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Coupling of oxygen-enriched combustion and CO₂ capture by membrane processes

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Abstract

This study aims to investigate a new technological solution for CO₂ capture from fossil fuel burning power plants. It consists of coupling an oxygen-enriched combustion (typically 30-80% O₂) with a CO₂ capture by membrane separation processes. This offers a CO₂ capture process with a greatly reduced energetic cost compared to conventional post-combustion or oxycombustion processes. The overall purpose of the present work is to maximize the energy production by combustion while ensuring a correct operation of the global process in compliance with environmental legislations. First, a feasibility study is performed with numerical simulations of the energy required for this “hybrid” process. In parallel, combustion kinetics simulations are performed in order to determine the best combustion conditions. This numerical approach is now under experimental validation in a counter-flow burner at LCD and in a model gas turbine chamber at CORIA.

Introduction

Carbon dioxide Capture and Storage (CCS) represents a promising option for the reduction of greenhouse gas emissions from fossil fuel-fired power plants [1]. Much of the research in this area focuses on minimizing the energy required for CO₂ capture. While pre-combustion capture offers the most promising alternative for integrated coal gasification combined cycle or natural gas combined cycle power plants [2], post-combustion is usually inescapable for other industrial plants (cement, steel, glass, refineries, chemical plants, etc). The application of this latter technology is still not developed because of high cost (around 40 € per ton of CO₂ captured) for which the capture step dominates, typically 60-80% of the overall cost of the capture-transportation-injection for storage chain. A reduction of this cost is then required. From a practical point of view, CO₂ capture in post-combustion process is currently envisaged through two aspects:

- i) High purity oxygen supply (oxycombustion) to avoid dilution with nitrogen, leading to the capture of concentrated CO₂ by a simple drying operation;
- ii) CO₂ capture in the exhaust gas of a conventional process with air supply (CO₂ content is usually between 4 and 15 % depending on the fuel type) using separation process like absorption in liquids (amine washing). The global objective is to ensure a CO₂ capture rate of 80 to 90% while producing a flue gas containing 80% of CO₂ (to allow transportation and sequestration) with a minimal energy consumption (typically less than 2GJ per ton of CO₂ captured) [3].

The investigation of a technological solution, allowing minimization of the energy requirement while ensuring high CO₂ concentration, is the major purpose of this study. The basic concept relies on a novel approach based on an association of combustion and capture,

which could present an alternative solution between oxycombustion (i.e. combustion with pure oxygen) and the conventional post-combustion capture. In this study we investigate a “hybrid” solution for CO₂ capture based on an oxygen-enriched combustion (typically 30-80% O₂) in order to produce a high content of CO₂ in the flue gas (>30% at 1 bar), for which membrane separation processes can provide separation for post-combustion applications at a greatly reduced energetic cost [4]. The overall purpose of the investigation is to maximize energy production by combustion while ensuring a correct operation in compliance with environmental legislations. A special attention is given to NO_x and unburnt compounds emissions. Methane (major constituent of natural gas) is studied here. First, a feasibility study for this “hybrid” process coupling CO₂ capture with oxygen-enriched combustion conditions is performed with numerical simulations of the energy required. In parallel, combustion kinetics simulations (Chemkin/Premix code) are performed in order to determine the best combustion conditions in terms of burning velocity, temperature, and pollutants emissions required for a proper operation of the system. This numerical approach is now undergoing experimental validation in a counter-flow burner at LCD and in a model gas turbine chamber at CORIA. The first results are presented here.

Numerical approach

Numerical validation of the “hybrid” process

The approach starts from the principle that the energy required for the capture of a specific component in a mixture is proportional to the dilution rate of the component to extract and/or the level of enrichment required. The feasibility study consists then of the numerical investigation of a *hybrid* process associating two technologies for a lesser energy consumption:

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- i) oxygen-enriched air production (typically 30 to 80% of oxygen) for combustion process supply, using a flexible and energetically interesting process (cryogeny for large units, membrane permeation for other units);
- ii) CO₂ capture in the flue gas using a membrane process particularly well adapted to high CO₂ concentrated mixtures [4].

