The Role of CO₂ on Oxy-Colorless Distributed Combustion

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5 Abstract

Oxy-fuel combustion is one of the routes to have carbon dioxide as the main component of the combustion products stream, enabling carbon capture and sequestration. However, oxy-fuel combustion presents challenges in terms of higher temperatures and flame speed, dictating the need for dilution using entrainment of non-reactive diluents. This need for
10 dilution presents opportunities for developing oxy-fuel combustion using distributed combustion technique. Distributed combustion has been investigated in different configurations and geometries, demonstrating near zero emissions, uniform thermal field and much reduced combustion noise. Key element to achieve distributed combustion is mixture preparation with controlled entrainment of hot reactive species from within the
15 combustor and their subsequent mixing with the fresh reactants to form reduced oxygen concentration-high temperature oxidizer to achieve distributed combustion in the combustor. This necessary entrainment can be beneficial in oxy-fuel combustion as it satisfies the need to utilize CO₂ back into the reaction zone for dilution. In this paper, distributed combustion was investigated with focus on oxy-methane combustion.
20 Experiments were performed on a swirl flame combustor with oxygen concentration ranging between 40-21% of the oxidizer mixture. Results showed the possibility of achieving distributed combustion using oxy-fuel combustion. This is demonstrated through OH* chemiluminescence wherein the reaction zone extended to cover larger portion of the combustor as opposed to that of a traditional swirl flame. Emissions measurements showed
25 the elimination of NO emission with low CO emissions, demonstrating the benefits of incorporating distributed combustion concept using oxy-fuel combustion for carbon capture with the product stream containing mostly CO₂.

Keywords: Colorless distributed combustion, Oxy-fuel combustion, Ultra-low pollutants emission, OH* Chemiluminescence, Gas turbine combustion.

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1. Introduction

The increased awareness of global warming along with efforts to mitigate greenhouse gas emissions have motivated researchers to look for new methods to utilize available fossil fuels while limiting the amounts of carbon dioxide (CO_2) emitted to the atmosphere. Over the past decades, oxy-fuel combustion has been investigated as means to convert fuel chemical energy into electricity/heat with exhaust gases mainly being CO_2 and water vapor. This makes the separation of CO_2 an easy process (as opposed to air combustion, where the exhaust contains large amounts of nitrogen) for its subsequent sequestration. This CO_2 stream can then be compressed into liquid form and then stored (carbon capture and sequestration (CCS)). Oxy-fuel is not the only route to capture CO_2 , others include Pre-combustion and Post combustion CO_2 capture. In a technical and economic review comparing these three routes, it was concluded that oxy-combustion is more suitable for coal combustion, with post combustion more suitable for natural gas combined cycle. These conclusions were based on the specific assumptions and case studies and support that oxy-combustion is an important method for CO_2 capture [1]. Another study outlined that though combining oxy-fuel and integrated gasification combined cycle was technically challenging, it was energetically favorable [2]. Oxy-fuel combustion not only helps to capture CO_2 with relatively easy separation process, but also eliminates the formation of thermal and prompt NO_x from the lack of nitrogen in the oxidizer, thus limiting the thermal NO_x formed. It is noteworthy that the majority of NO_x formed in gaseous fuels is from thermal NO_x following the Zeldovich mechanism [3].

Oxy-fuel combustion characteristics is different than that of air combustion in several aspects. First, oxy-fuel combustion results in higher adiabatic flame temperature (typically 30% more than that of air for the same conditions), consequently large amounts of exhaust gas need to be

recirculated to maintain the same adiabatic flame temperature to prevent excessive heat [4].

55 Second, oxy-fuel flames have a much higher flame speed [5], consequently higher injection velocities (through adding more diluents) are needed to stabilize the flame in the desired location. Exhaust gas recirculation, being mainly CO₂, aids significantly in reducing flame speed to achieve similar flame velocity for safe operation [5,6].

