates at relatively low temperature and has good combustion efficiency even in limited conditions with high concentrations of H_2O and CO_2, in comparison with those of conventional combustor, resulting in a reduction of thermal NOx, CO, and

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UHC emissions [4], [5], is introduced to MCFC systems. Catalytic combustion has generally been accepted as an environmentally preferred alternative for heat and power generation systems, allowing fossil fuels to be burned efficiently, in fuel concentrations outside flammability limits, at temperatures lower than those used in flame combustion, and with fewer undesirable combustion by-products [6]-[8].

Meanwhile, catalytic combustion involves complicated reaction processes that are controlled by heterogeneous chemistry (for examples, the diffusion of reactants to the catalytic surface, adsorption, surface reaction, desorption, diffusion of products from the surface) and transport phenomena of mass, momentum, and energy, in addition to homogeneous chemistry [9]. Consequently, the analysis and optimization of operating conditions for the stable operation of methane-based catalytic combustion are necessary to apply such a system to natural gas-based MCFC power generation systems. To ensure stable operation in such systems, the combustion of CH_4 is most important among off-gas components, because the reaction of CH_4 starts at a relatively higher temperature than that of H_2 and CO [10], [12]. In this study, therefore, CH_4 catalytic combustion characteristics are the main focus. Here, the Pd-based catalyst commonly used for catalytic combustion of CH_4 is adopted.

Several recent efforts have begun to address the catalytic combustion characteristics of CH_4 with a Pd-based catalyst for real applications. Dalla Betta et al. [13] showed that preheating is required for the ignition of CH_4 by illustrating the ignition/extinction catalyst performance. Kuper et al. [14] and Griffin et al. [15] showed that the PdO/Pd transition temperature range within which the activity of a catalyst is reduced is between 750 and 850°C. Hong [3] and Lee et al. [16] conducted an experimental study to investigate the importance of various parameters such as inlet temperature, space velocity, gas composition, and the excess air ratio for complete combustion. Recently, Deshmukh and Vlachos [17] proposed a reduced mechanism for methane and one-step rate expressions for fuel-lean catalytic combustion of small alkanes on noble metals.

In this paper, therefore, numerical investigations on the CH_4 catalytic combustion characteristics according to various parameters are conducted to examine the optimal operating conditions. Firstly, after introducing the governing equations adopted in this work, the numerical approach, which entails a comparison with experimental data given by Hong [3], is validated. Next, catalyst performance studies with different excess air ratio and space velocity are reviewed, and the optimal design characteristics are determined from them. The

design points of combustor systems are fixed and used to scale up the catalytic combustor and the following parametric studies according to variations in operating conditions for the performance evaluation of catalytic combustors. The effects of various operating conditions such as inlet temperature and H_2 addition on reaction behavior in the adopted catalytic combustor under actual conditions in the 250kW MCFC system are then investigated. Finally, some concluding remarks are presented.

II. MATHEMATICAL FORMULATION

A. Governing Equations

The catalytic combustor considered in this work is a part of the balance of plant (BOP) of the MCFC power generation systems depicted in Fig. 1. Since the catalytic reactions occur on the catalyst surface, the reactants have to be transported to the external gas-solid interface. Modeling the overall combustion process, therefore, requires consideration of both the physical transport and the chemical kinetic steps [18]-[20]. In general, there is a boundary layer between the bulk fluid stream and the solid surface, within which velocity, concentration, and temperature vary. Species transport, from the bulk fluid stream to the solid catalytic surface, can have a limiting effect on the rate of the catalytic reaction. In this work, the reactions are considered a one-step global reaction in terms of fuel composition [21], [22]. Therefore, the influence of adsorption and desorption of species on the catalytic surface must to be considered in formulating the reaction rates. Here, the commonly used Langmuir-Hinshelwood-Hougen-Watson type rate equations [15] are used to model the catalytic reactions.

