The Effects of Carbon Dioxide in Oxy-fuel Atmosphere on Catalyst Reaction in a Small-Scale Channel

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Abstract

In this study, the effect of carbon dioxide on catalyst reaction in a small-scale channel in oxy-fuel atmosphere is experimentally investigated. In the oxy-combustion, carbon dioxide in the flue gas is usually recirculated to dilute the oxidizer stream in order to reduce the flame temperature. However, the specific heat of carbon dioxide is relatively higher than that of nitrogen, and it causes significant reduction on flame temperature and combustion stability. Furthermore, carbon dioxide in flames does not only act as an inert diluent, but also involves in flame reactions and modifies flame behaviors and combustion characteristics. During the miniaturization, the surface-to-volume ratio of the combustion chamber will be increased, and the mixing and reaction residence time will be decreased. It causes flame quenching, such as thermal quenching and radical quenching.

Segmented catalyst with cavity in a micro-channel is expected to induce gas reaction and surface reaction simultaneously, and enhance fuel conversion. The experimental results of the segmented catalyst with cavities show the improvement of oxy-combustion behaviors in a micro channel by reducing the requirement of excessive oxygen concentration in the oxidizer stream for flame stability. When the flow rate is 10 m/sec and corresponding equivalence ratio of 0.6, oxy-hydrogen combustion in a channel can be stabilized in a condition of 23% oxygen concentration in the oxidizer stream. Besides, the gas analysis shows that carbon monoxide is yielded in oxy-hydrogen combustion, and it speculates that gas reaction and surface reaction somehow induce the inverse reaction of carbon dioxide. However, the producing carbon monoxide can be consumed in downstream segmented catalyst.

Keywords: oxy-fuel, oxy-combustion, micro reactor, hydrogen, catalyst.

1. Introduction

The research and development of meso-scale power devices has been motivated by the increasing need and demand for smaller scale and energy dense power sources. The fossil fuel has inherently enormous energy density compared to the conventional batteries, so that concept and demonstration of novel small-scale fuel-firing power and heating generation system have been proposed [1]. However, the flame in confined and miniaturized space is usually associated with the problems of low flame temperature, narrow stability limits as well as low combustion efficiencies. Catalytic combustion is a well-known technique to enhance the combustion stability in the fuel-lean conditions, and to extend flammability limit of the low-heating-value combustion [2]. Besides, owing to reduce carbon dioxide emission, the post combustion technique, namely oxy-combustion, integrating with carbon capture and storage (CCS) system has been intensively studied. The oxy-combustion is to recuperate the flue gas as diluent gas to replace nitrogen in air, and to obtain high concentration of carbon dioxide and water steam in downstream flue gas [3, 4]. Nevertheless, carbon dioxide and water steam in hydrocarbon fuel as diluent gas would alter the flame behaviors via three effects, dilution effect, thermal effect and chemical effect, respectively. Dilution effect is to reduce the concentration of oxygen in reaction zone and further influence the reaction rate, and thermal effect is caused by the difference in thermal capacity and thermal radiation, and the chemical effect is to increase the radical concentration and further shift the chemical pathway. Kimura et al. [5] discovered that the ignition delay and flame instability would occur in oxy-combustion condition, and proposed that an increase of gas temperature and oxygen concentration in flue gas can mitigate the combustion instability. Besides, the increasing percentage of water steam in flue gas can improve the combustion efficiency of oxy-fuel flame. Haler et al. [6] experimentally and numerically investigated the flame behaviors of methane/air in CO_2-diluent, N_2-diluent, and CO_2-N_2-diluent (71.6% N_2 + 28.4% CO_2). It found that CO_2-diluent has inherently high thermal capacity compared to N_2-diluent, and induces pre-dissociation phenomenon. Besides, Glarborg and Bentzen [7] found that the CO concentration in the flue gas of oxy-fuel combustion is greater than in air combustion.

In this paper, the small-scale reactor with various catalyst deployments is performed in oxy-fuel combustion. In the procedure of miniaturization, the increasing surface-to-volume ratio will lead to increasing the possibility of radical quenching and fame instability. However, the oxy-fuel environment will amplify the above-mentioned challenges. Catalytic surface in a micro channel is expected to overcome the beforehand shortcomings and reduce the requirement of excessive oxygen in oxidizer. Furthermore, the catalyst capability in the environment of oxy-fuel combustion is still not clear. The objective of this paper is to determine the combustion behaviors of various catalyst deployments in oxy-fuel condition, and examine the minimum oxygen concentration requested for stabilizing catalytic combustion in a channel.