Oxy-fuel combustion has been studied for both gaseous and solid fuels [5, 7-12]. These
60 studies focused on flame speed [5], flame shape [5,7, 8], emissions [8,9], combustion efficiency, and performance [10-12], focusing mainly on furnace applications that have low combustion intensity and larger residence times. Oxy-fuel combustion is characterized by high laminar speed. Oxy methane laminar flame speed is roughly 9 folds that of methane air at stoichiometry (315 cm/s vs. 37 cm/s [5]). In one of the studies, the authors demonstrated that the flame has less
65 radial expansion and is elongated axially with higher oxygen concentration [7]. They also encountered problems stabilizing the flame for O₂ concentration less than 21% in the oxidizer mixture for methane [7]. In another study, it was concluded that CO emissions from CO₂ diluted oxy-fuel combustion is minimal near stoichiometric and increases rapidly, as compared to air combustion, when moving towards lean combustion [8]. In the same study, there was no data
70 available for oxygen concentration below 22% at an equivalence ratio of 0.95 [8], indicating possible instabilities below this value as suggested in a previous study [7]. One of the studies, focusing on coal combustion, concluded that the incomplete combustion loss for oxy-fuel combustion was much lower than that of air combustion, as well as higher sulfur conversion to SO₂ [10]. This was further confirmed in another study [11] wherein the authors also
75 demonstrated lower nitrogen oxides emission. Oxy-fuel combustion was also investigated with focus on chemical kinetics on the role of CO₂ on reaction pathways [13]. Recently, efforts have

been directed to combine novel combustion technologies with oxy-fuel combustion. In their work, the authors established the boundaries of achieving MILD combustion using oxy-combustion with different amount of CO₂ dilution, however, their work focused on low intensity
80 furnace combustion [14]. Meanwhile, Sabia *et al.* and Mardani *et al.* have numerically investigated oxy-fuel MILD combustion with focus on chemical kinetics providing useful insights on reaction routes at different equivalence ratios using methane and methane/hydrogen mixtures as the fuels [15, 16]. The potential of oxy-fuel combustion has been shown for gas turbines [17] though higher CO emissions were recorded. Kutneet *et al.* investigated oxy-fuel flames in a swirl
85 combustor with comparison to air combustion; they attributed the significant changes between both the combustion modes to higher heat capacity of CO₂ [18].

In this paper, oxy-fuel combustion is investigated with focus on achieving colorless distributed combustion (CDC) using oxygen diluted with CO₂ rather than air. CDC relies on the internal recirculation and entrainment of reactive hot species from within the combustor and their
90 subsequent mixing with the fresh mixture to form low oxygen concentration and high temperature mixture prior to ignition. This mixture results in a distributed combustion zone that extends in most of the combustor volume at a lower temperature increase and lower reaction rate to result in the similar fuel consumption. Such low reaction rate is achieved through the low oxygen concentration and sustained by the high mixture temperature. CDC have been thoroughly
95 investigated, demonstrating significant emissions reduction under different configurations [19, 20], fuel flexibility [21, 22], thermal field uniformity and noise reduction [23], with the required conditions to achieve CDC as described in detail [24].

The mixture preparation requirement for CDC presents significant opportunities for oxy-fuel combustion, as such method ensures the entrainment of significant amounts of reactive and

product species (mainly CO_2) which lowers the flame speed and flame temperatures. However, the challenge here is how to handle the high oxygen concentration in oxy-fuel combustion as opposed to air combustion, which needs to be lowered to achieve distributed combustion. In the following sections, oxy-fuel combustion will be examined in a swirl burner with focus on distributed combustion in the burner via CO_2 dilution. CO_2 was injected upstream of the burner, simulating the entrainment of hot reactive gases in a controlled manner. The amount needed for dilution to achieve distributed combustion and favorable performance is used as guideline for combustor design.

2. Experimental Facility

The experiments were performed using a swirl burner. Details of the swirl burner can be found elsewhere [25]. For all the cases reported here, methane was used as the fuel. Laminar flow controllers with an accuracy of $\pm 0.8\%$ of reading and $\pm 0.2\%$ of full scale were used to control the air and carbon dioxide flow rates, leading to an overall accuracy of about 1.5% of the reading. Methane and oxygen flow rates were controlled through gravimetric flow controllers with an accuracy of 1.5% of full scale. Fuel was injected at the center of the swirler in a non-premixed configuration, relying on the swirl for mixing. Oxygen and carbon dioxide were supplied upstream of the swirler with enough time to ensure good mixing. Figure 1 shows the flow configuration of the swirl, while figure 2 shows the flow arrangement to the burner.

