Experimental Study on Fuel-Rich Partial Oxidation of Methane/Carbon Dioxide in Porous Media: Postprint

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Abstract

This study employs a porous media burner to experimentally investigate the fuel-rich partial oxidation of methane/carbon dioxide mixtures, focusing on the influence of CO2 addition in the fuel on non-catalytic partial oxidation reforming for syngas production. At an air flow rate of 5 L/min, the inlet CO2/CH4 ratio and equivalence ratio were adjusted to determine the stable operating regime of fuel-rich combustion in the porous media burner, and the temperature distribution and outlet species concentrations were measured under stable conditions. At an equivalence ratio of 1.3, the CO2/CH4 ratio could reach 1.5 under stable operating conditions. When the equivalence ratio was 1.6 and the CO2/CH4 ratio was 0.5, the fuel reforming efficiency could attain 47.7%. The addition of CO2 to the fuel can promote the reverse water-gas shift reaction to a certain extent, recover partial sensible heat, enhance fuel reforming efficiency, and simultaneously reduce net CO2 emissions.

Full Text

Preamble

Experimental Study on Partial Oxidation Reforming of CH4/CO2 with Rich Combustion in a Porous Media Burner

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Abstract: Rich combustion in a porous media burner was used for the partial oxidation reforming of CH4/CO2, which is a potential non-catalysis way for syngas production from biomass-derived gas. The effect of CO2 injected in methane was studied in the experiment. As the inlet air flow rate was 5 L/min, for various inlet CO2/CH4 and equivalence ratios, the flammability of rich combustion in the porous media was determined. Within the flame stability limit, the temperature distributions and species profiles were measured. When the equivalence ratio was 1.3, the ratio of CO2/CH4 reached 1.5. As the equivalence ratio was 1.6 and the ratio of CO2/CH4 was 0.5, the reforming efficiency reached 47.7%. With the injection of CO2 in the fuel, the inverse process of water gas shift reaction was promoted that increased the fuel reforming efficiency, meanwhile, the net emission of CO2 was reduced.

Key words: Porous media; Rich combustion; Partial oxidation; Carbon dioxide

Introduction

With socio-economic development, energy demand continues to grow, drawing increasing attention to the consumption of traditional fossil fuels and their associated environmental impacts. The development of renewable energy is crucial for alleviating the current severe energy situation and addressing environmental problems arising from energy utilization. As an abundant renewable energy source, the rational and efficient use of biomass energy has become a practical issue that must be addressed alongside the continued high-efficiency utilization of conventional fossil fuels.

Biogas and landfill gas represent renewable biomass energy resources that are abundant, inexpensive, and readily available. Their main components are 50%~80% CH4 and 20%~50% CO2 [1], which differ significantly from conventional natural gas in composition. Reforming biogas or landfill gas to produce syngas for further use in chemical synthesis, internal combustion engines, or fuel cells can simultaneously utilize both methane and carbon dioxide, two major greenhouse gases [2,3]. Current research on dry reforming or autothermal reforming of methane and carbon dioxide has been extensive, particularly focusing on various catalysts and performance enhancement. However, due to the high carbon content and strongly endothermic nature of methane-CO2 reforming reactions, coking occurs readily, severely affecting catalyst activity [4,5]. To address this issue, some researchers have proposed adding a certain amount of O2 during reforming to reduce hotspot formation and coking in the catalytic bed [6], thereby achieving autothermal reforming. However, the strong oxidation reactions upstream can easily cause sintering of catalysts in the reforming zone [7]. This study considers utilizing the advantages of porous media combustion to investigate non-catalytic rich partial oxidation reforming of methane-carbon dioxide mixtures with air, avoiding problems associated with catalyst use such as deactivation, coking, hotspots, and sintering. Simultaneously, the substantial heat generated from partial oxidation reactions can sustain the strongly endothermic methane-CO2 reforming reaction without requiring additional external heat sources.