A diagram of principle is given in Fig.1.

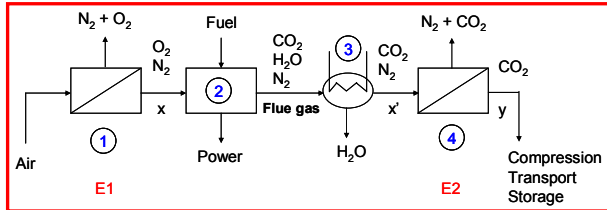


Figure 1: Synoptic of the hybrid process including a oxygen-enriched combustion section (oxygen production unit: 1, combustion unit: 2) and a CO₂ capture section in view of sequestration (drying process: 3, capture process: 4). The oxygen mole fraction x is varied between 0.21 and 1, CO₂ purity (y) is fixed to 0.9.

The main purpose of this work is the estimation of the energy required to capture one ton of CO₂, expressed in GJ per ton. This quantity is associated to the minimal work of concentration W (in Joule per mole of mixture, assuming an ideal gas phase). W depends on the mole fraction (x) of the component to be extracted in the mixture considered, and the level of purity to be attained (y , mole fraction of the component to be extracted after the separation process). A diagram of principle is given in Fig. 2.

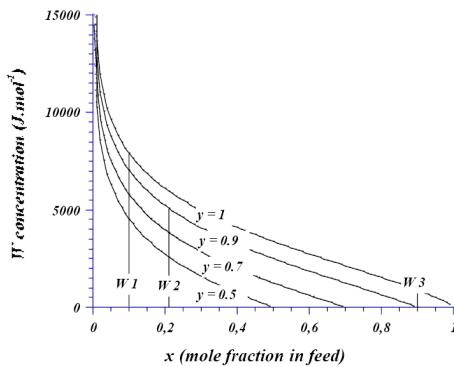


Figure 2: Evolution of the minimal work of concentration (W , $J.mol^{-1}$) of a binary gas mixture as a function of the mole fraction in the mixture (x) and the level of purity (y) required.

The oxycombustion strategy, represented by the W2 segment, aims to concentrate oxygen from 21% to more than 99%. The conventional post-combustion process, marked as W1, treats a flue gas containing about 10% CO₂ and must attain a mole fraction higher than 0.9. With a hybrid process strategy, coupling a moderated oxygen enrichment upstream ($W^2 < W2$) and a CO₂

extraction from the exhaust gas containing a high concentration of this compound (represented schematically by the W3 segment for $x=0.9$), the total work of separation required W^2+W3 can be lower than W2 or W1.

This hypothesis has been validated by numerical simulation. For that purpose, the energy E1 (see Fig. 1) required for “oxygen-enriched air” production and the energy E2 required for the capture of one ton of CO₂ with a purity of 90% has been calculated. Results are presented in Fig. 3. They show that coupling an oxygen-enriched air production by cryogeny (requiring a specific energy E1) with a CO₂ capture using a membrane process (specific energy E2) leads, for the oxygen content in the oxidizer about 60-70%, to a total energy consumption lower than the one required for oxycombustion or the post-combustion processes.

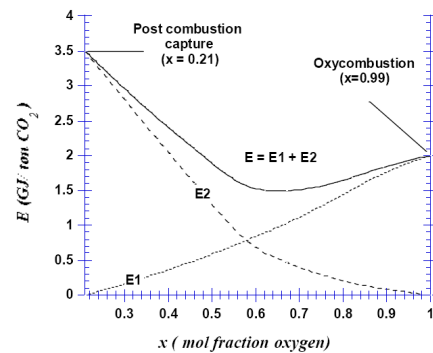


Figure 3: Energy requirement for CO₂ capture versus oxygen content in the feed stream. E1= specific energy for oxygen production, E2= specific energy for capture process by membrane (see Fig. 1). Capture ratio=90%, Purity of 90% is imposed.