Under the assumption that the radial transport effects of a honeycomb-type catalytic converter are smaller than those of axial heat transfer, the entire converter can be represented by a single channel [18], [23], [24]. While the effects taking place are convective, diffusive and conductive transport occur in the gas phase, and mass and energy can transfer through the boundary layer, diffusion and catalytic conversion in the washcoat and conduction in the solid phase also can occur. In addition, neglecting the radial gradients in the channel, a transient and one-dimensional (in the axial direction) conservation equation suffices to describe thermodynamic and fluid dynamic characteristics. Under these assumptions, the differential conservation equations for the mass, momentum, and energy of a single channel can be written as follows [25].
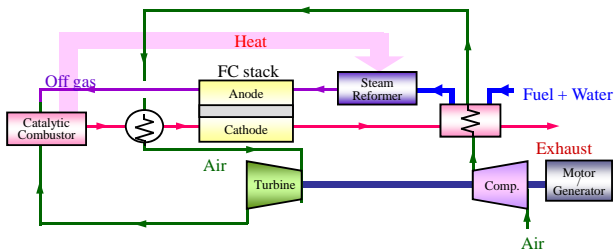

Fig. 1 Schematic diagram of the MCFC power generation system

TABLE I
BASIC GAS COMPOSITION OF THE CATALYTIC COMBUSTOR BASED ON OFF-GASES FROM THE ANODE

Species	Mass flow rate (kg/hr)		Mole fraction
	5 kW	250 kW	
H_2	0.15	7.67	0.045
CO	0.33	16.75	0.007
CO_2	7.89	394.36	0.105
CH_4	0.15	7.41	0.005
H_2O	4.12	206.13	0.135
Air (λ=4)	34.55	1,727.73	0.702
Total	47.2	2,360.04	1.000

Under the assumption that the radial transport effects of a honeycomb-type catalytic converter are smaller than those of axial heat transfer, the entire converter can be represented by a single channel [18], [23], [24]. While the effects taking place are convective, diffusive and conductive transport occur in the gas phase, and mass and energy can transfer through the boundary layer, diffusion and catalytic conversion in the washcoat and conduction in the solid phase also can occur. In addition, neglecting the radial gradients in the channel, a transient and one-dimensional (in the axial direction) conservation equation suffices to describe thermodynamic and fluid dynamic characteristics. Under these assumptions, the differential conservation equations for the mass, momentum, and energy of a single channel can be written as follows [25]. More detailed information regarding governing equation can be found in [3].

The one-step global reactions for H_2, CO, and CH_4 are used to conduct a characteristic analysis of the catalytic combustion, i.e.,

$$H_2 + 1/2\,O_2 \rightarrow H_2O \tag{1}$$

$$CO + 1/2\,O_2 \rightarrow CO_2 \tag{2}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3}$$
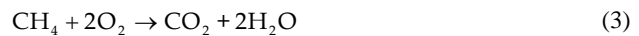
The reaction rate expressions are, of the Langmuir-Hinshelwood type which is most commonly used for analyzing catalytic combustion with inhibition terms [15], [16] such as

$$\dot{r}_1 = K_1 y_{H_2} y_{O_2}/D, \; \dot{r}_2 = K_1 y_{CO} y_{O_2}/D, \; \dot{r}_3 = K_1 y_{CH_4} y_{O_2}/D \tag{4}$$

$$D = T_s \left(1 + K_2 y_{CO} + K_3 y_{CH_4}\right)^2 \left(1 + K_4 y_{CO}^2 y_{CH_4}^2\right)\left(1 + K_5 y_{NO}^{0.7}\right) \tag{5}$$

$$K_i = k_i \exp\left(-T_{A,i}/T_s\right) \tag{6}$$

where k_i and $T_{A,i}$ are the frequency factor and the activation energy, respectively and y_k is the mole fraction of species k. The kinetic parameters are calculated by comparing the light-off characteristics of the catalytic reaction with the optimization process by using iSIGHT^{TM} [26]. The kinetic

parameters of catalytic combustion of methane are as follows :