The presence of CO2 in biogas or landfill gas reduces the fuel’ s flammability limits. When the CO2 content in the fuel gas exceeds 30%, the gas cannot burn normally under free-space conditions [8]. Porous media burners leverage the excellent thermal conduction and radiation properties of porous media materials to transfer heat from the downstream combustion zone upstream, preheating the incoming premixed fuel/air and thereby extending the fuel' s flammability limits. Porous media combustion can be broadly classified into two categories based on flame movement characteristics: filtration combustion and stable combustion [9]. Due to the flame propagation through the reactor during filtration combustion, the reactor undergoes continuous thermal cycling, imposing high material requirements and relatively complex operational processes. Consequently, many researchers have focused on stable combustion in porous media. Pedersen-Mjaanes et al. from Cambridge University used a two-stage porous media burner with methane fuel, achieving a methane reforming efficiency of 45% at an equivalence ratio of 1.85 [10]. Wang et al. used an alumina ball-packed porous media burner for stable combustion to produce syngas, directly coupled with solid oxide fuel cells, achieving a maximum reforming efficiency of 49% at an equivalence ratio of 1.7 using methane fuel [11]. Current research on syngas production via stable rich combustion in porous media has primarily used methane and similar fuels, while the effects of large amounts of CO2 in biomass-derived gases remain to be investigated.

Due to its non-combustible, non-oxidizing nature and relatively high specific heat capacity, CO2 significantly differs from pure methane in terms of combustion temperature and outlet species composition during rich reforming. This study designed and constructed a two-stage porous media burner experimental system based on alumina balls of different diameters to investigate rich partial oxidation reforming of methane/carbon dioxide mixtures. The stable rich combustion limits were determined, and the effects of CO2 addition in the fuel on temperature distribution, fuel reforming efficiency, and carbon emission reduction under various equivalence ratios were examined.

1 Porous Media Burner Experimental System

The two-stage porous media burner experimental system used in this study is shown in [Figure 1: see original paper] and consists of three main parts: the gas supply system, reactor system, and measurement system. The gas supply system provides three separate gas streams, with methane, air, and CO2 flow rates controlled by mass flow meters provided by Beijing Sevenstar Electronics Co., Ltd. The flow ranges are 5 SLM for methane and CO2, and 30 SLM for air. The reactor system comprises a premixing chamber, flashback prevention chamber, and combustion chamber, with all chamber shells fabricated from 430 stainless steel. The premixing chamber has six uniformly distributed inlet ports on its circumference. Methane, air, and CO2 enter from different directions, with each gas stream split into two paths via a three-way valve before entering opposing inlet ports to ensure thorough mixing. A flashback prevention chamber filled with quartz sand and an upper stainless steel perforated plate for heat dissipation is installed between the premixing chamber and combustion chamber to prevent flashback and ensure uniform gas flow. The combustion chamber shell has an inner diameter of 54 mm, wall thickness of 3 mm, and height of 200 mm. The interior contains integrated aluminum silicate insulation with an inner diameter of 30 mm, outer diameter of 54 mm, and height of 200 mm. The stainless steel chamber is wrapped with 8 cm thick insulation, with the exterior near room temperature during experiments. The combustion chamber uses freely packed alumina balls as the porous media matrix, with a total porous media height of 80 mm. The upstream section contains alumina balls 2-3 mm in diameter with a packing height of 20 mm, while the downstream section contains 7.5 mm diameter alumina balls with a packing height of 60 mm.

The study focuses on monitoring the temperature distribution in the porous media reaction zone and the outlet gas composition. To monitor the axial temperature distribution and changes in the combustion chamber's porous media region and detect the flame front position, seven S-type thermocouples (T0-T6) are uniformly arranged axially at 10 mm intervals from upstream to downstream. After flame stabilization, the burner outlet gas composition is measured by gas chromatography.

Under conditions of methane/air equivalence ratio of 0.8 and total flow velocity of 0.15 m/s (total flow rate of 6.36 L/min), an electric spark igniter is used at the outlet. The flame first preheats the downstream porous media, then gradually propagates upstream into the porous media interior. When the T0 temperature reaches 600 °C, the burner is considered to have completed preheating and is adjusted to the desired experimental condition. When the flame stabilizes, the corresponding axial temperature distribution is recorded, and the outlet gas composition is measured. Due to measurement errors in thermocouples, primarily considering radiation effects at high temperatures, the experimentally measured temperature data were corrected for radiation [12]. The corrected experimental data have relatively small uncertainty, within ±2%.

