Oxy-combustion in gas turbine applications

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CONTENTS

ABSTRACT

Faced with the increasing concern about the effect of greenhouse gases in global warming, Carbon Capture and Storage technologies are developed. Oxy-combustion is one of these techniques; it consists of separating the nitrogen from the air and using the O_2 (diluted in CO_2) as an oxidant so that the resulting flue gases are mainly composed by carbon dioxide and water vapour and the capture of CO_2 can be done easily after condensing the steam. Changing the working fluid from air to O_2/CO_2 modifies combustion properties what might have consequences on the range of operability of the combustor. In order to design a combustor for oxy-fuel cycles in gas turbine applications, the differences between air and oxyfuel's operational zone at low and high pressures are studied. For comparing their stability, laminar flame speed is computed for air-fuel and oxy-fuel mixtures near stoichiometric equivalence ratios (1-0.95). Diffusion effect is studied as a possible cause of the change in combustion properties when modifying the working media by computing the residence time of blowout of the same mixtures.

INTRODUCTION

The effect of the greenhouse gases in the atmosphere is pointed as the cause of Global warming. Faced with the increasing public concern about this phenomenon, technologies for capturing and storing carbon dioxide are being developed. Carbon Capture and Sequestration techniques allow capturing the CO_2 emitted by Fossil Fuel Power Plants and store it such that it never arrives to the atmosphere.

CCS procedures consist of three stages: the capture of carbon dioxide, its transport to suitable storage places and its sequestration in underground geological formations or in the ocean.

Engineers propose three different solutions to capture carbon dioxide [1]: pre-combustion, post-combustion and oxyfuel combustion. In post-combustion capture technology, CO_2 is removed from the flue gases after combustion using acid gas separation processes. In contrast, pre-combustion capture technology takes out the CO_2 before the combustion: it modifies the fuel to convert it into H_2 (used as fuel) and carbon dioxide. The third technology used is oxyfuel combustion.

Oxy-combustion refers to burning fuels in pure oxygen or a mixture of oxygen and carbon dioxide. The main idea is that, when burning with oxygen, exhaust gases are composed almost exclusively of carbon dioxide and steam. Subsequently, carbon dioxide capture can be done easily and efficiently by condensing the water of the exhaust gases. Because excessive temperatures attained with pure oxygen prevent undiluted combustion, the flue gases are cooled and re-circulated to the compressor; the oxidizer becomes a mixture of oxygen and carbon dioxide.

This method also offers the advantage of drastically reducing NOx emissions since there is little nitrogen involved in the reaction. Although theoretically the amount of nitrogen participating in the reaction would be zero, in practice is not, as there is some nitrogen left in the working media. The air is split into oxygen, nitrogen and argon in the Air Separation Unit (ASU) which needs energy to operate. Thus, the quantity of nitrogen left in the air is a balance between the oxygen purity needed and the energy required to obtain it. This balance is normally fixed at 95% pure oxygen [2] and explains the presence of NOx in the exhaust gases.

Oxyfuel’s major drawback is the energy required by the ASU, which reduces the efficiency of the power plant. Thus, it is required to reduce to minimum the oxygen used in the combustion.

Besides, changing the oxidizer from air to oxygen diluted in carbon dioxide has implications for the combustor, turbine and compressor as well as for the cycle itself (e.g. oxy-combustion applied in combined cycles may operate at high pressures to be efficient). Machinery design for oxyfuel gas turbine´s applications is in a preliminary state, as little investigations has been made in this subject and no power plant is working with this method yet.

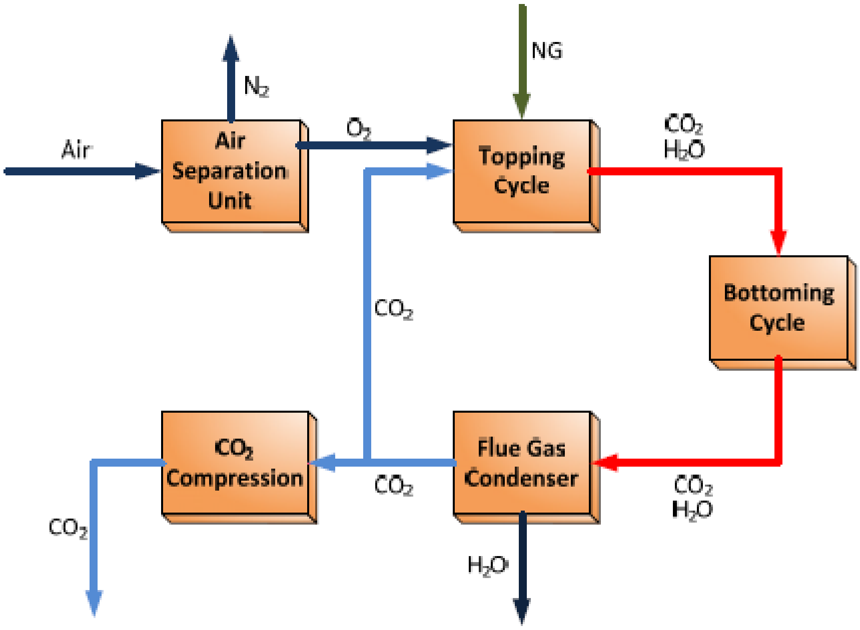


Figure1. Oxyfuel cycle

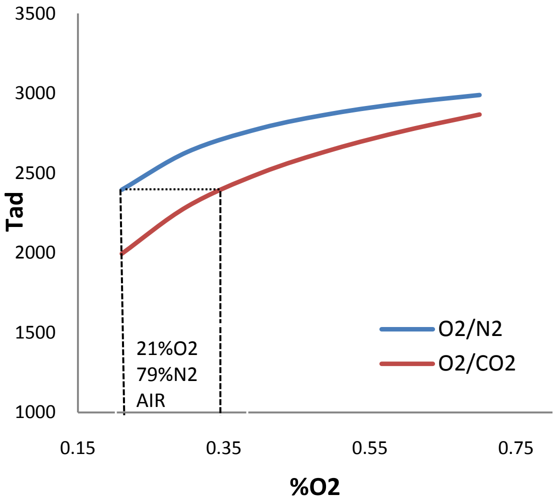
CO_2 effects on combustion properties when comparing to air

Oxidizer alteration affect combustion properties as it modifies:

- i) heat properties of the mixture and adiabatic temperature
- ii) transport and thermal properties
- iii) chemical rates of reaction
- iv) radiative heat transfer.

Since CO_2's specific heat per mole and per mass is higher than nitrogen's; more energy is required to raise the temperature of the mixture. Therefore, at the same equivalence ratio and same percentage of oxygen in the oxidizer, the adiabatic temperature reached by CO_2/O_2 is expected to be lower than N2/O2 (Figure 1)· For obtaining the same temperature as air, oxy-combustion needs more percentage of oxygen in the oxidant. For instance, to obtain the same adiabatic temperature as air at stoichiometric conditions, 35%O_2 diluted in CO_2 is needed.

Adiabatic temperatures in the range of work of combustors in combined cycles (1600-2200K) would be achieved by using between 14 and 25% concentration of oxygen in the oxidant. Even if 2200K is high to be considered as the average working temperature in a combustor, it can be reached in the primary zone of a combustor for gas turbine applications.



$C_{p\ CO2}$	$C_{p\ N2}$
1076 J/kg K	1074 J/kg K
47300 J/mol K	30009J/mol K

Figure 2. Adiabatic flame temperature dependence on %O2using O2/N2 and O2/CO2 as an oxidant for stoichiometric flames. (Tin=667K, p=1atm,$\varphi_{air}=\varphi_{oxy}=1$) Specific heats per mass and per mole at 673K are also showed.

The higher specific heat capacity of CO_2 might also have consequences on the laminar flame speed, as heat transfer from the hot products to the cool reactants is essential to heat the unburned products so that reactions can occur. A higher specific heat capacity is associated with lower flames temperatures; the flame speed of oxyfuel flames is expected to be reduced when compared to air.

Although N_2 and CO_2 have similar thermal diffusivity and viscosity, they present different mass diffusivity which affects the transport properties of the mixture. CO2 has a lower mass diffusivity and, thereby, less molecular diffusion.

CO_2 has also chemical effects on the combustion. Many studies point out that CO_2 is not an inert gas but participates in the reaction basically through $CO_2 + H \leftrightarrow CO + OH$ [3][4][5]. This reaction competes for H radicals with the chain branching reaction $H + O_2 \leftrightarrow O + OH$, it reduces considerably the concentration of H and O radicals in the reaction and, thus, the burning rate of fuel [6]· F.Liu et al. [5] showed the chemical and transport/thermal effect of CO_2 on the burning velocity by creating a compound with the same transport and thermal properties than CO_2 but chemically inert; the differences between thermal-diffusion and chemical effects can be clearly seen in that paper. CO_2 has also chemical effects on CO emissions, which are increased. The main causes of this augment are CO_2 reaction with hydrogen, its reaction with methylene group $CH_2 + CO_2 \leftrightarrow CH_2O + CO$ and, at high temperatures, its thermal dissociation [7]. Other studies point out that not only the CO equilibrium emissions are higher, but also CO emissions at a fixed residence time increase; this is due to the slow burning rate of intermediate CO[8].

There is some discrepancy on CO_2 third body efficiency. Some studies show that CO_2 has a third body efficiency between 2,4 and 2,6 higher than nitrogen in the reaction of recombination $H + O_2 + M \leftrightarrow HO_2 + M$ [9][10], meaning that this reaction will also compete for H radicals with the chain branching reaction and decreases the stability of the flame. On the other hand, this theory is refuted by molecular studies which defends that CO_2 has no anomalous third efficiency [11].

Finally, CO_2 is considered as a radiating specie. A high concentration of it increases non-luminous radiation and, therefore, mixture emissivity and radiative heat transfer[12][13]. Lower concentrations of oxygen are required to reach a comparable adiabatic flame temperature as a consequence of the increase of radiative heat; the decrease of oxygen is approximately of 2-3% of oxygen due to this reason.