The injection of carbon dioxide simulates the entrainment of product gases from within the combustor, albeit at lower temperature. Controlled injection of CO_2 helped to determine the amounts of dilution needed to achieve favorable conditions. These amounts can then be used for practical combustor designs.

NO emissions were measured using a NO–NO_x chemiluminescent gas analyzer with an accuracy of ± 0.5 PPM, CO emissions were measured using the non-dispersive infrared method with an accuracy $\pm 5\%$. O₂ concentration was also measured, to correct the measured NO and CO emission to the standard 15% oxygen concentration, using galvanic cell method. For every experimental point, measurements were repeated at least three times. The experiments were repeated at least three times to ensure good repeatability of the data obtained.

For capturing the OH* chemiluminescence, an intensified charge coupled device (ICCD) camera coupled to a narrow band filter, centered at wavelength 307 nm wavelength, was used. For all the cases, the flames were confined in the quartz tube having an internal diameter of 3 inches and length of 12 inches. Thermocouples were fitted along the reactor walls to confirm the existence of reaction zone at low oxygen concentration as the flame was invisible with almost no combustion noise.

3. Experimental Conditions

The experimental investigations reported here were focused on obtaining the global flame characteristics and pollutants emission under oxy-fuel combustion with different amounts of carbon dioxide dilution with focus on seeking distributed combustion. Table 1 summarizes the operating conditions for each of the experimental case investigated here. The fuel flow rate was kept constant for all the experiments to result in a constant thermal load. The lower limit for the oxygen concentration in the oxidizer was determined based on the observed instabilities of the flame and flame blowout when the oxygen was further reduced below these values. Higher oxygen concentration (higher than 40%) were not examined as the flame shifted towards the swirler due to the higher flame speed, overheating the swirler body. The heat load was kept

constant at 3.25KW to give a heat (thermal) release intensity of 2.4 MW/m³-atm. The experiments were performed at room temperature and pressure with no preheat to any of the gases. The percentage values mentioned herein are based on volumetric basis, wherein the oxygen concentration is expressed as a percentage of oxygen in air or percent oxygen in the oxygen-carbon dioxide mixture.

4. Results and Discussion

4.1 Global Flame Structure

To characterize the performance of oxy-methane flame and examine the possibility of achieving distributed combustion using oxygen as the oxidizer, global flame images were first recorded for the different conditions. Figure 3 shows the global flame images obtained at an equivalence ratio of 0.9, which is of relevance to oxy-fuel combustion [8]. Also included is the flame image using air as the oxidizer as a reference case. It is noteworthy that for these images, the exposure time and iso-settings were kept constant.

At oxygen concentration of 40%, considered high concentration in this work, the flame formed had limited radial expansion with the flame significantly elongated axially. This is evident when compared to the normal air flame case, see Fig. 3. As the amount of CO₂ was increased (decreasing the oxygen concentration) the flame slowly restores the traditional swirl shape as seen at O₂ concentrations of 35% and 30%. Further reduction in O₂ concentration resulted in a slow transition to distributed combustion, similar to that demonstrated using air combustion [24]. A more uniform combustion is evident at O₂ concentrations of 25% and 23%. At the low end of 21%, the flame starts to separate out to form two regions, with a continuous cycle of separation and reattachment. Further reduction in O₂ concentration resulted in flame

170 blowout. Operating the burner at a lower equivalence ratio of 0.7 resulted in a similar behavior to that observed at equivalence ratio of 0.9, see Fig. 4. However, the flame incurred instabilities at O_2 concentration of 25% rather than 21%.

4.2 OH^* Chemiluminescence

175 The OH^* chemiluminescence was employed to outline the reaction zone distribution. Previous experiments have demonstrated the strong correlation between OH^* chemiluminescence distribution and thermal field uniformity for this swirl burner used herein [23].

Figure 5 shows the OH^* chemiluminescence at an equivalence ratio of 0.9 with varying
180 amounts of oxygen concentration. As the oxygen concentration was reduced, a more uniform reaction zone was formed, as opposed to the swirl lobes evident at oxygen concentration of 30% and higher. For the high end of O_2 concentration, the reaction zone was concentrated at the center with unfavorable performance in terms of reaction zone distribution, which results in sharp temperature increase within the flame zone, to subsequently form local hot spots.