Combustion kinetics simulations

This part of the work aims to identify the combustion conditions (initial gas mixtures composition, oxygen content, equivalence ratio, exhaust gas composition,) allowing a correct operation of the entire process in terms of flame velocity, temperature, pollutants emission (NOx, CO, unburnt compounds), CO₂ content in the exhaust gas and oxygen consumption.

Simulations have been performed with the PREMIX code [5] from the Chemkin II package [6] and the GRImech3.0 mechanism [7]. The PREMIX code allows the calculation of flame velocity, temperature profiles and species mole fraction profiles in premixed laminar flames. The present calculations have been performed with the freely propagating flame option. The GRImech3.0 mechanism, containing 53 species involved in 325 reversible reactions, is a reference mechanism largely employed in literature concerning methane combustion.

First, the influence of a progressive oxygen enrichment (from 21 to 100% O₂) is studied for stoichiometric and slightly rich ($\phi = 1.1$) CH₄/O₂/N₂ flames at three different pressures (1, 4 and 8 bar) and for an inlet temperature of 600K. Figure 4 shows the variations of the flame velocity S_L and the adiabatic temperature T

when the O_2 content increases from air (21%) to oxycombustion (100%) conditions for the slightly rich $CH_4/O_2/N_2$ flame ($\phi=1.1$). Figure 5 shows the calculated NOx ($X_{NO} + X_{NO_2}$) emission (in ppm@15% O_2 in the exhaust gas) and the CO_2 final mole fraction for the same conditions.

The results show, as expected, an increase of the adiabatic flame temperature and the flame velocity when the O_2 content increases. For the same O_2 content, the adiabatic temperature increases with pressure while the flame velocity decreases. The plot of NOx emissions versus the % O_2 gives a bell-shape profile with a maximum for 60-70% of O_2 . NOx emissions increase drastically as the pressure increases due to an increase in temperature (the thermal-NO mechanism predominates for the present temperatures). As expected, no NOx are formed for oxycombustion (100% O_2) condition, however the adiabatic flame temperature is very high (more than 3000K). For a real industrial application, this would require a thermal protection of the combustion chamber walls and of the turbine blades. CO_2 final mole fraction slightly increases with O_2 content and pressure but remains too low (about 10% at 1 bar) for an economically favourable application of CO_2 capture by membranes processes.

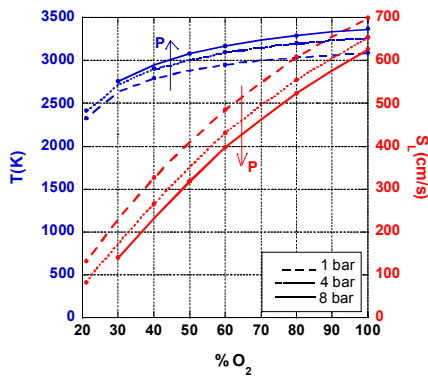


Figure 4: Adiabatic flame temperature T (K) and laminar flame velocity S_L (cm/s) versus the percentage of O_2 in "air" for three different pressures (1, 4 and 8 bar) for a slightly rich $CH_4/O_2/N_2$ flame ($\phi=1.1$).

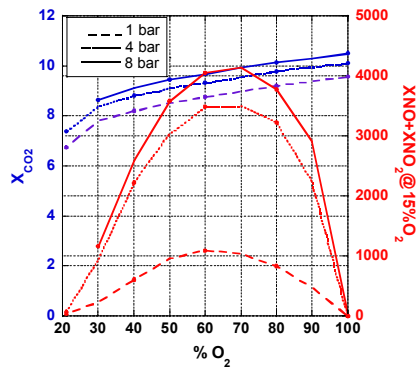


Figure 5: CO_2 mole fraction and NOx emissions ($X_{NO}+X_{NO_2}$) in the burnt gases of the slightly rich $CH_4/O_2/N_2$ flame ($\phi=1.1$) versus the percentage of O_2 in "air" for three different pressures (1, 4 and 8 bar).