High pressure effects on combustion properties

Oxy-fuel cycles have to work at high pressures as the efficiency of a combined cycle is only acceptable under these conditions due to the working fluid change. Besides, high pressure helps to the removal of sulphur dioxide after combustion and to the capture of nitrogen leakage in the combustor. Furthermore, the volume of CO_2 is lower under high pressure and its sequestration becomes easier. Increasing the pressure has also consequences in the combustion properties.

From a thermal point of view, heat capacity increases logarithmically with pressure.

Kinetics is also affected by pressure. Reactions rates increase with pressure. On the other hand, Westbrook and Dryer show that the increase in pressure benefits third order reactions; the reaction of recombination $H + O_2 + M \leftrightarrow HO_2 + M$ comes into play and competes for hydrogen with the chain-branching reaction $H + O_2 \leftrightarrow O + OH$, which reduces the pool of free radicals H and O and, therefore, it slows down the speed of the flame [14]. CO emissions might be reduced as CO equilibrium concentration is reduced with pressure. Besides, the effect of CO intermediate would be less critical at low residences times as the reactions are accelerated.

Regarding the radiative power' dependence on pressure, studies demonstrate that the non-gray radiation increases with pressure [15].

Operability zone of oxy-fuel cycles

Changing the working fluid of the cycle from air-fuel to CO_2/O_2-fuel might reduce the operability of the system. Oxy-combustion seems to be a trade-off between stability, emissions and temperature.

Outlet temperature is one of the parameters which should be considered when designing a combustor, since an excessive temperature can damage the machinery. Thereby, temperature has to be controlled. In air-fuel mixtures, controlling the outlet temperature can be achieved by changing the equivalence ratio. In oxy-combustion one degree of freedom is added as the composition of the oxidant can be changed. Hence, in oxyfuel cycles the temperature can be controlled by changing the $\%O_2$ in the oxidizer or the equivalence ratio.

However, all the O_2 introduced that cannot be converted in a profitable energy (meaning putting more O_2 without increasing the combustion efficiency) is penalized with a loss of efficiency of the cycle due to the high cost of separating the oxygen from air. For these reasons the cycle should operate near stoichiometric conditions.

O_2 emissions are also of interest, as it corrodes pipelines and other materials. Figure 3 shows the concentration of O_2 in the equilibrium dependence with the equivalence ratio. It has to be pointed that combustion in a CO_2 environment produces more oxygen emissions than air, as more oxygen is involved in the reaction for reaching the same adiabatic flame temperature. Higher limitations for O_2 emissions established for pipelines are 200ppm, that are reached for oxy-fuel mixtures at equivalence ratios of 1, 1.05 and 1.2 for adiabatic flames temperatures of 1600K, 1800K and 2200K.

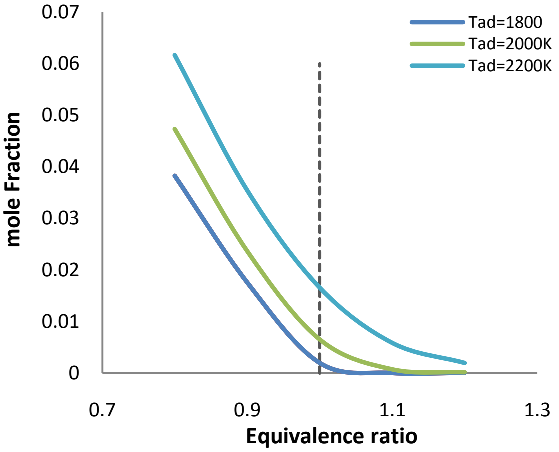


Figure 3. Equilibrium O_2 concentration for oxyfuel mixtures at different adiabatic flame temperatures and different equivalence ratios

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CO emissions are associated to an energy that had not been used in the reaction and, thereby, a decrease in the combustion efficiency. Furthermore, machinery as pipelines has limit specifications for these emissions.

Besides, CO emissions imply an increase of fuel (and thereby of costs) for the same power output. CO_2 is not inert but it participates in the reaction reducing the mean fuel consumption rate in the flame region [6]. Increasing the equivalence ratio of the mixture above a limit might lead to promote the reaction between fuel and carbon dioxide without increasing the amount of oxygen burned

While increasing the adiabatic flame temperature increases CO emissions (Figure 4). Limits of 0,1%CO imposed by pipelines are reached at equivalence ratios of 1.02, 1 and 0.3 for adiabatic flames temperatures of 1600K, 1800K and 2200K.

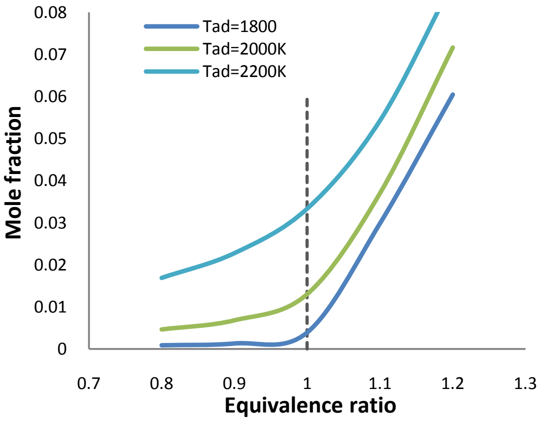


Figure 4. CO equilibrium emissions dependence with equivalence ratio in oxyfuel mixtures at different adiabatic flame temperatures.

Stability is also a parameter to take into account in oxy-fuel flames. There are four critical stability issues that might limit the operability zone of the flame: blowout, flashback, combustion instabilities and autoignition. Blowout refers to the flame blown away from the combustor and it occurs when the local flame velocity is not greater than the local gas velocity at any point causing a system failure. On the contrary, flashback occurs when the local flame velocity is greater than the local gas fluid causing the flame to move towards the unburned mixture which may cause explosion in fuel/air supply. Combustion instabilities [16] are damaging pressure fluctuations caused by fluctuations of heat release in the combustor. Finally autoignition refers to the spontaneous ignition of the unburned mixture.

Since changing the working media from N_2 to CO_2 is believed to diminish the local flame velocity [5], blowout seems more likely to occur in oxyfuel mixtures than flashback or autoignition. Thus, blowoff seems to be an operability issue to consider in these mixtures.

The operability zone of oxy-fuel mixtures might be limited by stability, CO emissions, O_2 unburned and higher temperatures. Figure 5 shows the operability zone of oxy-fuel mixtures, each point of this operability zone is associated with an equivalence ratio and adiabatic flame temperature and, therefore, mole fraction of oxygen involved in the reaction.

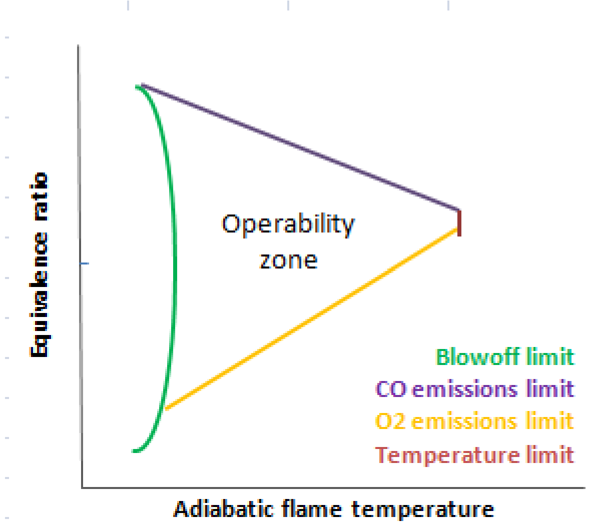
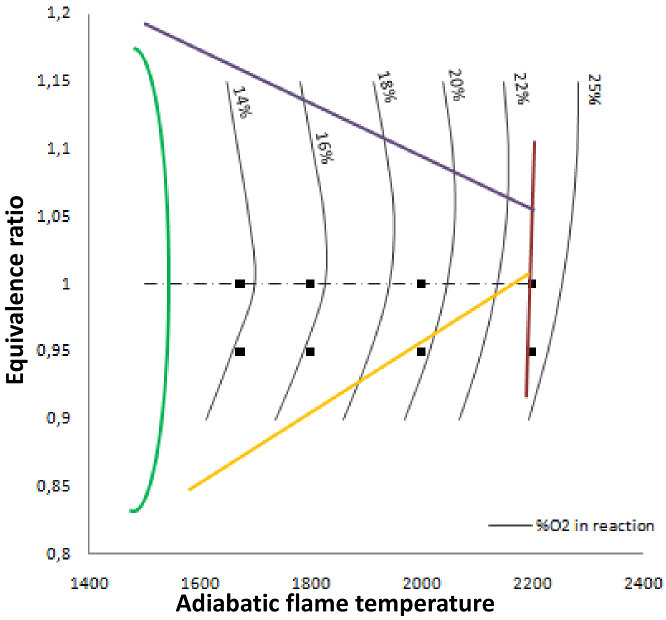


Figure 5. Operability zone for oxyfuel mixtures

While doing this work, other studies about oxyfuel flames stabilities appeared. These studies show that the timescales associated with oxyfuel combustion are maximum when the minimum concentration of O_2 is involved in the reaction [17] Therefore, at minimum oxygen involved in the reaction it is expected to have the less concentration of O_2 in the unburned mixture but the slower kinetics (less stability of the flame).



The stability of oxy-fuel mixtures marked in Figure 6 are studied in the following and it is compared to air mixtures. It is worthy to mention that even if a combustor for gas turbine applications would never operate in average higher than stoichiometric conditions due to the increase of CO emissions, the primary zone of a combustor can work under these conditions.

MATERIALS AND METHODS

Flames extinguish when the reaction is slower than the rate of supply of reactants; when does it occur depends on laminar flame speed, pressure and residence time. To study the operational differences between air and oxy combustion, laminar flame speed and blowout residence time are studied for both of them, as they are characteristic parameters of the stability of the flame. In order to compare the stability under the same operational conditions, all the mixtures are considered to reach the same the adiabatic flame temperature.