185 To examine the reaction distribution at low oxygen concentrations, the OH^* chemiluminescence intensity distributions at O_2 % of 25 and lower are shown in Fig. 6 at a scale of 0-3000 a.u. as opposed to 0-18500 a.u. used in Fig 5. The intensity distribution uniformity was slightly enhanced at $O_2=25\%$ (as compared to higher $O_2\%$). At $O_2=23\%$, the reaction zone was distributed across the burner, and even better distribution was achieved at $O_2=21\%$. It is
190 noteworthy that for all these cases, the amount of fuel was the same.

The OH^* chemiluminescence was also recorded at lower equivalence ratios of 0.8-0.6. Figure 7 shows the OH^* chemiluminescence data for equivalence ratio of 0.8. The trend observed was

similar to that observed at equivalence ratio of 0.9, where the high end of O₂ concentration (40%) resulted in a concentrated flame reaction zone, while further reduction in O₂ concentration resulted in restoration of the typical swirl flame shape (e.g., at O₂=35 & 30%). Further reduction in O₂ concentration resulted in distributed reaction (27.5%-23%). The flame was observed to be unstable below 23% O₂ concentration at equivalence ratio of 0.8 (as opposed to below 21% at $\phi=0.9$). In addition, the overall intensity was lower for $\phi=0.8$ (scale 0-15000 as opposed to 0-18500 a.u, for $\phi=0.9$).

Figures 8 and 9 show the OH* distribution at equivalence ratios of 0.7 and 0.6. The same trend was observed, however, the stability limit was reduced, with unstable combustion below oxygen concentration of 25% ($\phi=0.7$) and 27.5% ($\phi=0.6$). For both equivalence ratios, the scale was lower than the two previous (high) equivalence ratios (0-12000 for $\phi=0.7$ and 0-9000 for $\phi=0.6$).

The consistent increase in OH* signal at the O₂ concentration of 40% in oxidizer mixture as compared to that of air can be explained by the increase in reaction rate and higher temperatures achieved with oxygen combustion. Equilibrium calculations showed that addition of CO₂ significantly decreased the adiabatic flame temperature (AFT) from 2366K (40%O₂ in mixture) to 1674K (21%O₂ in mixture), at an equivalence ratio of 0.9 (where the AFT of air combustion is 2133K, lower than that of 40% O₂). The same trend was demonstrated for the other equivalence ratios examined. For instance, at $\phi=0.6$, the AFT decreased from 2023K (40% O₂) to 1561K (27.5% O₂) while that of air combustion was 1665K, lower than the 40% O₂ case.

One can conjecture that the change in behavior is related to the increase in velocity with increased CO₂ dilution flowrate, however; previous experiments have shown that this behavior

was due to the dilution effect and the chemical effects of adding CO₂ and lowering O₂ concentration as opposed to the increased flow velocity [26].

4.3 Pollutants Emission

The pollutants emission for the different cases were recorded with focus on NO and CO emissions. Figures 10 and 11 show the emission of NO and CO for the different cases as a function of equivalence ratio. NO emissions approached zero PPM using the O₂-CO₂ mixture rather than air. This is attributed to the fact that the fuel (methane) contains no nitrogen, and in absence of air, there is no nitrogen to form NO_x. As for CO emissions, the values for O₂-CO₂ mixture were higher than air combustion regardless of the equivalence ratio and the amount of CO₂ in the O₂-CO₂ mixture. This increase can be related to the increase of CO₂ in the combustion products which in return increases the amount of CO by dissociation. Although the emissions increased, they were still considerably low, being around 20PPM or less for favorable operational condition.

To further examine the impact of CO₂ addition on CO emission, the emissions were plotted vs. the oxygen concentration in the oxidizer, as opposed to equivalence ratio, and the results are shown in Fig.12.