A possible solution consists in diluting the initial mixture by CO_2 (the captured CO_2 for example) in order to decrease the combustion temperature and then NOx emission, as well as to increase the final CO_2 content. The aim is to obtain low NOx emissions that meet current environmental legislations for gas turbines (i.e., ~ 15 ppm @15% O_2). Figure 6 shows the variations of the laminar flame velocity and the adiabatic temperature when the O_2 (from 50 to 100%) and CO_2 (from 0 to 60%) initial contents increase at a pressure of 4 bar and for the slightly rich $CH_4/O_2/N_2$ flame ($\phi=1.1$). Figure 7 shows the NOx emissions and the CO_2 final mole fraction for the same conditions.

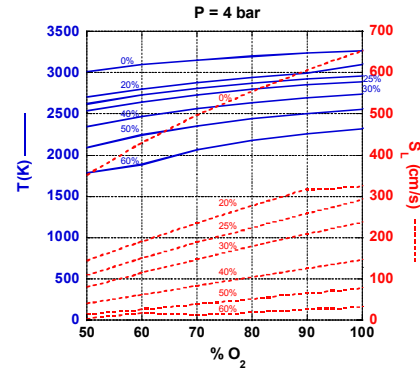


Figure 6: Adiabatic flame temperature T (K) and laminar flame velocity S_L (cm/s) versus the percentage of O_2 in "air" and the CO_2 content in the initial mixture at $P=4$ bar for a slightly rich $CH_4/O_2/N_2/CO_2$ flame ($\phi=1.1$).

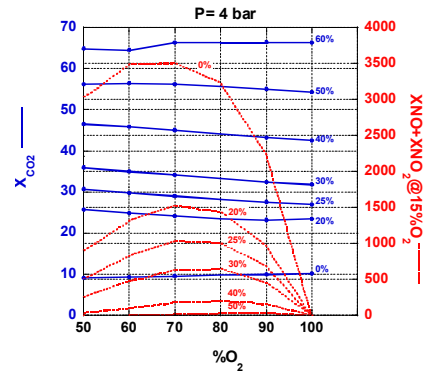


Figure 7: CO_2 mole fraction and NOx emissions ($X_{NO}+X_{NO_2}$) in the burnt gases of the slightly rich $CH_4/O_2/N_2/CO_2$ flame ($\phi=1.1$) versus the percentage of O_2 in "air" and the CO_2 content in the initial mixture at $P=4$ bar.

CO_2 dilution plays its expected role: it decreases the adiabatic temperature (due to its high heat capacity) and increases the final CO_2 content in the burnt gases which is advantageous for the membrane capture process. However, a high CO_2 dilution (60% CO_2) is necessary to reach the NOx emissions critical value (~ 15 ppm @15% O_2). In this case the flame velocity becomes very low (< 20 cm/s for 50 to 80% O_2).

This numerical study shows therefore that oxygen-enriched combustion (60-80 % O_2) allows to obtain a high CO_2 content in the exhaust gas while guaranteeing

low NOx emissions provided a dilution of the initial gas mixture by high quantities of CO₂. Future calculations will focus on the effect of Exhaust Gas Recirculation on the oxygen-enriched combustion of methane.

Experimental approach

Experimental study of CO₂ dilution in a counter-flow laminar flame burner

The objective of this part is to enhance the knowledge of the combustion regime generally called MILD (Moderate Intense Low-oxygen Dilution Combustion) or flameless combustion. Experiments were performed in a counter-flow burner. We have investigated the influence of the diluent composition (nitrogen/carbon dioxide), concentration (dilution rate) and preheat temperature of the reactants on the flame stability and on the broadening of the reaction zone. The experimental results are necessary to analyse the thermochemical effects of the flue gas recirculation on the flame stability behaviour.