Blowout residence time is determined by simulating a Perfectly Stirred Reactor. Even if this combustor is an idealization for combustion and may not predict accurate results for realistic flames, the trends predicted are considered correct [18]. In PSR, combustion is considered a balance between the rate of heat generation by the reaction and the rate at which heat is removed from the reactor by bulk fluid motion (transport properties are not considered); thus, combustion occurs if the heat transfer term is not excessive compared to heat generation term. As heat generation has associated timescales, combustion will be successful only if the residence time is higher than the time required for reacting and, for that reason, blowout residence time is considered a parameter to measure the stability of the flame.

Laminar flame speed of a free propagating, adiabatic, planar premixed flame is also calculated. In that case, the rate of heat generation balances both diffusion and convection heat. Laminar flame speed is inversely proportional to the reaction time; the faster is the burning rate of the flame, the less time is needed for the reactions to occur and, therefore, it is more stable. A chemical timescale can be easily obtained by dividing the thickness of the reaction zone by the flame speed as showed bellow.

$$\tau_c = \frac{\delta}{S_L}$$

Calculations are made at 1atm and 39bar, not only to compare the real circumstances under which an oxyfuel cycle must operate (39bar) with the circumstances under which experimental data can be obtained easily, but also to investigate the pressure effect in the operability zone. These parameters are also determined for different oxyfuel equivalence ratio (Phi=1 and Phi=0.95), with the purpose of determining if there is a meaningful difference between these conditions.

Cantera programming

Program assumptions

GR-Mech 3.0. [19] chemical reaction mechanism and NASA polynomial thermodynamic data base are supposed when using Cantera. Next, a discussion about the validity of these assumptions is provided.

Ideal gas is assumed when using Cantera software. This assumption is valid at low pressures when particles are separated enough to assume that their volume is negligible and that attraction forces don’t act between particles. However, at high pressures, the molecules are closer and the attractive forces come into play. Hence, in order to validate Cantera simulation, it becomes necessary to verify the accuracy of ideal gas supposition at 39bar.

With the aim of quantifying the error done by assuming ideal gas in the simulation, enthalpies obtained by Cantera are compared to those obtained by REFPROP [20]

To implement a gas mixture in Cantera software a specific constructor which includes thermodynamic, kinetics and transport properties is needed. This constructor assumes the Ideal Gas Equation of State and it uses NASA polynomial parameterization to characterize the thermodynamic properties of species. This parameterization consists in considering thermodynamic properties as seven term’s polynomials depending on temperature but independent of pressure. Each specie has different thermodynamic properties, and, thus, has different polynomial coefficients. In contrast, REFPROP is a software that uses the most accurate equations available for the thermodynamic and transport properties to calculate the state points of the fluid or mixture. Therefore, REFPROP is often used to simulate real gases.

In this context, enthalpy of the same specie (CO2) is calculated with both softwares at two different pressures. In order to eliminate the influence of different reference values when calculating enthalpy, the variation of enthalpy between the same temperatures is computed. The results are showed bellow:

REFPROP	**Enthalpy [kJ/Kg]**			**NASA**	**Enthalpy [kJ/kg]**		
	T=1400K	**T=1300K**	**ΔH(kJ/kg)**		**T=1400K**	**T=1300K**	**ΔH(kJ/kg)**
P=10bar	2140,6	2006,6	**134kJ/kg**	**P=10bar**	1652,4	1518,5	133.9kJ/kg
P=39bar	2141,4	2007,2	**134kJ/kg**	**P=39bar**	1652,4	1518,5	**133.9kJ/kg**

Table 1. Enthalpy increments at high temperatures at two different pressures calculated using NASA polynomials and REFPROP

From the results, it can be seen that NASA polynomials don´t consider the effect of pressure, but REFPROP does. Even if it does, the effect of pressure at 39 bars can be neglected since the results are almost the same at high and low pressures. However, the question raised before was if NASA polynomials, assuming ideal gas, were a good approximation to a real gas at high and low pressures. From the calculations done it´s possible to conclude they are. The relative error between values at both, low and high pressure, is 0.07%, low enough to consider that working with Cantera ideal gases is not a source of error.

GRI-Mech 3.0 [19] is a list of typical chemical and rate reactions that can be found in the combustion of natural gas that is used by Cantera as chemical data. It also includes a thermodynamic package based on NASA polynomials and a transport package. It is important to point that this mechanism has been optimized for air/natural gas mixtures, at adiabatic flame temperatures from 1000 to 2500K, pressure from 10torr to 10atm and equivalence ratio from 0.1 to 5 in premixed flames.

It is extrapolated that the chemical mechanism is also suitable for different oxidizer (O2 /CO2). Reinke et al predict that is not enough accurate for calculating ignition delay times and provide an explanation of what is the mechanism which is missing [21]. However, seeing that the computation of laminar flame speed carried with MECH-GRI 3.0. by Liu [5] is in good agreement with the experimental data, the mechanism has been considered suitable for the purpose of the work. Besides, other studies show that CO emissions are well predicted under oxyfuel conditions [8].

Regarding the validity of the mechanism at pressures around 39bar, some studies [22] [23] show that deviation between simulation using GRI-MECH 3.0 and experimental data above 40atm can be neglected. On the other hand, Ogami and Kobayashi find out that, even if GRI-MECH3.0 is valid to predict combustion patterns at high pressures and temperatures, the previous version of this mechanism (GRI2.1) fits better the experimental data under these conditions [24]. GRI-MECH3.0 has been finally chosen; not only because the above mentioned study shows that trends are well-predicted at high pressures, but also because no data has been found to support the accuracy of GRI2.1' predictions in a CO_2 environment.

Thus, when using Cantera for calculating laminar flame speeds at different pressures, the increase in heat capacity with pressure would not be taken into account. Another observation to make is that the third body efficiency of carbon dioxide in the reaction of recombination is considered 1,5.

Perfectly Stirred Reactor and Laminar flame speed programing

The program consists of three parts: equivalence ratio or oxidizer composition's calculation, the Perfectly Stirred Reactor simulation and laminar flame speed computation.

All of them are encoded with Cantera; PSR simulation uses Cantera with MATLAB interface, while the laminar flame speed computations are made with Cantera's Python interface. The equivalence ratio and oxidizer composition's calculations have been written with both interfaces as they provide useful information for both, PSR and laminar flame, codes.

A summary of the program is shown in figure 7.

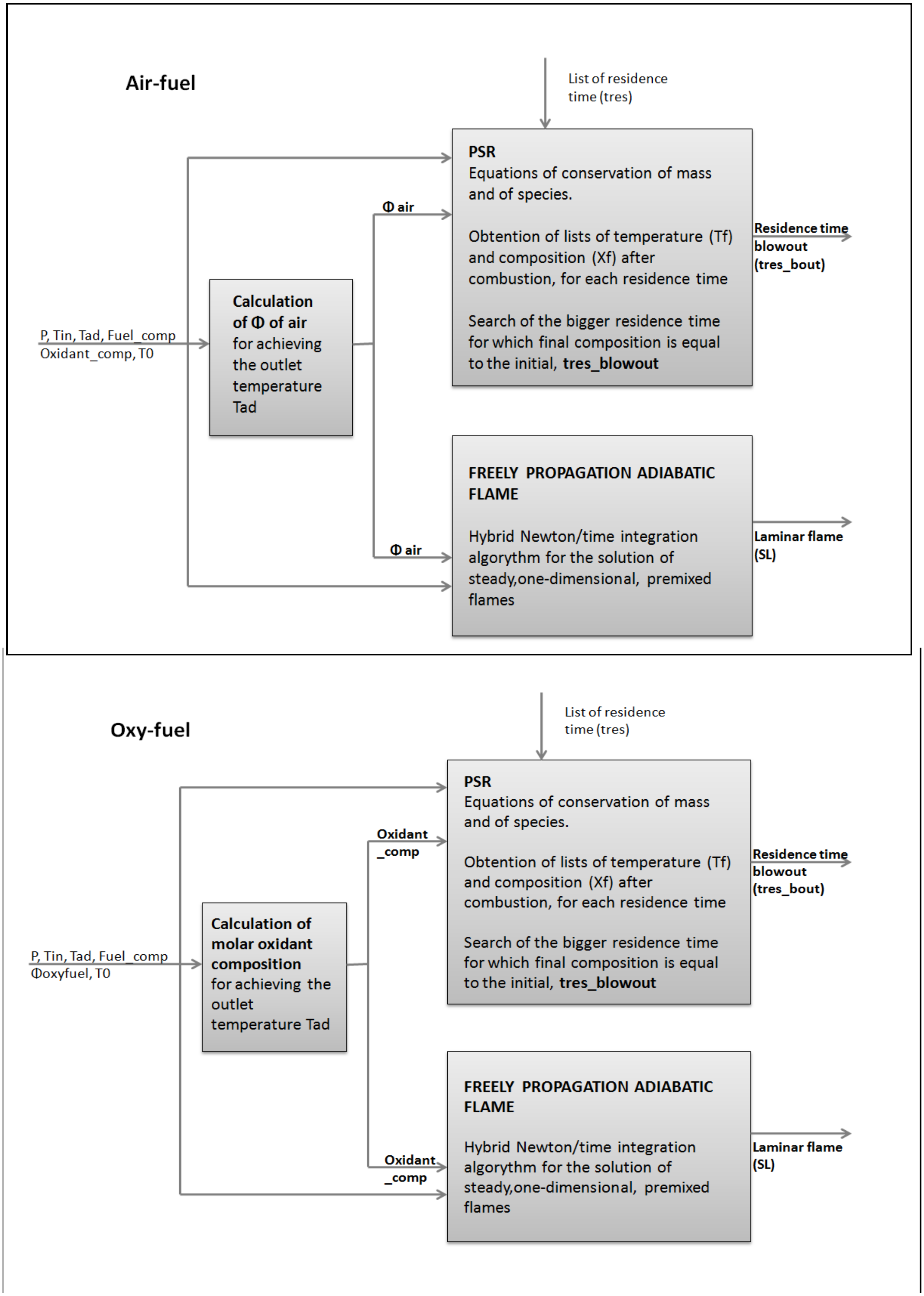


Figure7. Program design

The first step is to obtain the equivalence ratio for air-fuel mixtures and the percentage of CO_2 or oxidizer composition for the oxy-fuel mixtures that attain the required adiabatic flame temperature. For both of them, it has been done by assuming an initial equivalence ratio/oxidizer composition (depending on the mixture) and calculating which adiabatic flame temperature will be reached at constant pressure. The obtained value is compared to the target adiabatic temperature, so that the equivalence ratio/oxidizer composition can be corrected. Once the new equivalence ratio/oxidizer composition has been computed, the procedure is repeated as many times as is needed to accomplish the aimed temperature.