2. Experimental Apparatus

Figure 1 shows a replaceable channel burner with five substrates of various catalyst layouts. The overall dimension of the channel is 74mm in length, 42mm in width, and 15mm in depth with a spark igniter and parallel slots, where are allowed to embed a ceramic stick coasted with different catalyst layouts and configuration. There are five types of catalyst disposition considered, straight channel, cavity channel, 14mm single catalyst channel, segmented catalyst, segmented catalyst with cavities, respectively. The total area of catalyst disposition is kept constant for cases both with and without catalyst segmentation. Besides, the case of a multi-segment catalyst with cavity consists of seven 2 mm-long-segments and six cavities (2 mm (l) × 3 mm (w) × 1 mm (d)) in the channel. Hydrogen is used as fuel, while carbon dioxide and oxygen from high pressurized tanks are used to simulate oxy-fuel environmental conditions. The reactor is placed in a digital-control electric heater to maintain the surround temperature of the chamber at 600K. The camera is used to observe the combustion phenomenon in the channel, and thermocouple is embedded in the exit of a reactor to monitor the reaction occurrence. When the exit temperature is around or below 600K with dark red color appeared in the channel, it means that there is only heterogeneous reaction occurrence in the reactor. Similarly, when the exit temperature is larger than 1000K with bright white color anchored on the channel, it means that the hetero- and homo-geneous reaction is occurred in the reactor. Besides, the flue gas can be vacuumed into the collecting bag by the sampler (SKCUniversal-PCXR4). The flue gas will be tested by gas chromatography to determine the gas components.

3. Results and Discussion

Figure 2 shows the reaction phenomena of the channel burner with different substrate configurations in the condition of 0.6 equivalence ratio ($H_2/O_2/N_2$) and 10 m/s flow velocity. The result shows that straight channel has no reaction, and cavity channel has gas reaction. Regarding to catalyst channel, single catalyst channel has only surface reaction, but segmented catalyst with and without cavities can sustain gas reaction and surface reaction simultaneously. In $H_2/O_2/CO_2$ environment the excessive oxygen concentration (28%) in oxidizer stream is necessary to sustain gas reaction in the straight channel, as shown in Fig.3a. With the present of cavities in the channel the oxygen concentration can be reduced to 25%. In the cases with catalyst surface the oxygen concentration can further reduce to 23% in the channel with segmented catalyst and cavities. It is interested to note that the present of segmented catalyst and cavity can significantly reduce the required oxygen concentration in oxidizer stream and enhance catalytic combustion occurring in a small-scale channel.

However, fixed in the same condition of 23% O_2 concentration, 0.6 equivalence ratio and 10m/s flow rate, Fig. 4 shows the corresponding reaction phenomena in three different layouts. The result indicates that there is only surface reaction occurring in the cases of single catalyst and segmented catalyst channel. In the case of segmented catalyst and cavities the gas reaction accompanying with surface reaction is sustained. Table 1 shows the gas components of flue gas in three cases. It appears that the hydrogen conversion in the case of segmented catalyst and cavities approaches to 100% in correspondence to 47.4% for single catalyst case and 50.7% for segmented catalyst case. Nevertheless, carbon monoxide concentration is apparently increasing in the case of segmented catalyst and cavities case. Carbon monoxide is arguably derived from carbon dioxide of oxidizer stream. Apparently, catalytic combustion would booster the reaction of CO_2 decomposition via H radicals ($CO_2+H\rightarrow CO+OH$). There is a few amount of CO concentration in the other cases, and it demonstrates that the surface reaction is probably engaged in inverse reaction of CO_2 production on catalyst site. But the speculation has been further validated.

4. Conclusions

In this work, we discuss the reaction phenomena of various channels with different catalyst layouts and configurations in air-hydrogen and oxy-hydrogen conditions. Results demonstrate that the excessive oxygen concentration in oxidizer is necessitated to stably sustain combustion in a channel. However, deploying segmented catalysts and cavities in a channel can reduce required oxygen concentration. Besides, a large number of carbon monoxide will be yielded as the present of catalytic combustion in oxy-hydrogen condition.

5. Acknowledgements

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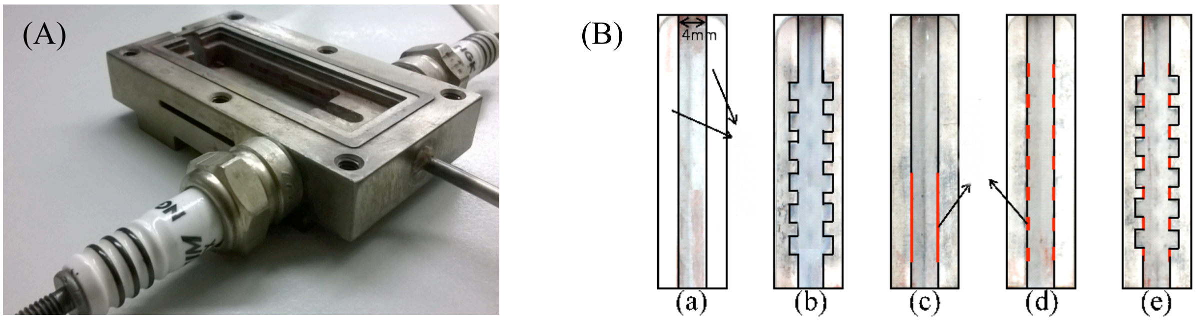

Figure 1. (A) Replace catalytic position burner. (B) Five different catalytic configurations: (a) Straight channel (b) Cavity channel (c) Single catalytic channel (d) Segmented catalytic channel (e) Segmented with cavity catalytic channel.