Experimental set-up and diagnostic

A counter-flow burner is used (Fig. 8), it consists of two identical vertically opposed nozzles. The fuel (mixture of CH₄/N₂/CO₂) is injected in the top burner and the oxidizer (mixture of O₂/N₂/CO₂) in the bottom burner. The separation distance (H) between the nozzles and the internal injection diameter D are both fixed to 35mm. An annular concentric co-flow of nitrogen provides a curtain to isolate the flame from reaction of fuel with surrounding air. The two laminar opposed flows are heated electrically up to 700°C. The flow characteristics are kept constant to those of the cold stream velocity of $u_c = 0.5$ m/s, corresponding to a constant volume flow rate of $Q_c \approx 4.82 \times 10^{-4}$ m³/s. As the two reactant flows are heated up, their effective velocities u_h at the exit change the flow strain rate. The average exit velocity after preheating follows the law: $u_h = (u_c / T_c) \cdot T_{pr}$, where u_h is the real exit velocity of the hot reactants, u_c is the inlet cold flow velocity, T_c is the ambient temperature ($T_c = 298$ K), and T_{pr} is the preheat temperature (298-1023K).

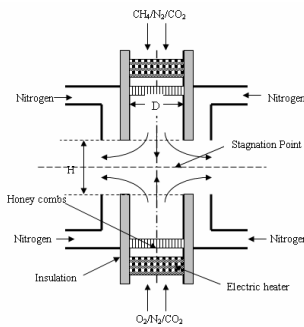


Figure 8: Schematic of the counter-flow burner

The non-premixed diluted CH₄/Air flame is experimentally established in the mixing zone of the reactants diluted in nitrogen and carbon dioxide. The

volume fraction of methane X_{CH_4} in the fuel stream varies from 6 to 30%, and the oxygen volume fraction X_{O_2} in the oxidizer stream ranged from 10 to 21%. The volume fraction of carbon dioxide X_{CO_2} varies from 0 to 20% and kept constant on the fuel and oxidizer sides. The remaining part of the diluent is nitrogen: $X_{CH_4} = 1 - X_{CO_2} - X_{N_{2f}}$ and $X_{O_2} = 1 - X_{CO_2} - X_{N_{2o}}$ where $X_{N_{2f}}$ and $X_{N_{2o}}$ are the volume fraction of nitrogen in the fuel and oxidizer flows respectively. Visualization of the reaction zone is performed by Planar Laser Induced Fluorescence of OH.

Results and discussion

The flame stability diagram is determined by extinction tests as a function of the strain rate S. Fig. 9 presents the flame stability diagram using S versus the oxygen concentration X_{O_2} . The extinction strain rate (linearly dependant of T_{pr}) increases with the oxygen concentration X_{O_2} for both nitrogen ($X_{CO_2} = 0$) and nitrogen/carbon dioxide dilutions, which means that dilution reduces flame stability whatever the diluent composition. The effect of CO₂ content on the flame stability is noticeably increased as the oxygen concentration is low.

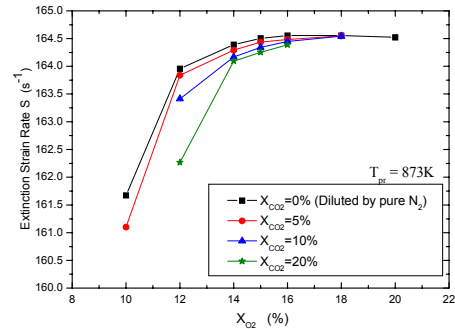


Figure 9: Flame stability diagram versus X_{O_2} for different CO₂ dilutions

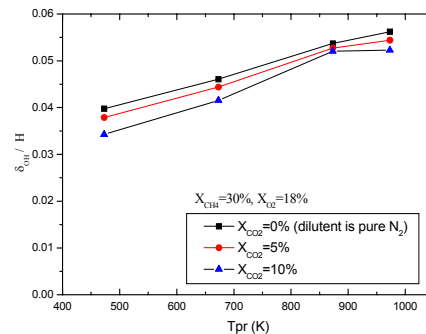


Figure 10: Effects of the preheat temperature T_{pr} and CO₂ dilution on the reaction zone thickness δ_{OH}/H

Figure 10 presents the reaction zone thickness versus the preheat temperature of reactants for different X_{CO_2} content in the diluent. The reaction zone thickness increases with increasing preheat temperature and decreases with increasing CO₂ concentration. This result is attributed to the higher heat capacity of CO₂ compared to N₂. But, according to some analyses [8] for

a mild combustion model, the CO₂ content in diluents may change the behaviour of the diluted combustion not only because it affects the heat capacity of the system but also because it contributes to the chemical reactions.