$k_1 = 1.1 \times 10^6 \, \text{kmol}/(\text{m}^2 \cdot \text{s})$, $k_2 = 65.5$, $k_3 = 2.08 \times 10^3$, $k_4 = 3.98$, $k_5 = 4.79 \times 10^5$, $T_{A,1} = 6.45 \times 10^{3°}\text{C}$, $T_{A,2} = -9.61 \times 10^{2°}\text{C}$, $T_{A,3} = -3.61 \times 10^{2°}\text{C}$, $T_{A,4} = -1.1611 \times 10^{4°}\text{C}$, and $T_{A,5} = 3.733 \times 10^{3°}\text{C}$.

B. Numerical Analysis

In this study, methane originating from natural gas is used as the main fuel of the catalytic combustor. The conditions simulated correspond to the experimental study done by Hong [3]. Table I shows the basic gas composition used as the inlet condition, based on the off-gas composition from the anode, under a fuel utilization rate of 60% of the MCFC stack. A Pd/Ce/Ni-Al$_2$O$_3$ catalyst, which contains not only Pd(2 wt.%), but also Ce and Ni, is used because the concentration of H$_2$O obstructing catalyst activity is high [27]. The physical properties of the catalysts used in this study are as follows: monolith volume of 0.00141m^3, length of monolith of 0.1m, cell density of 300cpsi, wall thickness of 8 mil, washcoat thickness of 5 mil, number of grid points of 20, density of 2500kg/m^3, thermal conductivity of 3W/mK, and specific heat of 800 J/kgK.

The governing equations are analyzed with BOOST^{TM} of AVL [15] by adopting the thermo chemical properties of the fuel and catalysts used in this study. Here, the number of grid points is 20 and the adiabatic condition is used at the wall, while the outlet condition of the catalytic combustor is assigned an atmospheric pressure of 0.1MPa.

III. RESULTS AND DISCUSSION

A. Model Validation

First, a comparison between the numerical and experimental results of the CH$_4$ mole fraction and the outlet temperature is conducted using the basic gas composition indicated in Section II *B* and the operating conditions such that the inlet temperature is 290°C, the space velocity is 24,000 hr^{-1}, and the excess air ratio is 4 under the conditions of a 5kW MCFC system. In order to completely combust CH$_4$, supplemental fuels such as CO and H$_2$ are added in ordered intervals as shown in Fig. 2. Here, it can be found that CH$_4$, which is initially supplied at *t*=110s, remains unconverted over the catalyst before any supplemental fuel is supplied. After CO is supplied, however, CH$_4$ starts to react, the temperature increases by 50°C, a small amount. Dramatic variations of the CH$_4$ mole fraction and temperature are observed when H$_2$ is used as an additional fuel. In Fig. 2, it is found that the CH$_4$ mole fraction and temperature increase steeply when 40% H$_2$ is supplied. In addition, when 70% H$_2$ is supplied, almost all of the CH$_4$ is converted into the products, and the temperature reaches almost 580°C. The final temperature increase to 640°C is due mainly to the H$_2$ reaction, which is supplied at *t*=1,700s. Note that the simulation data using the kinetic parameters indicated in Section II *A* agrees well with the experimental data [3].
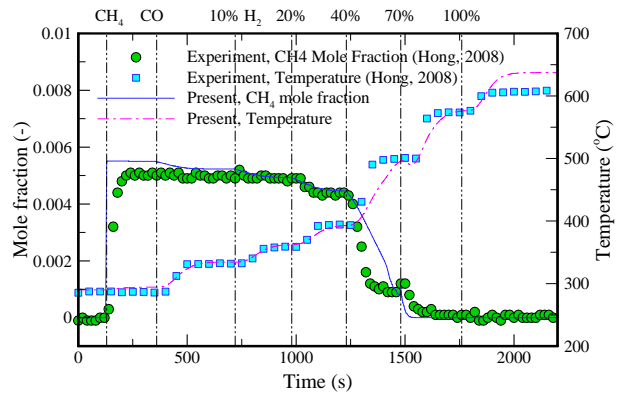