For equivalence ratios of 0.8 and 0.7, one can see that the CO emissions do not vary much with increase in CO₂ dilution, with values around 20PPM. At $\phi=0.6$, the emissions were slightly higher and increased at the low end of oxygen concentration as the flame started to show unstable behavior. On the other hand, at $\phi=0.9$, CO emissions did not show any consistent trend with the values lying between 48 and 68 PPM. At or close to the distributed combustion conditions, CO emission were about 20PPM (for $\phi=0.8$ and 0.7, O₂=25%), 60PPM (for

phi=0.6, O₂=27.5%) and 54PPM (for phi=0.9, O₂=23%). In general, the increase in CO emission
for all the examined oxy-fuel mixtures, as compared to air combustion, can be attributed to the
increased amounts of CO₂ in the product gases, allowing for more dissociation of CO₂ to O₂ and
CO. This dissociation was further enhanced at higher temperatures (i.e. at phi=0.9) to result in
higher CO emissions as compared to other (lower) equivalence ratios.

The emission reduction encountered was not only in terms of pollutants, but also in terms of
noise. The combustion noise decreased significantly upon transitioning to distributed combustion
with the disappearance of the characteristic swirl oscillation frequency. The overall sound noise
level decreased from 85 dB (with air combustion) down to 75 dB (with 27.5% O₂ in O₂-CO₂) and
to 64 dB (for 23% O₂ in O₂-CO₂ mixture). When O₂-CO₂ mixture was used instead of air, the
resonant frequency moved from around 500Hz to around 400Hz. This can be related to the
change in density and temperature inside the combustor. As the oxygen concentration was
reduced, this resonant frequency decreased in amplitude until it disappeared at the low end of
oxygen concentrations. This behavior was similar to that shown previously with air as oxidant
under conditions approaching distributed combustion[23].

5. Conclusions

Colorless distributed combustion was investigated in a swirl burner with focus on oxy-fuel
combustion to foster carbon capture and sequestration. Global images showed that, upon diluting
the oxygen with enough carbon dioxide, distributed combustion was achieved with a uniform
reaction zone across the combustor. This was evident through regular flame images and OH*
chemiluminescence. For equivalence ratio of 0.9, favorable distribution was shown below O₂

concentration of 25% in the O₂-CO₂ intake mixture. Similar behavior was demonstrated for lower equivalence ratios (down to 0.6).

For pollutants emission, NO emissions approached zero, since most of the NO_x formed was essentially from thermal NO_x as the fuel used (methane) had no nitrogen. CO emissions increased for oxy-fuel combustion as compared to air combustion. However, emissions below 20PPM of CO were achieved at favorable conditions. These results outline the benefits of incorporating colorless distributed combustion for oxy-fuel combustion with focus on ultra-low emissions and thermal field uniformity to prevent local burnout of the equipment which may occur under high temperature oxy-fuel combustion.

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References

- [1] Kanniche M, Gros-Bonnivard R, Jaud P, Valle-Marcos J, Amann J, Bouallou C. Pre-combustion, Post-combustion and Oxy-combustion in Thermal Power Plant for CO₂ Capture. Applied Thermal Engineering, 2010;30:53-62
- [2] Kunze C, Spliethoff H. Assessment of Oxy-fuel, Pre- and Post-Combustion-Based Carbon Capture for Future IGCC Plants. Applied Energy, 2012;94:109-116
- [3] Correa SM. A Review of NO_x Formation under Gas-Turbine Combustion Conditions. Combustion Science and Technology 1992;87:329-62.