This is the only difference between air-fuel and oxyfuel programming, PSR and laminar flame speed would be determined in the same way for both oxidizers.

After calculating the composition of the inlet mixture of the Perfectly Stirred Reactor from the data obtained before, PSR code is called.

This program receives all the information of the inlet mixture and calculates the critical residence time below which the flame will blowout. In order to do that, it creates a list of different times and evaluates the PSR outlet's composition and temperature for all of them. Then, it searches for the residence time in which the final composition is almost the same that the initial one; meaning that it searches for the border residence time from which the mixture will not have time to react and the flame will blowout. In order that the inlet and outlet composition are considered the same, the difference between the compositions of all the species have to be lower than a set value. This limit has been fixed in 0.0001.

For obtaining the final composition Perfectly Stirred Reactor's mass, species and energy equations are considered:

$$\left.\begin{array}{ll} mass\ continuity: & \dot{m}_{in} = \dot{m}_{out} = \dot{m} \\ species\ continuity: & \frac{dy}{dt} = \frac{\dot{m}}{\rho V}(y_{in} - y) + \dot{w}_i \frac{Mw}{\rho} \\ energy\ equation: & \frac{dh}{dt} = \frac{\dot{m}}{\rho V}(h_{in} - h) \end{array}\right\} \xrightarrow{t_R=\frac{\dot{m}}{\rho V}} \left\{\begin{array}{l} \frac{dy}{dt} = \frac{1}{t_R}(y_{in} - y) + \dot{w}_i \frac{Mw}{\rho} \\ \frac{dh}{dt} = \frac{1}{t_R}(h_{in} - h) \end{array}\right.$$

Thus, the compositions during all the combustion are obtained by solving these ordinary differential equations.

Laminar flame speed is obtained using a hybrid method between Newton procedures and time integration [25] [26] for an adiabatic, freely propagating, one dimensional premixed flame already implemented in Cantera. Newton's method is a fast convergent algorithm to solve premixed flames; the problem is that it only works when the initial estimate solution is in its domain of convergence. On the other hand, implicit time integration invariably reaches the steady state but is slower.

The method used by Cantera starts from a very coarse grid and, after finding its solution points are added where the gradient changes rapidly. The coarse grid solution is used as initial guess to find the solution of the finer one. This method first tries to find the solution by using Newton algorithm, but, if it fails to converge, time integration is used to find a new estimation of the solution. Then, Newton method begins again. This procedure is repeated until a solution with enough accuracy is found.

For guaranteeing the accuracy of the solution found the program first obtain the species profile using a fixed temperature profile and without taking into account the energy equation. The solution obtained is used as initial guess for finding the real solution which considers the energy equation.

Cantera has implemented the Newton-time integration step algorithm in the function solve of the flame library. Thus, it is only necessary to define a)the criteria used to refine the domain (the ratio at which new points are added and which criteria is used to add this points e.g. maximum slope and curvature), b) the tolerances for the steady state at which it can be said that the solution is found, c) the maximum number of times the jacobian can be used before re-evaluating it in both steady and time integration states and d) the time integration and sequence of time steps for the time integration procedure e) a fix temperature for bounding conditions.

Freely propagating flames known boundary conditions are the cold boundary temperature and the fact that the gradient of temperature and species concentrations in steady state and at the hot boundary is nearly zero. As the mass flow rate is not an input data in one dimensional adiabatic freely propagating flames, from the flame governing equations showed in (figure 8) it can be seen that it is necessary to set another boundary condition in order to solve the problem For this reasons it is required to set a fixed temperature of a point. It is the user responsibility to choose that point so that the temperature and species gradients vanish in the steady state. In the case of doing a bad choice fixing this temperature, the resultant mass flow rate will be too low as some heat would be lost through the cold boundary.

$$Continuity \qquad \dot{m} = \rho u A$$

$$Energy \qquad m\frac{dT}{dx} - \frac{1}{c_p}\frac{d}{dx}\left(\lambda A\frac{dT}{dx}\right) + \frac{A}{c_p}\sum_{k=1}^{K}\rho Y_k V_k c_{pk}\frac{dT}{dx} + \frac{A}{c_p}\sum_{k=1}^{K}\dot{w}_k\, h_k W_k$$

$$Species \qquad \dot{m}\frac{dy_k}{dn} + \frac{d}{dn}(\rho A y_k v_k) - A\dot{w}_k W_k = 0$$

$$Ideal\ gas \qquad \rho = \frac{p\bar{W}}{RT}$$

Figure 8. Governing equations of an adiabatic freely propagating flame

RESULTS

Validation of the laminar flame speed computations

As explained before, the user has to set a temperature in a point in order to run the computations of laminar flame speed. The value set is considered correct if the mass flow rate obtained is high enough. Otherwise, it would mean that heat has got lost in the cold boundary and, thereby, that the flame cannot be considered adiabatic. In order to validate the computations made the results of mass flow rate obtained are presented in Table 2.

	MASS FLOW RATE $\left(\frac{kg}{s\,m^2}\right)$					
	P=1atm			**P=39bar**		
Tad	**Air**	**oxy ϕ=1**	**oxy ϕ=0,95**	**Air**	**oxy ϕ=1**	**oxy ϕ=0,95**
1673	0,221	0,037	0,049	1,154	0,750	0,797
1800	0,324	0,074	0,090	1,821	1,067	1,158
2000	0,502	0,178		3,337	1,850	2,030
2200	0,668			5,333	3,285	3,554

Table 2. Mass flow rates obtained for different mixtures

The trends showed in the mass flow rate are considered correct, as it increase with pressure and with increasing the adiabatic flame temperature as showed by Glassman [18]. Furthermore, oxyfuel mass flow rate being lower than air matches with its associate slower kinetics and mass burning rate [6] [27]

Residence time of blowout and laminar flame speed computations

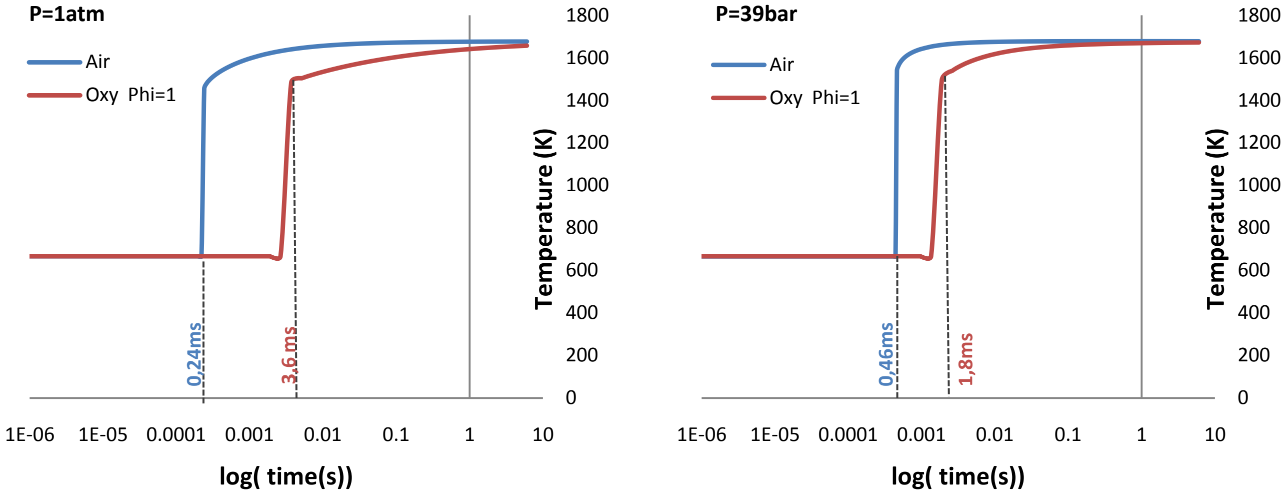
Combustion in a Perfectly Stirred Reactor is simulated for both air and oxyfuel oxidizers in order to calculate the residence time of blowout. As stated before, the adiabatic flame temperature is fixed for both systems in order to compare the combustion under the same operability conditions. Inlet and outlet temperature have been set at 667K and 1673K; these values are based on studies of oxyfuel cycles [28]. All the simulations have been done at inlet temperature 667K.

Adiabatic flame temperature of 1673K is obtained at atmospheric pressures in air at an equivalence ratio of 0,447, in stoichiometric oxyfuel mixture at 14,6%O_2 in the oxidizer and in oxyfuel mixture of equivalence ratio 0,95 at 15,3%O_2. At 39bar, the same adiabatic temperature is obtained, respectively, at an equivalence ratio of 0,447, 14,5% O_2 and 15,2%O_2. (table 3)

AIR			**OXYFUEL**			
					Φ=1	**Φ=0,95**
Φ	**P=1atm**	0,477	**%O_2**	**P=1atm**	14,6	15,3
	P=39bar	0,477		**P=39bar**	14,5	15,2

Table 3. Equivalence ratio for air and %O_2 in the oxidant for oxy-combustion required to reach T_{ad}=1673K

The dependence of the final temperature reached in the combustor and the residence time of the mixture is showed bellow for $CH_4/O_2/CO_2$ and CH_4/air flames at different pressures.