Fig. 2 Comparison of simulation and experiment results of the CH$_4$ mole fraction and outlet temperature for the case of T_{in}=285°C, λ=4 and SV= 24,000hr^{-1}
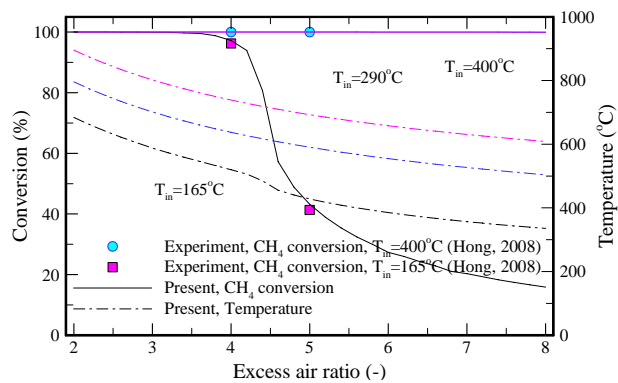

Fig. 3 Effects of the excess air ratio on the CH$_4$ conversion rate and the outlet temperature when SV= 24,000hr^{-1}

B. Effect of the Excess Air Ratio

The excess air ratio is the volumetric ratio of air to fuel present combustion. It is known that a low excess air ratio can lead to deactivation of the catalyst because of high combustion temperatures. In contrast, a high excess air ratio creates unburned fuel, which is supplied to the cathode and may cause unexpected problems in the MCFC stack. Consequently, the decision of the proper excess air ratio is quite important for the stable operation of a catalytic combustor.

Fig. 3 shows the effect of the excess air ratio on the CH$_4$ conversion and the outlet temperature with three different inlet temperatures of 400, 290, and 165°C with the basic gas composition. Here, the space velocity is 24,000hr^{-1} at λ=4, but steadily increases because of the increase in volumetric flow resulting from the air supply addition, even though the reactor volume is the same. When the inlet temperatures are 400°C and 290°C, all of the CH$_4$ is converted into products, regardless of the excess air ratio, because the inlet temperature is high enough for the fuel to react completely. In particular, when the inlet temperature is 400°C, it is very important that the outlet temperature exceeds 800°C, at which point the deactivation of the Pd catalyst may occur if the excess air ratio is less than three. Meanwhile, when the inlet temperature is as low as 165°C and the excess air ratio exceeds five, the CH$_4$ conversion

rate decreases sharply. For this reason, the excess air ratio has to be maintained between three and five for stable operation of the catalytic combustor considered in this study.
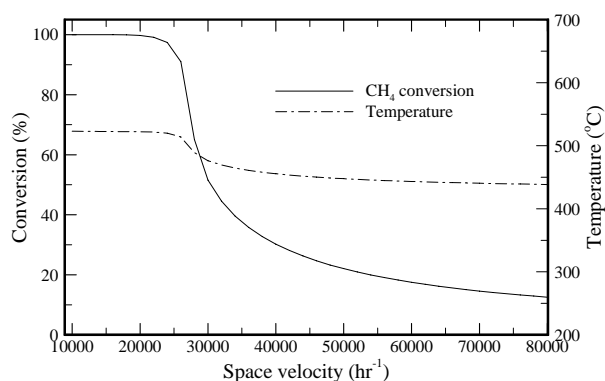

Fig. 4 Effects of the space velocity on the CH_4 conversion rate and the outlet temperature when T_{in}=165°C and λ=4
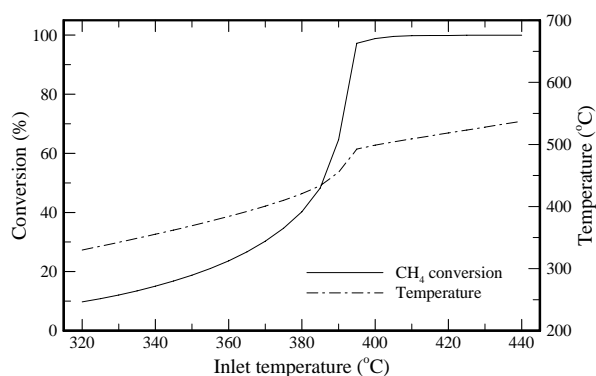