- [4] Buhre BJP, Elliot LK, Sheng CD, Gupta RP, Wall TF. Oxy-fuel Combustion Technology for Coal-fired Power Generation. *Progress in Energy and Combustion Sciences*, 2005;31:283-307
- 285 [5] Shi B, Hu J, Ishizuka S. Carbon Dioxide Diluted Methane/Oxygen Combustion in a Rapidly Mixed Tubular Flame Burner. *Combustion and Flame*, 2015;162:420-430
- [6] Galmiche B, Halter F, Foucher F, Dagaut P. Effects of Dilution on Laminar Burning Velocity of Premixed Methane/Air Flames. *Energy & Fuels*, 2011;25:948-954
- 290 [7] Nemitallah M, Habib M. Experimental and Numerical Investigations of an Atmospheric Diffusion Oxy-combustion Flame in a Gas Turbine Model Combustion. *Applied Energy*, 2013;111:401-415
- [8] Williams T, Shaddix C, Schefer R. Effect of Syngas Composition and CO₂-Diluted Oxygen on Performance of a Premixed Swirl-Stabilized Combustor. *Combustion Science and Technology*, 2007;180(1):64-88
- 295 [9] Heil P, Toporov D, Forster M, Kneer R. Experimental Investigation on the Effect of O₂ and CO₂ on Burning Rates during Oxyfuel Combustion of Methane. *Proc. Of Combustion Institute*, 2011;33:3407-3413
- [10] Czakiert T, Sztekler K, Karski S, Markiewicz D, Nowak W. Oxy-fuel Circulating Fluidized Bed Combustion in a Small Pilot-scale Test Rig. *Fuel Processing Technology*, 300 2010;91:1617-1623.
- [11] Duan L, Sun H, Zhao C, Zhou W, Chen X. Coal Combustion Characteristics on an Oxy-fuel Circulating Fluidized Bed Combustor with Warm Flue Gas Recycle. *Fuel*, 2014;127:47-51

- [12] Hecht E, Shaddix C, Geier M, Molina A, Haynes B. Effect of CO₂ and Steam Gasification Reactions on the Oxy-combustion of Pulverized Coal Char. Combustion and Flame, 2012;159:3437-3447
- [13] Le Cong T, Dagaut P, Dayma G. Oxidation of Natural Gas, Natural Gas/Syngas Mixtures, and Effect of Burnt Gas Recirculation: Experimental and Detailed Kinetic Modeling. J. Eng. Gas Turbines Power, 2008;130(4):041502
- [14] Li P, Dally B, Mi J, Wang F. MILD Oxy-combustion of Gaseous Fuels in a Laboratory-scale Furnace. Combustion and Flame, 2013;160:933-946
- [15] Sabia P, Sorrentino G, Chinnic A, Cavaliere A, Ragucci R. Dynamic Behaviors in Methane MILD and Oxy-Fuel Combustion. Chemical Effect of CO₂. Energy Fuels, 2015;29(3):1978-1986
- [16] Mardani A, FazlollahiGhomshi A. Numerical Study of Oxy-Fuel MILD (Moderate to Intense Low-Oxygen Dilution Combustion) Combustion for CH₄-H₂-fuel. Energy, 2016;99:136-151
- [17] Richards GA, CasletonKH, Chorpening BT. CO₂ and H₂O Diluted Oxy-fuel Combustion for Zero-Emission Power. Proc. Inst. Mech. Eng. Part A, 2005;219(2):121-126
- [18] Kutne P, Kapadia BK, Meier W, Aigner M. Experimental Analysis of the Combustion Behavior of Oxyfuel Flames in a Gas Turbine Model Combustor. Proc. Combust. Inst, 2011;33(2):3383-3390
- [19] Arghode VK, and Gupta AK. Effect of Flowfield for Colorless Distributed Combustion (CDC) for Gas Turbine Combustion. Applied Energy, 2010;78:1631-40.
- [20] Khalil AEE, and Gupta AK. Swirling Distributed Combustion For Clean Energy Conversion In Gas Turbine Applications. Applied Energy, 2011;88:3685-93.

[21] Khalil AEE, and Gupta, AK. Fuel Flexible Distributed Combustion With Swirl For Gas Turbine Applications. Applied Energy, 2013;109:327-334.

[22] Khalil AEE, and Gupta AK. Clean Combustion in Gas Turbine Engines Using Butyl Nonanoate Biofuel. Fuel, 2014;116:522-528

330 [23] Khalil AEE, and Gupta AK. Thermal Field Investigation under Distributed Combustion Conditions. Applied Energy, 2015;160:477-488

[24] Khalil AEE, and Gupta AK. Impact of Internal Entrainment on High Intensity Distributed Combustion. Applied Energy, 2015;156:241-250.

[25] Khalil AEE, Brooks JM, Gupta AK. Impact of Confinement on Flowfield of Swirl Flow
335 Burners. Fuel, 2016;184:1-9

[26] Khalil AEE, and Gupta AK. On the Flame-Flow interaction under Distributed Combustion Conditions. Fuel, 2016;182:17-26