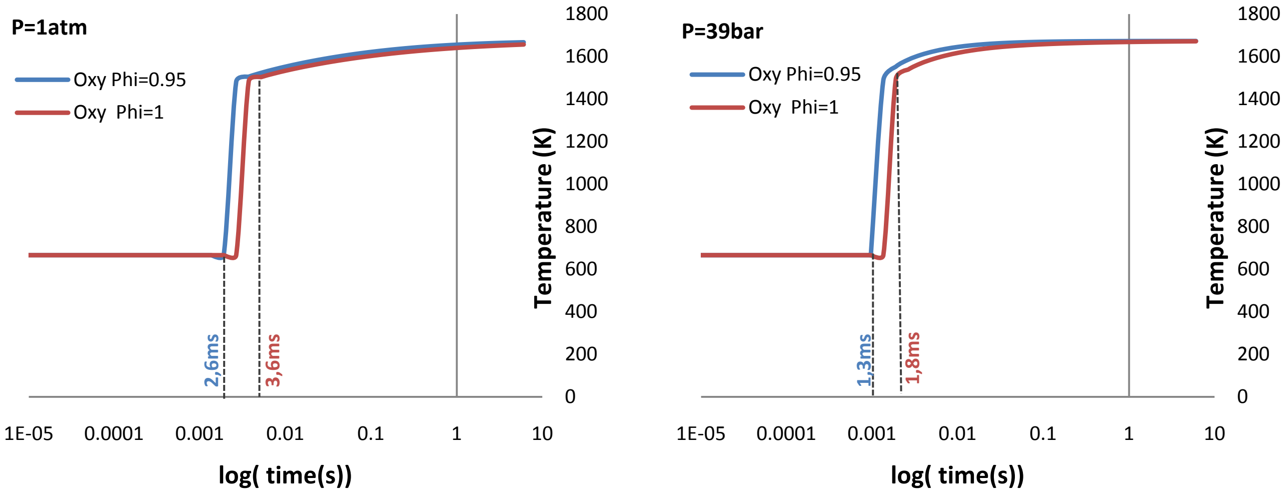


<u>Figure 9.</u> Final temperature reached in a PSR with different residence times for different reacting blends, air-mathane and CO_2/O_2-methane at p=1atm and p=39bar. T_{ad}=1673K

The results show that oxy-combustion needs more time than air to attain the same outlet temperature for both low and high pressures. The residence time of blowout in air is 0,24ms while in CO_2/O_2 is 3,6ms. The residence time of blowout of air increase with pressure while the one of CO_2/O_2 decreases.

Oxy-combustion with different equivalence ratio are also computed (Figure 10). For an equivalence ratio of 0,95, the residence time of blowout is 1ms which is less than for stoichiometric conditions and, therefore, the time required for reacting is shorter. Pressure effect is to reduce the residence time of blowout. By increasing the pressure the gap between both mixtures is reduced from 1ms to 0,5ms.

Table 4 resumes the blowout residence time results found.



<u>Figure 10.</u> Final temperature reached in a PSR with different residence times for oxyfuel mixtures at two different equivalence ratio: φ=1 and φ=0.95 and for pressures 1atm and 39bar. T_{ad}=1673K

		AIR	OXYFUEL	
	Phi	0,447	1	0,95
Residence time of blowout [ms]	P=1atm	0,24	3,6	2,6
	P=39bar	0,46	1,8	1,8

Table 4. Residence time of blowout *for air-methane and* CO_2/O_2-methane mixtures at p=1atm and p=39bar. T_{ad}*=1673K.*

For the same mixtures laminar flame speed of a freely propagating adiabatic flame is computed.

		AIR	OXYFUEL	
	Phi	0,447	1	0,95
Laminar Speed [cm/s]	P=1atm	42,78	5,06	6,67
	P=39bar	5,80	2,63	2,81

Table 5. Laminar flame speeds (cm/s) for air-methane and CO_2/O_2-methane mixtures at p=1atm and p=39bar. Equivalence ratio of 1 and 0.95 has been considered in oxyfuel's case. Reactant conditions are T_{in}*=667K.* T_{ad}*=1673K*

Laminar flame speed is larger in air, comparing to oxyfuel mixtures at both pressures; stoichiometric oxyfuel mixtures presents the slower velocity. As observed before, the difference of laminar flame speed between air/CH_4 and $CO_2/O_2/$ CH_4 is bigger at atmospheric pressure than at high pressures. The same trends are observed when comparing oxy-combustion at different equivalence ratios. Air reduces its laminar flame speed when increasing the pressure, which is consistent with the increase in residence time of blowout found before. Different tendencies are observed in oxyfuel cases; whereas residence time of blowout of oxyfuel mixtures decreases with pressure, laminar flame speed is also reduced. This disparity can be attributed to the fact that laminar flame speed is not a reaction timescale, even if it is strongly related to it, and, thereby, it cannot be directly compared to the residence blowout timescale. In order to compare the trends obtained in both experiments, laminar flame speed is used to calculate the chemical time of reaction ($\tau_c = \frac{\delta}{S_L}$). With this purpose, thickness reaction zone δ is computed using the definition $\frac{dT}{dz}\Big|_{zo} \delta = T_b - T_u$, where zo is the inflection point of the flame temperature profile $\frac{d^2T}{dz^2}\Big|_{zo} = 0$ obtained from the laminar flame speed computation.

		AIR	OXYFUEL	
	Phi	0,447	1	0,95
Thickness [mm]	P=1atm	0,736	3,387	2,612
	P=39bar	0,125	0,214	0,193

		AIR	OXYFUEL	
	Phi	0,447	1	0,95
Chemical time [ms]	P=1atm	1,72	66,8	39,14
	P=39bar	2,15	8,12	6,88

Table 6 Thickness of the reaction zone and chemical timescales for air-methane and CO_2/O_2-methane mixtures at p=1atm and p=39bar. Equivalence ratio of 1 and 0.95 has been considered in oxyfuel's case. T_{ad}*=1673K*

When changing the oxidizer from air to CO_2/O_2, the thickness of the reaction zone is enlarged. Effect of pressure is to reduce the thickness in both environments as pressure accelerates the rates of reaction. However, its diminution is more significant in oxyfuel mixtures. As discussed before, effect of pressure in laminar flame speed is to reduce it in both pressures, even if the effect is more noticeable in air.

Since laminar flame speed diminish less than thickness with pressure, chemical timescale increases in oxyfuel mixtures. In contrast, laminar flame speed in air increases more than thickness with pressure and thus, chemical timescale decrease. (Table 7)

		AIR	**OXYFUEL**	
	Phi	**0,447**	**1**	**0,95**
%of change with pressure	**Laminar flame speed**	86,44%	48%	58%
	Thickness Reaction zone	83%	94%	92,61%
	Chemical time	25,24%	-87,85%	-82,42%

Table 7. Percentage of change from 1atm to 39bar of laminar flame speed, thickness reaction zone and chemical time. (relative to atmospheric pressure)

Chemical timescale and blowout residence timescale (Table 4) present the same trends; timescale of air is increased with pressure while the one of oxyfuel mixtures is reduced, the difference between both is then reduced. Though, the results obtained are significantly different due to the combustion' simplification used for residence time of blowout determination which does not consider diffusion. In order to quantify the diffusion effect in timescales, the difference between timescales is calculated as well as the percentage of reaction time that is due to diffusion.

	AIR	**OXYFUEL**			**AIR**	**OXYFUEL**	
Phi	**0,447**	**1**	**0,95**	**Phi**	**0,447**	**1**	**0,95**
P=1atm	1,48ms	63,2ms	36,54ms	**P=1atm**	86,05%	94,61%	93,36%
P=39bar	1,69ms	6,32ms	5,08ms	**P=39bar**	78,60%	77,83%	73,84%

Table 8. Diffusion effect, timescale enlarge because of diffusion and percentage of reaction time due to diffusion

When comparing the oxyfuel mixtures, the thickness of the reaction zone is larger in stoichiometric conditions at both pressures. Oxyfuel thicknesses are also reduced with pressure; effects of pressure are higher in stoichiometric oxyfuel. The difference between the chemical times of the two mixtures is also reduced with the pressure; at atmospheric pressure it is from 27,74ms and at high pressure 1,25ms.