Experimental study on premixed combustion with CO₂ dilution in a model gas turbine chamber

In addition, the effect of CO₂ dilution was studied in the case of lean premixed combustion in a gas turbine configuration. The study concerns a composition of 65%CH₄ and 35%CO₂, typical for biogas [9].

Experimental set-up and diagnostic

The injector of the burner is composed of an axial swirl injector with a central bluff-body producing an annular swirling jet; the swirl number is equal to 0.92. This high swirl number produces the Inner Recirculation Zone (IRZ) observed in the figure 11. The combustion chamber is equipped with a full optical access to allow optical diagnostics. The arrangement allows us to mix fuel and air far upstream injection to ensure a fully premixed combustion. Radius R of swirl injector is 10mm. The diameter of the combustion chamber is 80mm and its length is 250mm. A cold air stream is injected along the combustion chamber walls, both for cooling it and for diluting hot gases produced by combustion. Pressure in the combustion chamber can be settled by adjusting a sonic throat placed at the exit. More information concerning burner arrangements is provided in [10].

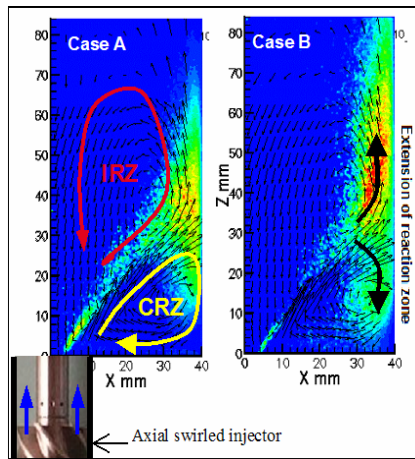


Figure 11: LDV flow velocity and CH* emission maps of two methane air flames, Case A: $\phi=0.75$ and Case B: $\phi=0.70$

To detect flame structure and to quantify the intensity of the reaction, a CH radicals chemiluminescence system is used [11-12]. It is composed of a band pass filter centred at 410 nm, and a 16 bits ICCD camera (Princeton 512x512). In order to provide an accurate visualization of the reaction zone, Abel deconvolution is performed from the averaged image obtained. A pressure sensor placed on the injection plane allows us to detect the apparition of unstable flame (i.e. the apparition of low frequencies peaks).

Results and discussion

The studied flames and their corresponding CH* emissions averaged images are reported in figure 12. For all cases, inlet velocity is set to 30m/s (air mass flow rate 7.80g/s), in atmospheric conditions. It shows the modification of flame structure and the modification of CH* emission intensity when the equivalence ratio and the mole fraction of CO₂ are changed.

Figure 13 quantifies the global CH* decrease of the flames when equivalence ratio is decreased and when CO₂ is increased. It means that the global reaction intensity [11] is decreased by CO₂ or air dilution. This observed decrease of reaction intensity can be related to the decrease of the turbulent flame velocity S_T due to the decrease of laminar flame velocity S_L as shown in

the following expression $\frac{S_T}{S_L} = 1 + c \left(\frac{v'}{S_L} \right)$ and in figure

14 where laminar flame velocity are computed from CANTERA and the GRImech 3.0 mechanism [7].

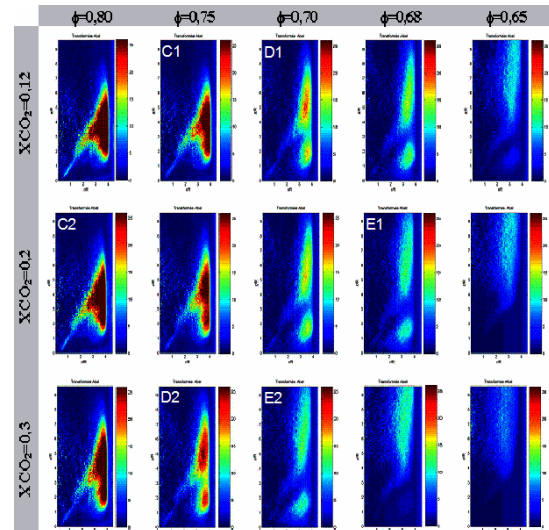


Figure 12: Abel inversion of CH* emission images from the (CH₄+aCO₂) – air flames. a=0.12;0.2 and 0.3