2.1 Flame Stability Limits

Ignition occurs under conditions of methane/air total flow velocity of 0.15 m/s (total flow rate of 6.36 L/min) and equivalence ratio =0.8. When the T0 temperature reaches 600 °C, the burner is fully preheated and adjusted to the required condition. Flame stability is considered achieved when temperatures measured by all thermocouples remain constant (temperature variation at the same position is less than 10 K within 20 min). With an inlet air flow rate of 5 L/min, adjusting the equivalence ratio and CO2/CH4 ratio yields the stable operating points shown in [Figure 2: see original paper].

Within the equivalence ratio range of 1.3-1.8, CO2/CH4 ratios of 0, 0.5, 1.0, and 1.5 were tested. The figure shows that at a given equivalence ratio, when CO2/CH4 reaches a certain level, the flame becomes unstable and tends to propagate downstream. At lower equivalence ratios, more heat is generated from combustion, allowing a larger proportion of CO2 to be added to the fuel. At an equivalence ratio of 1.3, stable combustion can be achieved at CO2/CH4=1.5, enabling stable rich reforming of biomass gas containing 60% CO2 and 40% CH4 within porous media. As the equivalence ratio increases, the maximum CO2/CH4 ratio in the fuel decreases, and the flame stability region narrows. With increasing CO2 content in the fuel, the rich flammability limit equivalence ratio decreases, and the flame stability region shrinks. At an equivalence ratio of 1.7, adding a small amount of CO2 causes the flame to propagate noticeably downstream. At an equivalence ratio of 1.8, the methane/air flame begins to propagate downstream and becomes unstable.

2.2 Temperature Distribution Patterns

Using methane/air partial oxidation reforming without CO2 addition in the fuel and with an inlet air flow rate of 5 L/min, the temperature distributions in the porous media combustion region after flame stabilization under different equivalence ratios are shown in [Figure 3: see original paper]. When the highest temperature measured by thermocouples occurs at the axial position of 10 mm, the flame stabilizes at a certain cross-section in the upstream region, with the flame front located between 0-10 mm. In this case, changes in downstream temperature can be used to judge the movement of the flame stabilization position. When the highest temperature occurs at the axial position of 20 mm, the flame front can be considered stabilized at the upstream-downstream interface. According to [Figure 3: see original paper], as the equivalence ratio increases, the overall downstream temperature rises, indicating that the flame stabilization position moves further downstream, suggesting that the upstream preheating required to maintain flame stability increases.

With an inlet air flow rate of 5 L/min, adjusting the CO2/CH4 ratio under different equivalence ratio conditions yields the temperature distributions in the porous media burner when the flame stabilizes within the stable region, as shown in [Figure 4: see original paper]. Under the same equivalence ratio condition, as the CO2/CH4 ratio increases, the required upstream preheating section increases due to CO2 addition, and the flame stabilization position shifts further downstream. At an equivalence ratio of 1.3 ([Figure 4a: see original paper]), stable combustion can be maintained within the CO2/CH4 ratio range of 0-1.5. When CO2/CH4=1.5, the flame front stabilizes at the upstream-downstream interface; when CO2/CH4=0-1.0, the flame front stabilizes at a certain cross-section in the upstream porous media, and based on the overall increase in downstream temperature with this ratio, the cross-section position can be inferred to move downstream. At equivalence ratios of 1.4 and 1.5 ([Figure 4b: see original paper] and [Figure 4c: see original paper]), stable combustion can be achieved within the CO2/CH4 range of 0-1.0, while flames propagate downstream and cannot maintain stable combustion when CO2/CH4>1. At =1.4 or 1.5 with CO2/CH4=1.0, the flame front can stabilize at the porous media upstream-downstream interface. At an equivalence ratio of 1.6 ([Figure 4d: see original paper]), the flame front can stabilize at the upstream-downstream interface when CO2/CH4=0.5, while it stabilizes at an upstream cross-section when CO2/CH4=0. At an equivalence ratio of 1.7 with CO2/CH4=0 ([Figure 4d: see original paper]), the flame stabilizes at the upstream-downstream interface, and adding a small amount of CO2 causes the flame front to move downstream, preventing stable stabilization at a cross-section.