Flame structure

Flame structure is analysed for air and stoichiometric oxyfuel by plotting the concentration of species CH_4, O_2, CO, OH and H dependence with the flame advance

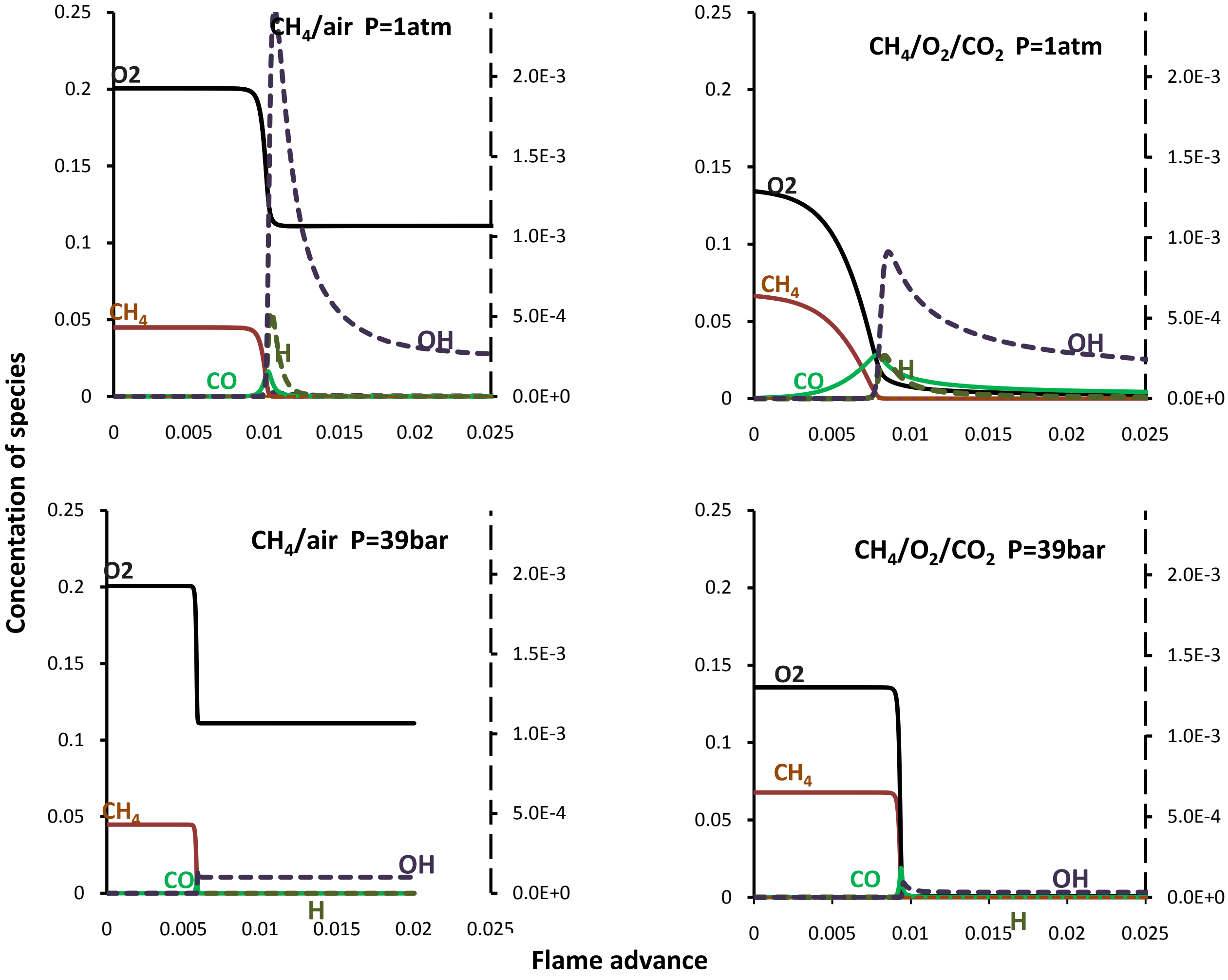
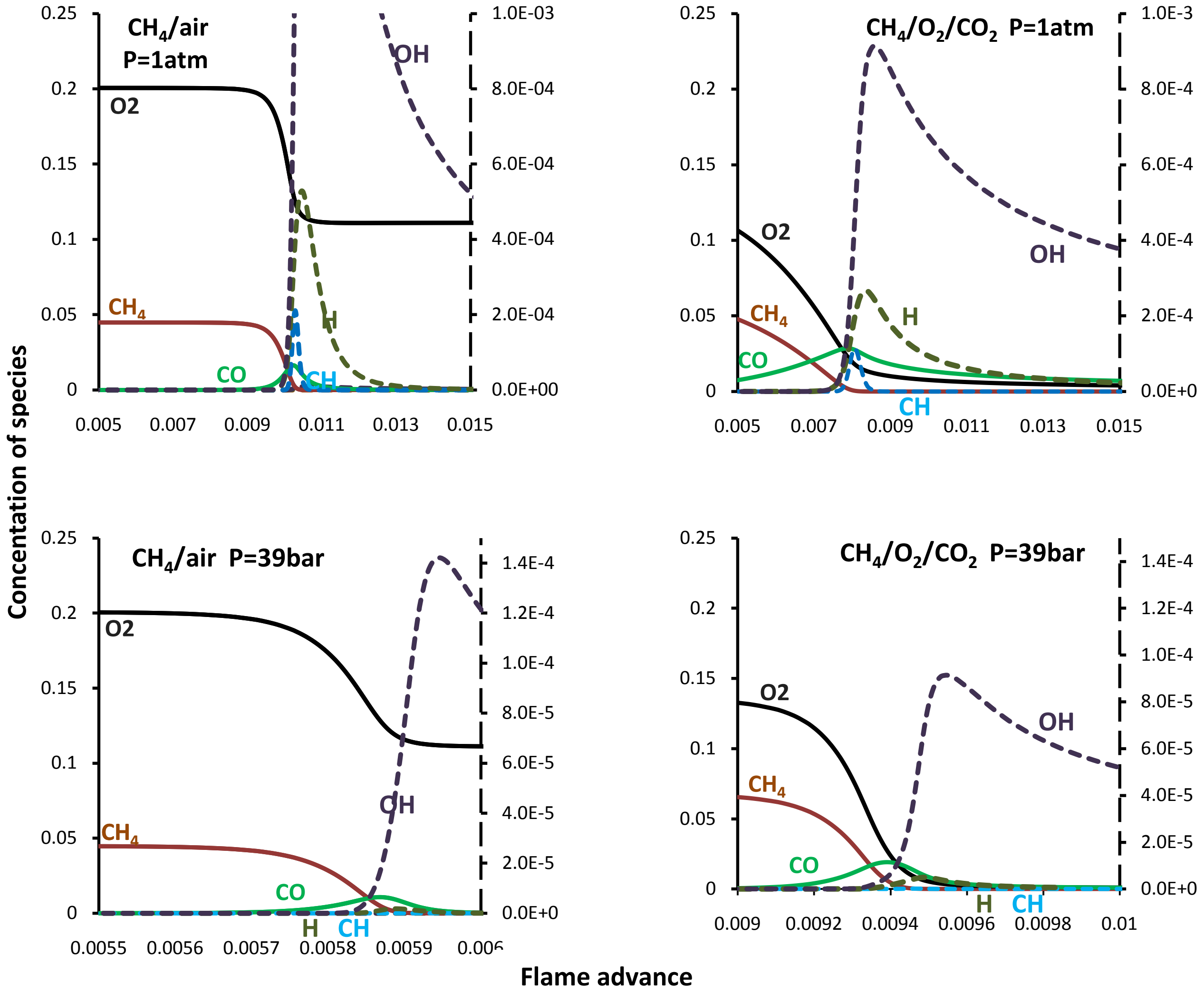


Figure 11. Flame structure of fuel-air and fuel-CO_2/O_2 mixtures at p=1atm and p= 30bar. T_{ad}=1673K.Dashed lines data is find in the right axe.

To identify better the reaction zone, a zoom is set. CH has been included; the concentration of CH radical has been multiplied by 10^4, so that it can be seen in the results.



<u>Figure 12</u>. Flame structure of fuel-air and fuel-CO_2/O_2 mixtures at p=1atm and p= 30bar. T_{ad}=1673K.

Differences between air and oxyfuel mixtures are noticeable when comparing flame structure. The first observation made is that O_2 concentration is higher in air since the %O_2 required to reach an adiabatic flame of 1673K is higher than in oxyfuel conditions where the temperature is controlled by adding CO_2. Besides, OH/H pool radicals are considerably reduced in a CO_2 environment, as well as CH radical. CH_4 and O_2 concentration's decrease in this ambient is more gradual than in air; same remarks are made for OH and H as well as for CO. In addition, intermediate CO concentration is increased significantly when changing the working media as well as CO equilibrium concentration.

When increasing the pressure, reactions are accelerated by pressure, as it can be seen from the diminution of the thickness reaction zone and from the increase of radical concentration, which is made in less flame distance in both cases. OH/H pool and CH radicals are considerably reduced in air and oxyfuel, even if pressure has more effects on air. The intermediate CO radical and CO equilibrium concentration are reduced with pressure in both cases, as well as the O_2 equilibrium concentration of oxyfuel.

The differences between air and oxyfuel at high pressures are reduced; thickness reaction zone' difference between them is diminished considerably. The radical pool of H and CH is greater in oxyfuel than in air under these conditions in contrast with the results at one atmosphere. OH radical concentration in oxyfuel remains smaller than in air even if the difference between them is littler at high pressures. Differences between CO equilibrium concentrations of both mixtures are considerably reduced with pressure. Table 9 shows the H, CH, OH, CO peak quantities as well as CO and O_2 in equilibrium. In order to quantify the differences between the two mixtures at both pressures, the percentage of concentration' change of oxyfuel when comparing to air is calculated. This percentage is also computed for comparing each mixture change with pressure, as well as for comparing the difference between mixtures change with pressure.

H peak	**Oxyfuel**	**Air**	**Difference**	
P=1atm	2,67E-04	5,94E-04	3,27E-04	**-55,05%**
P=39bar	4,93E-06	1,84E-06	-3,09E-06	**167,93%**
	-98,15%	**-99,69%**	**-100,94%**	

OH peak	**Oxyfuel**	**Air**	**Difference**	
P=1atm	1,00E-03	2,50E-03	1,50E-03	**-60,00%**
P=39bar	9,00E-05	1,40E-04	5,00E-05	**-35,71%**
	-91,00%	**-94,40%**	**-96,67%**	

CH peak	**Oxyfuel**	**Air**	**Difference**	
P=1atm	1,13E-08	2,11E-08	9,80E-09	**-46,45%**
P=39bar	1,25E-11	3,40E-12	-9,10E-12	**267,65%**
	-99,89%	**-99,98%**	**-100,09%**	

CO peak	**Oxyfuel**	**Air**	**Difference**	
P=1atm	2,84E-02	1,64E-02	-1,20E-02	**73,17%**
P=39bar	1,91E-02	1,08E-02	-8,30E-03	**76,85%**
	-32,75%	**-34,15%**	**-30,83%**	

CO eq	**Oxyfuel**	**Air**	**Difference**	
P=1atm	4,00E-03	8,83E-06	-3,99E-03	**45200,11%**
P=39bar	2,30E-04	1,11E-06	-2,29E-04	**20620,72%**
	-94,25%	**-87,43%**	**-94,27%**	

O2 eq	**Oxyfuel**
P=1atm	2,40E-03
P=39bar	7,10E-04
	-70,42%

Table 9. H,CH,CO,OH peak concentration and equilibrium concentrations of CO and O_2. Percentages of species concentrations' change when comparing to air are showed horizontally and when comparing to low pressures vertically. The percentage of change with pressure between mixture is also computed. All the data is concentration in fraction mol.

