CHEMICAL KINETIC EVALUATION OF OPTIMAL POST-COMBUSTION CONDITIONS FOR NON-CONDENSABLE SPECIES REDUCTION FROM CO_2-RICH EXHAUST STREAMS

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Abstract

The presence of a significant amount of oxygen and/or other incondensable species in flue gases of CO_2-capture-ready combustion systems is a relevant issue to be solved to avoid problems in CO_2 sequestration and storage process. As matter of facts, oxygen as well as other non-condensable species, increases the compression work required for the liquefaction of CO_2. Furthermore it was highlighted that residual oxygen in the CO_2 streams used for EOR (Enhanced Oil Recovery) operations reacts with hydrocarbons in oil field causing an overheating at the injection point, a higher oil viscosity and increased extraction cost.

Post-oxidation process is a feasible and economical possibility to reduce oxygen and non-condensable/oxidizable species (such as H_2 and CH_4) concentration to one digit ppm (or ppb) levels and obtain high purity CO_2 streams that can be used for sequestration or EOR.

This paper presents a numerical study of oxidation processes of a CO_2 rich gas stream, reproducing those typical at the exit of a CO_2-capture-ready combustion system, aimed to outline reaction conditions useful to achieve a significant reduction of the gas contaminants below the minimum required level allowing for a useful use of the resulting CO_2 stream for storage or EOR purposes.

High temperatures and elevated level of dilution of inlet streams put this post-combustion process in conditions typical of MILD combustion. For these reasons it appeared natural to face the problem with the approach usually followed by this research group in studying this class of combustion processes. Characteristic kinetics times and key species concentrations at steady state were evaluated in order to study the evolution and the completion of the oxidation process.

Such parameters were correlated to the main variables that influence post-oxidation process such as inlet temperature system, composition of feed mixture, fuel and nature of diluent species.

Introduction

The presence of oxygen and/or other incondensable species (i.e. nitrogen, argon, methane, hydrogen) in flue gases of CO_2-capture-ready combustion systems is a relevant issue to be faced with for several reasons.

Firstly, oxygen as well as other non-condensable species increases the compression work required for CO_2 liquefaction almost linearly with respect to their concentration in the CO_2

stream. The increase in compression work is approximately 2.5%, 3.5% and 4.5% for a concentration of 1% by volume of oxygen, nitrogen and hydrogen respectively [1].

In addition, the residual oxygen in the CO_2 streams used for EOR (Enhanced Oil Recovery) operations may react with hydrocarbons in oil field causing both an overheating at the injection point and an increase of oil viscosity thus implying higher extraction cost [1,2]. Another potential effect of oxygen is the increased biological growth even if the relevance of this effect on oil production has not been thoroughly exploited yet.

Moreover, in amines separation processes for CO_2 capture and sequestration, the presence of oxygen degrades most of the amine solvents not allowing for their regeneration, and also determines the formation of corrosive compounds, surfactants (foaming) and poisons the active adsorbing species [3]. These effects further increase the relatively high cost related to such a separation process.

Even if it has not yet been established unequivocally the maximum acceptable level of oxygen in the currents of CO_2, many studies, carried out as part of European projects focused on CCS technologies, have showed that the maximum volume fraction of non-condensable species such as O_2, N_2 and Ar in CO_2 stream to be stored, in less restrictive conditions, should not exceed 4 % in volume.

Companies as Praxair, Kinder Morgan and Statoil involved in the management and development of plants for CO_2 sequestration impose a maximum concentration of oxygen below 10 ppm as pipeline specification [4].

There are generally no great technical barriers to reduce oxygen and non-condensable species and provide high purity of the captured CO_2. The most common technique to reduce oxygen down to ppm range is to incorporate a distillation column of the liquid CO_2 in the typical purification process of CO_2 streams for sequestration or EOR [5]. However, such technique is likely to induce a remarkable additional costs and energy requirements resulting in an overall reduction of power plant efficiency. Therefore, it would be highly desirable the individuation of alternative more economical means to reduce concentration of oxygen and non-condensable species in the CO_2 captured stream to acceptable levels for transport and storage.

Post-oxidation process is a feasible and economical possibility to reduce oxygen and non-condensable/oxidizable species (such as H_2 and CH_4) concentration to one digit ppm (or to ppb) levels and obtain high purity CO_2 streams that can be used for sequestration or EOR. Additionally, this technique could also increment power plant efficiency by heat recovery.

The aim of the present work is to numerically study oxidation process of typical flue gas of CO_2-capture-ready combustion systems in order to identify the optimal working conditions of the oxidation processes for the elimination of oxygen and non condensable/oxidizable species from CO_2 streams.

The characteristic kinetic times (auto-ignition, oxidation) and key species concentrations at steady state were evaluated in order to study the evolution and the completion of the oxidation process. These parameters are very important for design and dimensioning post-oxidation stages. Initial conditions considered in the paper are those characteristic of the output streams of oxy-combustion plants. This technology appears to be one of the most promising capture-ready combustion systems allowing for obtaining higher CO_2 concentration in exhaust streams respect to other combustion technologies [6]. For these systems the fraction of residual oxygen in CO_2-exhaust stream to be treated into post-oxidation stage is a function of fuel used in the primary combustion chamber. In particular, the average volume fraction of residual oxygen in the exhaust stream is variable from 2 to 5% by volume depending on whether the plant is fueled with natural gas or pulverized coal [7]. High temperatures and elevated level of dilution (high concentrations of CO_2 and H_2O) of exhaust stream are such that the post-oxidation process evolves in typical conditions of MILD combustion [8]. Under such operative conditions, the evolution of the oxidation process is relatively different with

respect to conventional combustion systems. In the paper the values of characteristic kinetic times and mole fraction of key species at steady state were correlated to the main parameters that influence Mild combustion process such as inlet temperature system, composition of feed mixture, equivalence ratio ($\sqrt{}$), nature of fuel and diluents to provide preliminary information about optimal operating conditions of post-oxidation process.

