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Effects of carbon dioxide in oxy-fuel atmosphere on catalytic combustion in a small-scale channel

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ABSTRACT

The effect of CO_2 dilution on oxy-fuel reaction over catalytic surface is experimentally investigated in a small-scale channel in terms of heat transfer, chemical reactivity as well as interplay between hetero- and homogeneous reaction. There are two kinds of small-scale reactors, tubular reactor and channel reactor, respectively, used in this study. In the tubular reactor, the interaction between heterogeneous and homogeneous reaction on tubular platinum reactor are addressed based on the resulting surface temperatures of the tube and fuel conversion ratios. CO_2 would absorb chemically-induced heat release of hydrogen, but in the meantime heat up the flowing mixture via radiative and convective heat transfer. In the channel reactor, the results demonstrate that the segmented catalyst with cavities has minimal oxygen concentration to hold catalytically stabilized thermal flame in a channel, and performs approximately complete fuel conversion. Beside, CO content in flue gas is increased in the case of segmented catalyst with cavities. It speculates that CO_2 decomposes CO through the reaction of $CO_2+H = CO + OH$ in gas phase in the vicinity of the catalyst surface, and the requested H radical and thermal energy are provided by the neighboring heterogeneous reaction.

1. Introduction

As the advent of industrial evolution, strong and correlated evidence elaborates that both the average global temperature and the atmospheric carbon oxide concentration have significantly increased. Technological solution to this problem is believed to rely heavily on a substantial improvement in energy conversion and utilization efficiencies, CCS (carbon capture and sequestration), and renewable sources such as biomass, hydro, solar, wind and geothermal energy. Accordingly, oxy-combustion integrating with CCS is considered as one of appropriate and practical approaches to timely curb the increasing CO_2 emission [1]. Oxy-fuel combustion is the technology for which instead of using air as oxidizer pure oxygen or a mixture of O_2 and recycled flue gas is used to generate high CO_2 concentration product gas to facilitate efficient carbon capture [2]. In general, O_2 is provided from air separation unit and CO_2 is recirculated from flue gas with water removal. The oxidizer in oxy-fuel combustion usually consists of O_2 and CO_2. However, the apparent difference in the thermal and chemical properties of N_2 and CO_2 leads to significantly different combustion behavior for oxy-fuel from air-fuel combustions [3]. The thermal and physical properties of N_2 and CO_2 relevant to oxy-fuel combustion are summarized in Table 1. For heat transfer, radiative and convective heat transfer are significantly different between oxy-fuel and air-fuel combustion. Unlike N_2, a symmetric diatomic gas, the oxy-fuel flue gases, mainly consisting of triatomic gases of CO_2 and H_2O, have large emissivity and absorption coefficients due to their non-transparency to radiation. The absorption and radiation in oxy-combustion are stronger than those in conventional air-fuel combustion with identical gas temperatures. Andersson et al. [4,5] investigated the radiation intensity of propane-fired oxy-fuel flames, and pointed out that the gas radiation in oxy-fuel combustion is apparently higher. For convective heat transfer, Smart et al. [6] demonstrated that the contribution of convective heat transfer in oxy-combustion increased with increasing flue-gas recirculating ratios. For thermodynamic properties, although the specific heats of CO_2 and N_2 are similar on mass basis, the CO_2 heat

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Table 1
Comparison of selected thermal and physical properties of CO_2 and N_2 at 1 atm and 1000 K.

Thermal and physical property	CO_2	N_2
Density (kg/m^3)	0.5362	0.3413
Specific heat capacity (kJ/kgK)	1.2343	1.1674
Volumetric heat capacity (kJ/m^3K)	0.662	0.398
Kinematic viscosity (m^2/s)	7.69e-5	1.2e-4
Thermal conductivity (W/mK)	7.057e-2	6.599e-2
Thermal diffusivity (m^2/s)	1.1e-4	1.7e-4
Mass diffusivity (m^2/s)[a]	9.8e-5	1.3e-4

[a] Mass diffusivity refers to the binary diffusion of O_2 in CO_2 and N_2.

capacity on mole basis is 1.66 times higher than that of N_2 because of its larger molecular weight. Therefore, there is a significant reduction in the flame temperature for oxy-fuel combustion. In order to match the gas temperatures and heat transfer performances with that of air-fuel combustion, a wide range of O_2 contents in the oxidizer (23–35%) are needed for oxy-fuel combustion, especially for plant retrofits. Croiset et al. [7] demonstrated that in order to match the gas temperatures and heat fluxes of air-combustion conditions, O_2 mole fraction in oxy-fired conditions for bituminous and sub-bituminous coals should be raised to between 28% and 35%.

On the other hand, unlike N_2 in air-combustion, CO_2 plays an important role in oxy-fuel combustion due that CO_2 can actively participate in the combustion chemical reactions. High CO_2 concentration may affect the combustion characteristics through direct chemical reactions of CO_2, for instance, laminar flame speed, a fundamental parameter describing many features related to reactivity, diffusivity and exothermicity of the combustible mixtures. Oh and Noh [8] examined the flame speed of oxy-fuel mixtures at a fixed oxygen concentration for various equivalence ratios. The results are much lower than the flame speeds of air-fuel mixture at the same condition. Hu et al. [9] numerically investigated the effects of CO_2 dilution on flame structure and reaction pathway in oxy-fuel combustion. Several studies have reported that CO_2 is not an inert in oxy-fuel combustion, but actively participates in chemical reactions primarily through the reaction $CO_2 + H = CO + OH$ [10,11]. According to aforementioned chemical reaction, the CO concentration in oxy-fuel combustion is generally found greater than that in air-fuel combustion [12,13].