Adiabatic flame temperature effects on residence time of blowout and laminar flame speed

In order to know how adiabatic flame temperature affects to the system the laminar flame speed and blowout residence time's dependance on adiabatic flame temperature is plotted (Figures 13, 14). Table 10 shows at which $\%O_2$ in the oxidant under oxyfuel conditions and equivalence ratio for air are these adiabatic flame temperature reached.

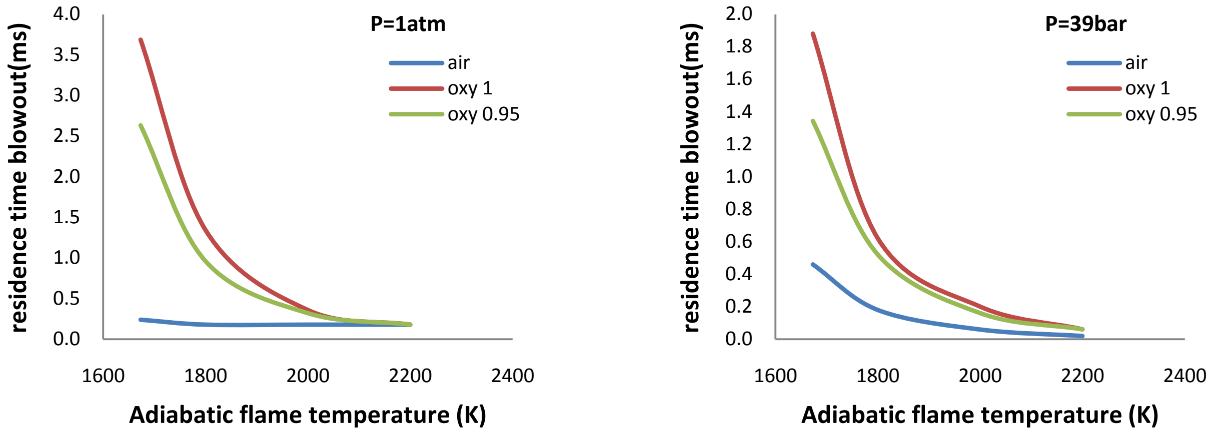


Figure 13. Residence time of blowout dependance with adiabatic flame temperature at p=1atm and p=39bar. T_{in}*=667K*

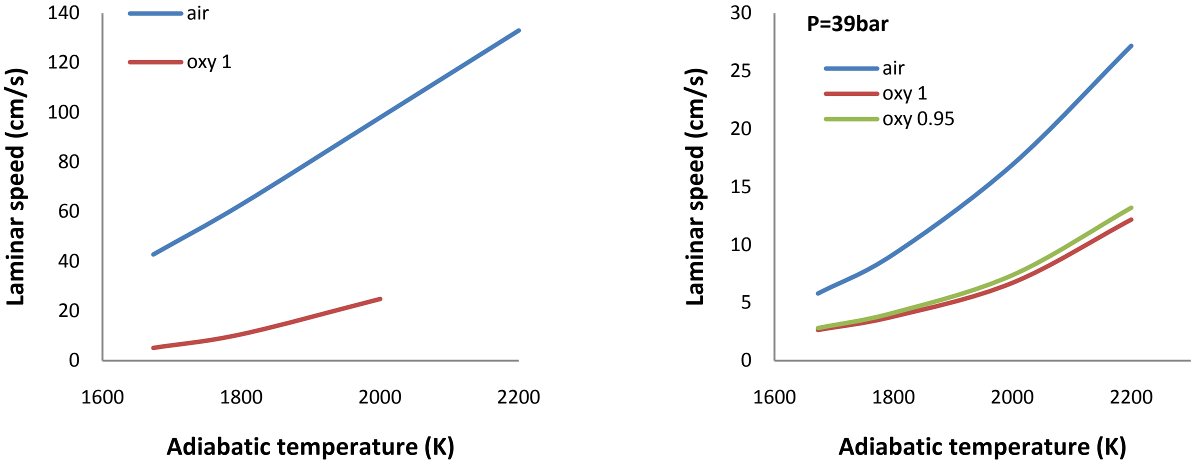


Figure 14. Laminar flame speed dependence on adiabatic flame temperature at p=39bar. T_{in}=667K

AIR		**Adiabatic flame temperature(K)**			
		T=1673K	**T=1800K**	**T=2000K**	**T=2200K**
Φ	**P=1atm**	0,45	0,52	0,67	0,73
	P=39bar	0,45	0,51	0,63	0,75

OXYFUEL			**Adiabatic flame temperature(K)**			
			T=1673K	**T=1800K**	**T=2000K**	**T=2200K**
%O_2	**Φ=1**	**P=1atm**	14,6	16,9	21,1	26,7
		P=39bar	14,5	16,7	20,3	24,4
	Φ=0,95	**P=1atm**	15,3	17,6	21,8	27,4
		P=39bar	15,2	17,4	21,1	25,1

Table 10. Equivalence ratio air-fuel and %O_2 required under oxyfuel conditions at equivalence ratio 1 and 0,95 to reach a determined adiabatic flame temperature.

At the same time as adiabatic flame temperature increases, residence time of blowout diminishes which might be logical as the equivalence ratio of air and the %O_2 in the oxidizer of O_2/CO_2 increases. The same trends are observed for laminar flame speed which increases while increasing adiabatic flame temperature (Figure 14).

At high pressures, less O_2 is required in the reaction. While the residence time of blowout for oxyfuel mixtures diminishes with pressure and adiabatic flame temperature, the one of air increases with pressure at low adiabatic flame temperatures and it diminishes with pressure at high adiabatic temperatures. In other words, at adiabatic flames temperatures of 1600K air needs more time to react at low pressure than at high pressure, at an adiabatic flame temperature of 1800K it needs approximately the same time at both pressures and for adiabatic temperatures higher than 1800K it is quicker at high pressures.

Laminar flame speed of both oxyfuel and air-fuel mixtures decreases with pressure for any adiabatic flame temperature. Effects of pressure in both, laminar flame speed and residence time are quantified by calculating the percentage of reduction of these parameters when increasing the pressure in each adiabatic flame speed.

RESIDENCE TIME OF BLOWOUT	**Adiabatic flame temperature(K)**			
%REDUCTION WITH PRESSURE	**T=1673K**	**T=1800K**	**T=2000K**	**T=2200K**
AIR	-91,67%	0,00%	66,67%	-88,89%
OXYFUEL ϕ=1	48,97%	53,87%	44,44%	

LAMINAR FLAME SPEED	**Adiabatic flame temperature(K)**			
%REDUCTION WITH PRESSURE	**T=1673K**	**T=1800K**	**T=2000K**	**T=2200K**
AIR	86,44%	85,40%	82,73%	79,57%
OXYFUEL ϕ=1	47,99%	64,16%	73,04%	

Table 11. Percentage of reduction of residence time of blowout and laminar flame speed from 1atm to 39bar at different adiabatic flames temperatures.

Results show that the percentage of reduction with pressure for residence time of blowout increases with adiabatic flame temperature for both air and oxyfuel mixtures; however, the rate of this increase is higher in air than in CO_2 environment. In addition, the percentage of reduction with pressure for laminar flame speed is reduced with adiabatic flame temperature for both mixtures and the rate of this increase is lower in air than in oxyfuel mixtures. For these reasons at the low adiabatic flame temperature considered, the differences in blowout residence time between mixtures tend to decrease with pressure, but at high adiabatic flames the gap increases.

DIFFERENCE BETWEEN OXYFUEL AND AIR	**Adiabatic flame temperature(K)**			
RESIDENCES TIME OF BLOWOUT	**T=1673K**	**T=1800K**	**T=2000K**	**T=2200K**
P=1atm	3,448	1,164	0,18	1E-06
P=39bar	1,422	0,44	0,14	0,04

Table 12. Difference between oxyfuel and air residences time of blowout.

Chemical effect analysis

Chemical effect is pointed as one of the main reasons for the increase of CO emissions. Besides, it has relationship with the stability of the flame, as it is pointed as one of the reasons for which oxy-fuel flames are slower than air ones.

In order to quantify this effect, a compound RCO_2 that has the same thermodynamic properties than CO_2 but it does not participates in the reactions has been created.

Results of CO and O2 emissions in the equilibrium at high and low pressures and for different adiabatic flames temperatures are showed in figure 14 and 15.