Concerning the structure of the flame, it is well known that the flame stabilization is difficult in zones with high velocity gradients, especially in the case of low flame velocity. In case A (methane/air flame @ $\phi=0.75$), figure 11 shows the position of the average reaction zone in the average velocity field [13]. It can be observed that the flame is anchored to the burner by a thin reaction zone in the inner annular swirling jet corresponding to the higher radial velocity gradient. Then, the main reaction is produced closed to the wall, where the velocities of the flow are lower. In case B, corresponding to a lower equivalence ratio and then to a lower flame velocity (Fig. 14), it can be observed that the flame anchorage is lower in intensity and area, and the zone of main reaction is larger. Due to a lower flame velocity, the time of combustion increases and then the reaction is convected farther in the flow, one part

downstream closed to the wall and the other part in the CRZ (Corner Recirculation Zone).

This phenomenon explains all the different structures of the flames observed in figure 12, when CO₂ and equivalence ratio are modified and seem only depend on the laminar flame velocity. Indeed, some similar structures of the flames observed in figure 12, like the couples C1-C2, D1-D2 and E1-E2, always lead to a similar flame velocity as shown in Fig. 14.

Other studies [13] show that this laminar velocity explains also the instability intensity of the flame in case of CO₂ dilution.

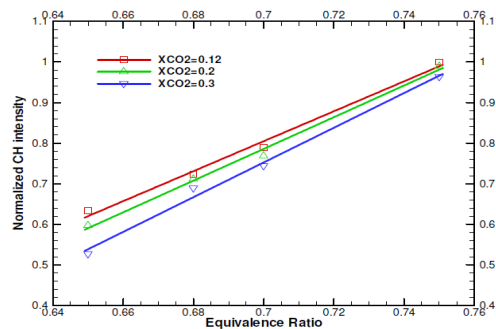


Figure 13: Normalized CH* emission for different mole fractions of CO₂ dilution versus equivalence ratio

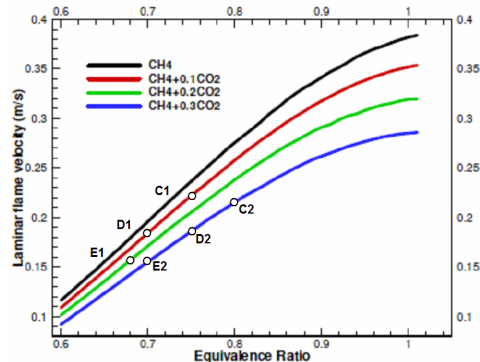


Figure 14: Calculation of the laminar flame velocity as a function of equivalence ratio and CO₂ dilution

Conclusions

This study is a preliminary effort to assess the feasibility of a low cost CO₂ capture process in oxygen-enriched air combustion of fossil fuels. The feasibility study is conducted for methane as fuel. The global objective of the project is to demonstrate that by combining careful analysis of the combustion process and that of oxygen generation and membrane CO₂ capture processes, an optimized hybrid process can be proposed in-between oxyfuel combustion and conventional post-combustion CO₂ capture. The optimisation should confirm reduced oxygen generation and CO₂ capture costs, flame stability and acceptable emission levels in particular for NO_x, CO and UHC.

Numerical simulations have been conducted to demonstrate the global energetic feasibility of the

process and to explore the flame and emission characteristics for various equivalence ratios, pressures, and CO₂ dilution rates relevant for gas turbine applications.

In addition experimental studies have been conducted to determine CO₂ dilution effects on laminar and swirl stabilized turbulent methane/O₂/N₂ flames.

The combined results of this integrated approach indicate that oxygen enriched air combustion of fossil fuels in association with CO₂ capture by membrane processes could be an innovative solution for low cost CCS technologies.

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