The replacement of N_2 with CO_2, when switching to oxy-fuel combustion, would also narrow the flammability limits and induce combustion instability. In order to overcome the shortcomings associated with the operation of oxy-fuel combustion in retrofitted or tailored furnace, many approaches and strategies on operation processes are addressed recently, such as oxygen enrichment in the oxidizer [7], optimized flue gas recycle ratios [14], or gas stream preheating [15]. However, the capital and operating costs associated with pure oxygen supply is considerably high, so that the reduction of oxygen concentration in oxy-fuel combustion is regarded as a priori challenge to implement and disseminate the application of oxy-fuel technology in industry sectors.

Catalyst is generally utilized to resist the thermal quench, enhance the combustion stability, extend flammability of low-calorie fuel [16,17], or cope with the toxic gas emissions [18]. In particular, catalytically stabilized thermal combustion is suited for low-calorific value fuels due to the enhanced combustion stability at moderate reaction temperatures [19]. The concept of catalytically stabilized thermal combustion is to achieve fractional fuel conversion in a heterogeneous reactor, and in turn the remaining fuel is combusted in an ensuing homogeneous burnout zone. Application of combined hetero-/homogeneous combustion has been demonstrated to suppress most of the intrinsic flame instabilities appearing in air-fired combustion [20]. Therefore, utilization of catalyst combustion in oxy-fuel combustion provides an alternative solution for improving low flammability and combustion instability in oxy-fuel combustion.

In this study, employing catalyst in the oxy-fuel environment is attempting to induce catalytically stabilized thermal combustion, namely the coexistence of heterogeneous and homogeneous reaction, with low oxygen concentration requirement in the oxidizer, and in the meantime to improve the narrow flammability and flame instability of oxy-combustion. However, there are some works discussing the effect of carbon dioxide addition or dilution in hydrogen or methane mixtures on catalyst reactivities and catalytic combustion [21,22], but limited papers for oxy-fuel environment [23]. Benedetto et al. discussed the effect of CO_2 addition (up to 30% in mixture content) on catalytic CH_4 combustion over a pervoskyte-based monolith at high pressure [22]. It indicated that the presence of CO_2 retards ignition and shifts the ignition pressure. In addition, once ignition has been attained, the catalytic surface temperature increases upon an increasing CO_2 content. Reinke et al. investigated the effect of flue gas dilution on the heterogeneous and homogeneous reaction of fuel-lean $CH_4/O_2/N_2$ mixture in experimental and numerical approaches [23]. The results illustrated that the addition of H_2O inhibits the catalytic methane conversion due to increasing OH radical occupying catalyst surface site, but the addition of CO_2 has no direct chemical impact on the catalytic pathway. However, the dilution of high CO_2 content in the mixture usually accompanied with a large amount of CO production. It is difficult to identify CO formation coming from the product gas of methane incomplete combustion or dissociation of CO_2 diluent gas in surface reaction or gas-phase reaction. In general, there are two kinds of catalysts extensively used in industry and transportation sectors, supported catalyst and metal catalyst (platinum and palladium), respectively. Supported catalyst is to coat or spray catalytic materials on ceramic substrates, such as honeycomb, mesh or bead. Meantime, honeycomb and tube are common and extensive configurations in catalyst applications. In order to simplify the experiment in this study, a tubular platinum tube and a ceramic catalytically-coated channel with various catalyst layouts are engaged to simulate a single catalytic channel of honeycomb in oxy-fuel environment and delineate the chemical reactivities of oxy-fuel over catalyst surface at conditions of broadly varying oxygen contents and flow throughputs.

2. Experimental apparatus

In this study, two different reaction sections are used to investigate the oxy-combustion phenomena in a catalytic channel. The first reaction section is a simple TP (tubular platinum) reactor, as shown in Fig. 1(a). The TP reactor consists of a 120 mm-long quartz tube (ID: 4 mm, OD: 6 mm) and 20 mm-long platinum tube (ID: 3 mm, OD: 4 mm). The platinum tube is positioned inside the quartz tube, and the distance between the inlets of the platinum tube and quartz tube is 40 mm. The second reaction section is a RCC (replaceable catalyst-channel) reactor with the dimension of 74 mm in length, 42 mm in width and 15 mm in height, as shown in Fig. 1(b). Two spark plugs are used for ignition in the reactor, and two slots are engaged to place in parallel ceramic sticks deployed with different catalyst layouts and configuration. The dimension of ceramic stick is 40 mm in length, 4 mm in width and 4 mm in height. The two ceramic sticks in parallel form a channel with the dimension of 60 mm in length, 4 mm in width and 4 mm in depth. The location of spark igniter is 5 mm from the inlet of the channel. Based on our previous studies [24–26], it indicates that varying