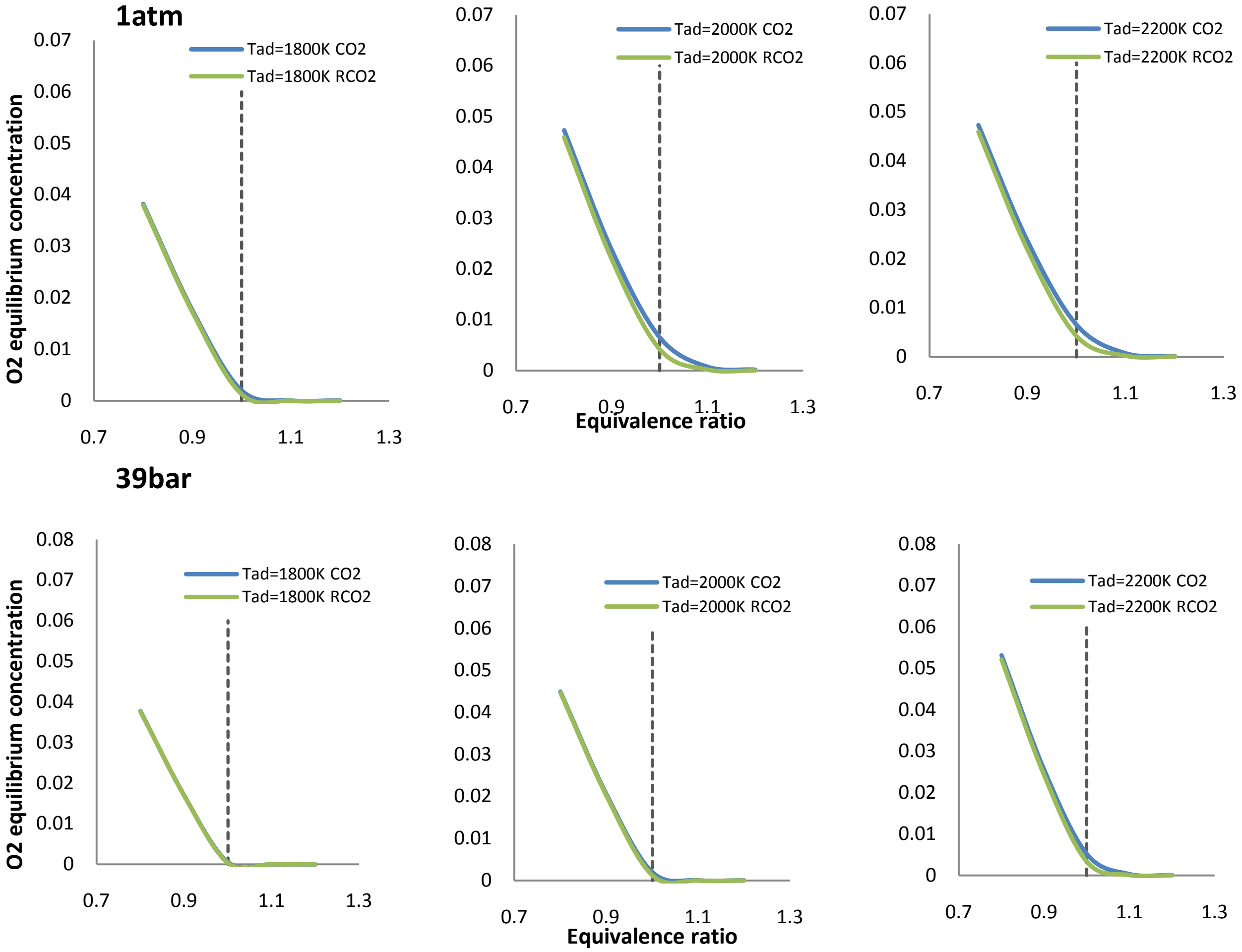


Figure 15. O_2 emissions in the equilibrium for RCO2 and CO2 mixtures at p=1atm and 39 bar for adiabatic flame temperatures of 1800K, 2000K and 2200K.

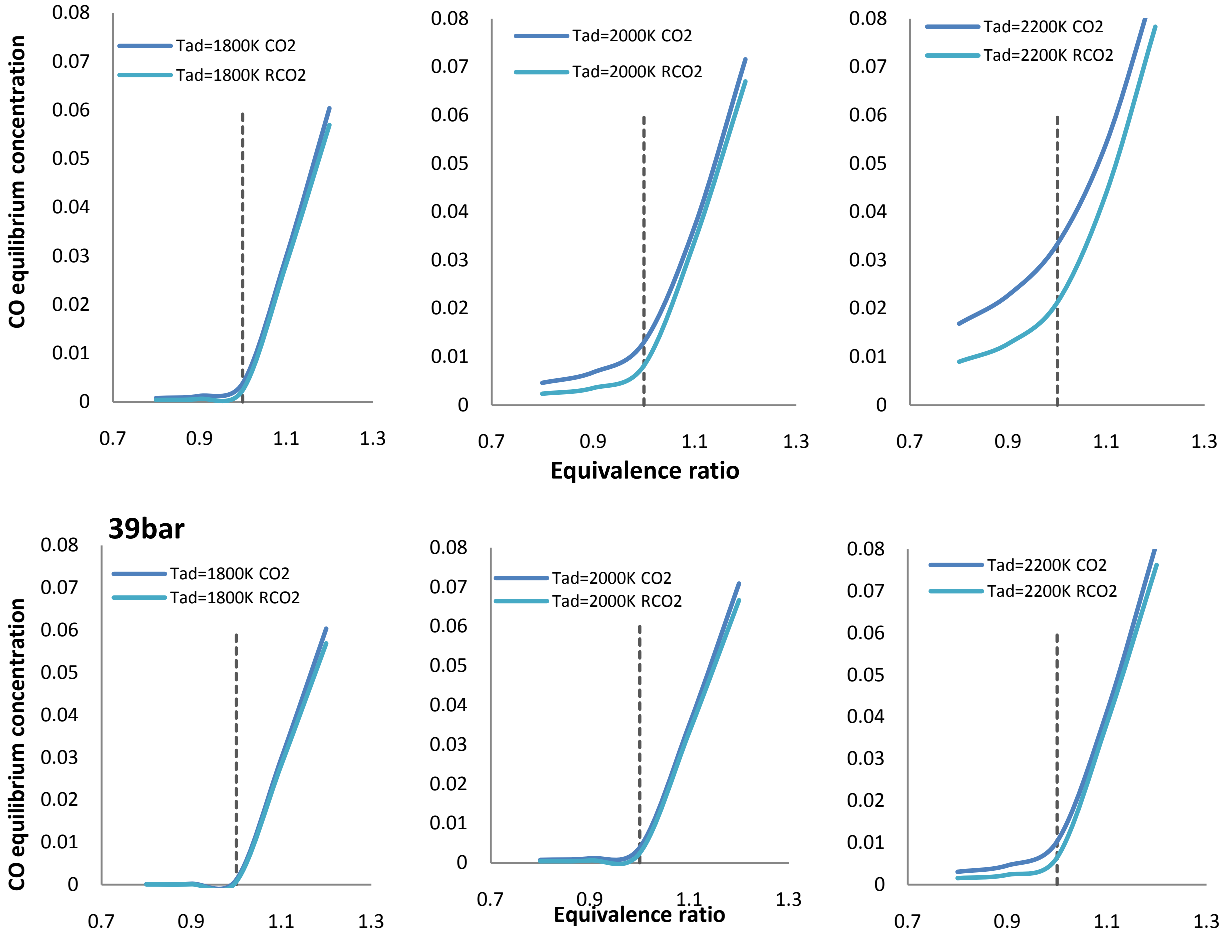


Figure 16. CO emissions in the equilibrium for RCO2 and CO2 mixtures at p=1atm and 39 bar for reaching adiabatic flame temperatures of 1800K, 2000K and 2200K.

The chemical effect of CO_2 increases when increasing the adiabatic flame temperature. However, this effect is significantly reduced with pressure.

Besides, it explains the higher reduction of laminar flame speed in air than in oxy-fuel mixtures. The inhibiting effect of CO_2 is less noticeable at high pressures, and thereby the reduction with pressure in the laminar flame speed due to recombination is less noticeable in oxy-fuel mixtures. The percentage of reduction with pressure of laminar flame speed in oxyfuel mixtures increases with adiabatic flame temperatures, as the chemical effect also does.

DISCUSSION

Combustion of air-fuel is more stable than in oxyfuel conditions, for the same adiabatic flame temperature, its chemical timescale is smaller, its laminar flame speed is larger and H/OH/CH radicals concentration is higher. Different mass diffusivity is discarded to be a major cause for the differences between air-fuel and oxy-fuel combustion, as the chemical timescales calculated with and without taking into consideration diffusion show the same trends. Differences are caused mainly by the higher heat capacity and chemical effect of carbon dioxide comparing to nitrogen. Chemical effect is perceived in oxyfuel's flame structure where CO concentration is higher than in air, and the chemical relaxation to the equilibrium is larger. Relationship with stability can be seen in laminar flame speed as it follows the same trends when increasing temperature and pressure.

At high pressures, the stability differences between the two cases decreases. This is due to the fact that decrease in the laminar flame speed with pressure in air is more significant than in oxyfuel mixtures. Recombination effect is more noticeable in air because of its higher concentration of H at atmospheric pressure as well as its higher concentration of O2. In addition, the decrease in reaction zone thickness with pressure is larger in oxyfuel mixtures, possibly due to the acceleration of the inhibiting reaction $CO_2 + H \leftrightarrow CO + OH$ with pressure and its slower concentration in the equilibrium.

As observed by Amato et al, the chemical effect of CO_2 is to increase CO equilibrium emissions (thermal dissociation of CO_2), as well as to increase intermediate CO (chemical effect) which causes emission's problems at short residence times. While increasing the pressure the equilibrium concentration of CO decreases as well as the rate of the reaction is bigger; in other words, the increase of pressure reduces the emission problems. [8]

The difference between chemical timescales for air and oxyfuel mixtures is reduced when increasing adiabatic temperature. This difference is reduced with pressure above a limit adiabatic temperature from which the difference between them increases; this is due to a bigger laminar flame speed reduction with pressure for oxyfuel while increasing adiabatic flame temperature compared to air. However, this effect does not seem to be important as the difference between them is small at this temperature.

Since less oxygen is involved in the reaction, stoichiometric oxyfuel mixtures presents slower kinetics than lean oxy-fuel ones, as remarked by Amato et Al. [17] However, at high pressures and at high adiabatic flame temperatures, the difference between chemical timescales for both mixtures is less significant.

CONCLUSIONS

The operability zone of oxyfuel cycles is largely reduced when comparing to air since oxy-combustion is shown to be more unstable and easier to blowout. However, at high pressures the differences in stability between both mixtures are smaller and CO emissions are reduced. Thus, the reduction of the operability zone by changing the oxidizer is not so significant at high pressures. Increasing the adiabatic flame temperature will also reduce the differences between them.

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