2.3.1 Outlet Species Measurement Results

The main reactions occurring during rich combustion are fuel partial oxidation and reforming reactions. The overall reaction can be expressed as:

$$\mathrm{CH_4}+\phi(\mathrm{O_2}+3.76\mathrm{N_2})+x\mathrm{CO_2} \rightarrow a\mathrm{CO}+b\mathrm{CO_2}+c\mathrm{H_2O}+d\mathrm{H_2}+3.76\phi\mathrm{N_2}+(1+x-a-b)\mathrm{C}$$

where is the equivalence ratio and x is the CO2/CH4 ratio.

With an inlet air flow rate of 5 L/min, adjusting methane and CO2 flow rates to vary the equivalence ratio and CO2/CH4, the measured outlet species contents of H2, CO, and CO2 under different stable flame conditions are shown in [Figure 5: see original paper]. The results show that at a fixed CO2 content in the fuel (i.e., constant CO2/CH4 ratio), as the equivalence ratio increases, H2 content increases ([Figure 5a: see original paper]), CO content increases ([Figure 5b: see original paper]), and CO2 content decreases ([Figure 5c: see original paper]), which can be derived from stoichiometric calculations of the reaction equations. Therefore, expanding the rich combustion stability region and increasing the stable rich equivalence ratio can improve fuel reforming efficiency. Under the same equivalence ratio condition, increasing the CO2/CH4 ratio decreases H2 content in the outlet species ([Figure 5a: see original paper]), increases CO content ([Figure 5b: see original paper]), and increases CO2 content ([Figure 5c: see original paper]). The CH4 content in the outlet species under rich conditions is very low, below 0.6% in all tested conditions, indicating near-complete methane conversion. Experimental results also show that increasing the CO2/CH4 ratio at the same equivalence ratio can reduce methane content in the outlet species and improve methane conversion. At an equivalence ratio of 1.3 and CO2/CH4 ratio of 1.5, methane content in the outlet gas can be reduced to 0.07%.

2.3.2 Fuel Reforming Efficiency

With an inlet air flow rate of 5 L/min, the fuel reforming efficiency under different equivalence ratio conditions calculated from the outlet species measurement results is shown as a function of CO2/CH4 ratio in [Figure 6: see original paper]. The fuel partial oxidation reforming efficiency is defined as:

$$\varepsilon = \frac{\text{Heating value of H}_2\text{ and CO in outlet gas}}{\text{Heating value of inlet fuel}}$$

At a given equivalence ratio, CO2 addition in the fuel does not reduce fuel reforming efficiency but instead improves it to some extent. At an equivalence ratio of 1.3, the fuel reforming efficiency increases from 28.3% to 34.9% when the CO2/CH4 ratio increases from 0 to 1.5. At an equivalence ratio of 1.4, the efficiency increases from 35.4% to 38.5% when CO2/CH4 increases from 0 to 1.0. At an equivalence ratio of 1.5, the efficiency increases from 39.1% to 45.3% when CO2/CH4 increases from 0 to 1.0. At an equivalence ratio of 1.6, the efficiency increases from 42.8% to 47.7% when CO2/CH4 increases from 0 to 0.5, which is essentially equivalent to the methane reforming efficiency of 47.7% for pure methane/air partial oxidation at an equivalence ratio of 1.7. Under the same equivalence ratio condition, fuel reforming efficiency increases with increasing CO2/CH4 ratio in the fuel, primarily due to the promotional effect of CO2 addition on the reverse water-gas shift reaction, as detailed in Section 2.3.3.