Fig. 5 Effects of inlet temperature on the CH_4 conversion rate and the outlet temperature when λ=4 and SV= 20,000hr^{-1}

C. Effect of Space Velocity

The space velocity (SV), representing the ratio of the volumetric flow rate and the reactor volume, is related to the residence time of fueling gases in a channel. Determining SV is very important because a low SV can make fuel and air mixtures react even under stringent conditions, such as with a low inlet temperature or a high excess air ratio. In this section, therefore, the effect of SV on CH_4 conversion and outlet temperature is investigated for a low inlet temperature of 165°C.

Fig. 4 shows the effects of the SV on CH_4 conversion and the catalyst outlet temperature at an inlet temperature of 165°C with the basic gas composition. As expected, both CH_4 conversion and outlet temperature decrease as the SV increases, because the residence time of the fuel decreases in the catalytic region. In addition, the most rapid decrease of the conversion rate is seen when the SV is between 20,000and 30,000hr^{-1}. For the stable operation of the catalytic combustor, the SV must be below 20,000hr^{-1}, at which level most of the fuel can react, although the inlet temperature is 165°C. Thus, in this study, the proper excess air ratio and space velocity are 4 and 20,000hr^{-1},

respectively. In addition, the design points are used to scale up the catalytic combustor by conducting parametric studies under the expected actual operating conditions of 250kWMCFC power generation systems.

D. Effect of Inlet Gas Temperature

Parametric studies, using various operating conditions such as inlet temperature and the H_2 supply rate under the 250kW MCFC system, are conducted preliminarily to assess the performance of the catalytic combustor under the actual conditions of MCFC power generation systems. In advance, the effect of inlet gas temperature on catalytic combustion characteristics is investigated because the inlet gas temperature is an important parameter for initiating and maintaining the reaction over the catalyst and should be raised to exceed the light-off temperature (LOT), so that the fuel component sufficiently reacts on the catalyst surface [28], [29]. Although some studies about inlet temperature are discussed in Section III *B*, a more extensive investigation of inlet temperature effects is conducted in this section.

In Fig. 5, both the CH_4 conversion rate and outlet temperature variations are illustrated with various inlet temperatures. Only CH_4, except for H_2 and CO, among the fuel components of basic gas composition is supplied when λ=4. As expected, the higher inlet gas temperature causes more fuel conversion and higher outlet temperatures. In particular, it can be seen that a value of T_{50} (i.e., 50% fuel conversion) is found between 380°C and 400°C. In addition, for inlet temperatures above 420°C, the CH_4 conversion rate reaches almost 100%, and the outlet temperature is approximately 550°C. This suggests that an inlet temperature of 380°C is needed for complete combustion of CH_4in this type of BOP for MCFC power generation applications.

IV. CONCLUSION

In this work numerical investigations are performed to examine the catalytic combustion characteristics under various conditions by altering parameters, such as the excess air ratio, space velocity, and inlet temperature. From this parametric study, the following conclusions can be drawn:

(1) The outlet temperature and conversion rate of the fuel component decrease with increases in the excess air ratio. An excess air ratio between 3 and 5 is best for ensuring the stable operation of the catalytic combustor.

(2) When the inlet temperature is 165°C, CH_4 conversion and outlet temperature decrease as the SV increases because the residence time of the fuel decreases in the catalytic region. In addition, the most rapid decrease of the conversion rate is observed when the SV is between 20,000 and 30,000hr^{-1}. For complete combustion of CH_4, the space velocity should be below 20,000hr^{-1}.

(3) The fuel conversion and outlet temperature increase as the inlet temperature increases. When the inlet temperature rises to 400°C, the most rapid increase of the CH_4 conversion rate is achieved.

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