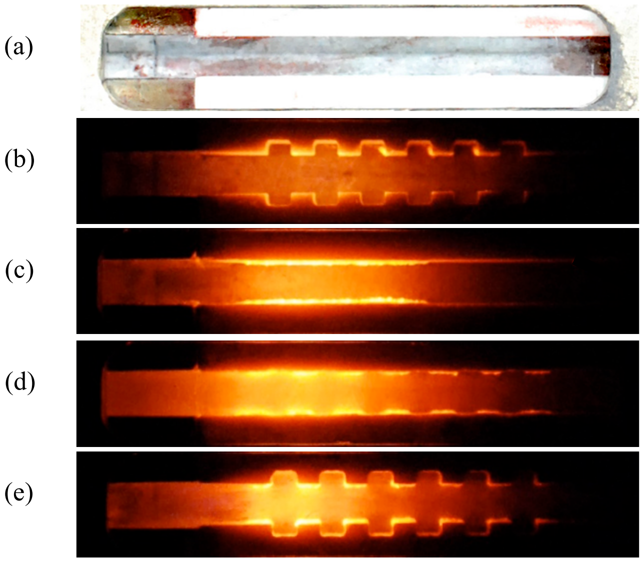

Figure 2. Images of burners in $H_2/O_2/N_2$ reaction: (a) straight channel: no reaction (b) cavity channel: gas reaction (c) single catalytic channel: gas and surface reactions (d) segmented catalytic channel: gas and surface reaction (e) segmented catalyst with cavities channel: gas and surface reaction, with the flow rate of 10 m/sec, and equivalence ratio of 0.6.

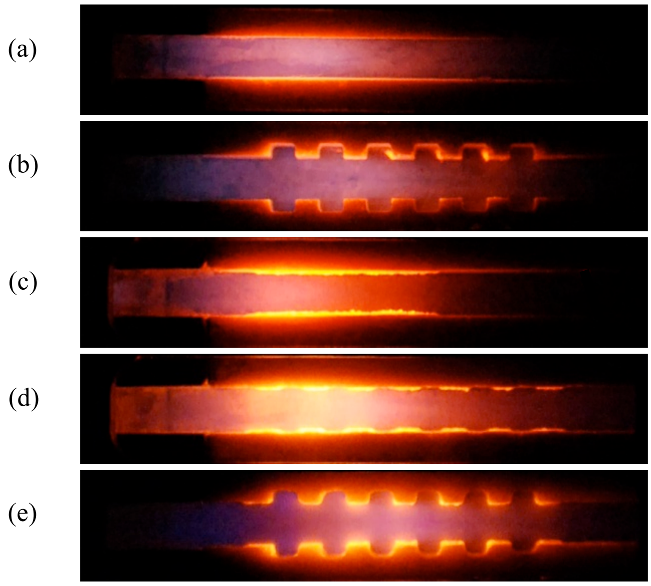

Figure 3. Images of burners in $H_2/O_2/CO_2$ reaction: (a) The least oxygen concentration in straight channel : 28% (b) The least oxygen concentration in cavity channel :gas reaction : 25% (c) The least oxygen concentration in single catalytic channel : 26% (d) The least oxygen concentration in segmented catalytic channel : 25% (e) The least oxygen concentration in segmented with cavity catalytic channel : 23%, with the flow rate of 10 m/sec, and equivalence ratio of 0.6.

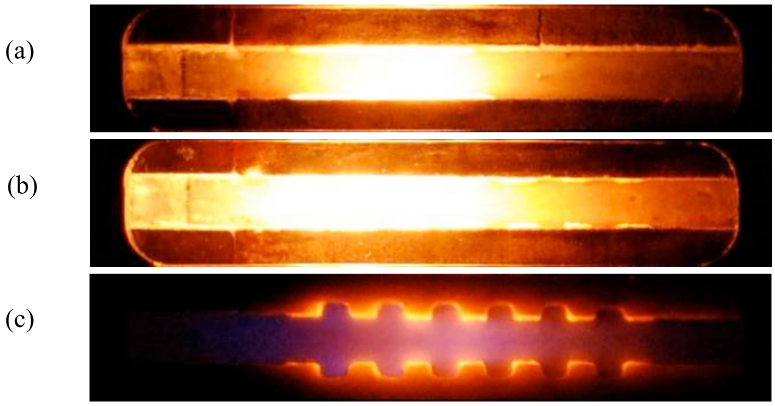

Figure 4. Images of burners in $H_2/O_2/CO_2$ reaction: (a) single catalytic channel: only surface reactions, (b) segmented catalytic channel: gas and surface reaction (c) segmented catalyst with cavities channel: gas and surface reaction, with the flow rate of 10 m/sec, equivalence ratio of 0.6, and fixed oxygen concentration of 23%.

Table 1. The gas components of flue gas in three catalyst layouts measured by GC.

Catalyst layouts	*CO concentration*	*H_2 concentration*	*H_2 conversion rate (%)*
single catalytic channel	0.02%	13.23%	47.4
segmented catalytic channel	0.02%	12.41%	50.7
segmented catalyst with cavities channel	0.54%	0.02%	99.94