2.3.3 Sensible Heat Recovery by Reverse Water-Gas Shift Reaction

During non-catalytic rich partial oxidation reforming of methane/CO2/air, the energy flow from the chemical energy of inlet methane can be divided into two main parts (as shown in [Figure 7: see original paper]): one part is converted into the chemical energy of CO and H2 stored in the produced syngas, which is usable energy for subsequent processes; the other part is converted into sensible heat, primarily used to maintain stable operation of the entire reaction process, with a significant amount of sensible heat lost in the outlet exhaust gas. Improving fuel reforming efficiency in the partial oxidation process, i.e., increasing the heating value of the produced syngas and reducing sensible heat loss, is a key objective.

The water-gas shift reaction is an important intermediate reaction in the partial oxidation reforming process, with the chemical reaction equation:

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO_2}, \quad \Delta H = -41.1\ \mathrm{kJ/mol}$$

Since this is an exothermic reaction, its reverse process can absorb part of the sensible heat and store it as chemical energy in the syngas, thereby improving fuel reforming efficiency. Under the same equivalence ratio condition, increasing the CO2/CH4 ratio in the fuel decreases H2 mole fraction in the outlet species ([Figure 5a: see original paper]) and increases CO mole fraction ([Figure 5b: see original paper]), indicating that CO2 addition promotes the reverse water-gas shift reaction during reforming, which in turn increases fuel reforming efficiency ([Figure 6: see original paper]). Therefore, experimental results demonstrate that adding CO2 to methane partial oxidation, i.e., using biogas or landfill gas instead of natural gas for rich partial oxidation reforming, can promote the reverse water-gas shift reaction and potentially recover part of the sensible heat, thereby improving fuel reforming efficiency.

2.4 Carbon Emission Reduction Analysis

During methane/CO2/air partial oxidation, CO2 participates in the reaction as a raw material gas, while a certain amount of CO2 is also generated during the partial oxidation process. Although CO2 content in the outlet species increases with increasing CO2/CH4 ratio in the fuel at the same equivalence ratio ([Figure 5c: see original paper]), the direct impact on net CO2 emissions cannot be conclusively determined.

This study calculated the CO2 mass fractions at the inlet and outlet of the porous media burner separately, using the difference between outlet and inlet CO2 mass fractions as the net CO2 emission for comparison and analysis. The calculation results (shown in) indicate that under the same inlet air flow rate and equivalence ratio conditions, both outlet and inlet CO2 mass fractions increase with increasing CO2/CH4 ratio in the fuel, but net CO2 emission decreases significantly. With an inlet air flow rate of 5 L/min and equivalence ratio of 1.3, when the CO2/CH4 ratio in the fuel increases from 0 to 1.5, net CO2 emission decreases from 10.8% to 3.8%. At an equivalence ratio of 1.5 and CO2/CH4 ratio of 1.0, net CO2 emission is only 1.9%. Adding CO2 to methane partial oxidation, or using biomass gas for rich partial oxidation reforming, can reduce net CO2 emissions to some extent, demonstrating positive effects for carbon emission reduction.

3 Conclusions

This study utilized rich partial oxidation in a porous media burner to investigate the non-catalytic rich reforming characteristics of methane-CO2 mixtures, achieving non-catalytic rich reforming of biomass-like gas to produce syngas while avoiding catalyst-related problems such as deactivation, coking, hotspots, and sintering that occur in methane-CO2 reforming.

With an inlet air flow rate of 5 L/min and equivalence ratio of 1.3, the CO2/CH4 ratio can reach 1.5 under stable operating conditions, enabling partial oxidation reforming of fuel containing 60% CO2. At an equivalence ratio of 1.6 and CO2/CH4 ratio of 0.5, fuel reforming efficiency can reach 47.7%, which is comparable to the methane reforming efficiency of 47.7% for pure methane/air partial oxidation at an equivalence ratio of 1.7.

At constant inlet air flow rate, under the same equivalence ratio condition, increasing CO2/CH4 ratio decreases H2 content and increases CO content in the outlet gas. This can promote the reverse water-gas shift reaction to some extent, recovering part of the sensible heat into the chemical energy of syngas, thereby improving fuel reforming efficiency. Meanwhile, CO2 addition in the fuel can reduce net CO2 emissions from the reaction process, demonstrating positive significance for carbon emission reduction.

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