Numerical Tools

Numerical simulations were performed by PLUG application of the Chemkin 3.7 software [9] and a detailed kinetic mechanism available on the web.

PLUG simulates the behavior of plug-flow chemical reactor. More specifically, the application is designed to model the non-dispersive, one-dimensional flow of a chemically reacting, ideal-gas mixture in a conduit of arbitrary geometry. Such configuration was chosen in order to study the oxidation process as function of the axial coordinate or equivalently of the residence time and in absence of complex fluid dynamics.

The detailed kinetic mechanism c1-c3 [10] is used in this paper . In a previous work, several oxidation kinetic mechanisms were tested to investigate oxidation characteristic times of highly diluted CH_4/O_2 systems at atmospheric pressure [11]. Among the tested mechanisms, the chosen one was found, on the basis of experimental evidences, the most reliable in predicting methane oxidation features and characteristic kinetic times in diluted and highly pre-heated systems [12]. As matter of fact, detailed kinetic mechanisms are validated on the basis of experimental data obtained in simple configuration exercised in traditional combustion conditions, thus their robustness and reliability is questionable whether they must be used to study oxidation processes in not-standard conditions.

Numerical simulations were carried out on methane-oxygen systems diluted in carbon dioxide at atmospheric pressure, varying mixture inlet temperatures and composition. Methane was chosen as reference fuel since it is a non-condensable/oxidizable species that likely is present in exhaust gases coming out from CCS systems.

The attention was focused on characteristic kinetic times of the process (i.e. auto-ignition delay and oxidation times).

Following a criteria described in details elsewhere [13], the auto-ignition time (τ_{ign}) was defined as the time corresponding to a temperature increase equal to 10 K with respect to mixture inlet one (T_{in}). The oxidation time (τ_{ox}) is the time corresponding to an oxygen molar fraction equal to 10 ppm in the exhaust gases or, alternatively, in case such condition is not reachable, to the time system needs to reach the steady state.

Results and discussions

Figure 1 shows the auto-ignition delay times as a function of parameter α ($= 1000/T_{in}$) for a $CH_4/O_2/CO_2$ system at atmospheric pressure for a value of equivalence ratio ($\sqrt{} = C/O_{mix}/ C/O_{stoich}$) variable from 1 to 1.4. For these $\sqrt{}$ values the oxidation of fuel is complete. The investigated temperature range is α =0.6-1.5 (that corresponds to $T_{in} = 700$-1500 K) while the residual oxygen molar fractions considered are 2 and 5%.

In general, the auto-ignition delay time decreases as the system inlet temperature increases.

Three different slopes of the auto-ignition delay time curve are identifiable. In particular for low and high temperatures, the auto-ignition delay time decreases as T_{in} is enhanced, while, for the intermediate temperature range, the auto-ignition delay time is almost independent on the system inlet temperature. Such behavior resembles the well known negative temperature coefficient (NTC) phenomenology [11].
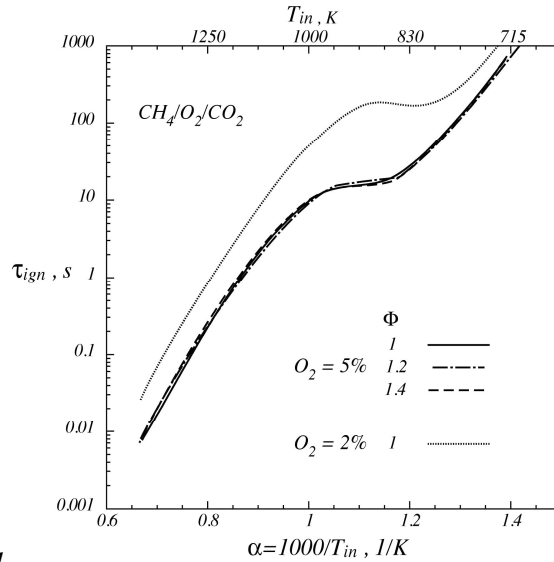
Fig. 1 *Auto-ignition delay times computed for different equivalence ratio and different residual oxygen mole fraction.*

For a residual oxygen molar fraction equal to 5% the auto-ignition delay time is slightly dependent on the equivalent ratio. As matter of facts, the profiles for $\surd = 1$, 1.2 and 1.4 are very close to each other for the whole considered temperature range.

This is also true for a residual oxygen molar fraction equal to 2%. In this case only the curve corresponding to stoichiometric conditions ($\surd = 1$) is reported. As expected the auto-ignition delay times is higher at lower oxygen concentration regardless of T_{in} and the NTC region shifts toward higher α values.

As a first indication about actual feasibility of post-combustion processes it has to be noted that inlet temperatures lower than 1000 K ($\alpha = 1$) implies auto-ignition delay times incompatible with practical industrial systems.

It is of interest to evaluate the dependence on the inlet temperature of the oxidation time, τ_{ox}, which is of the time needed to reach an oxygen molar fraction of 10 ppm. Figure 2 shows the oxidation times as function of α. According to the previous consideration the analysis is only restricted to the $\alpha < 1$ case (i.e. temperature higher than 1000 K).

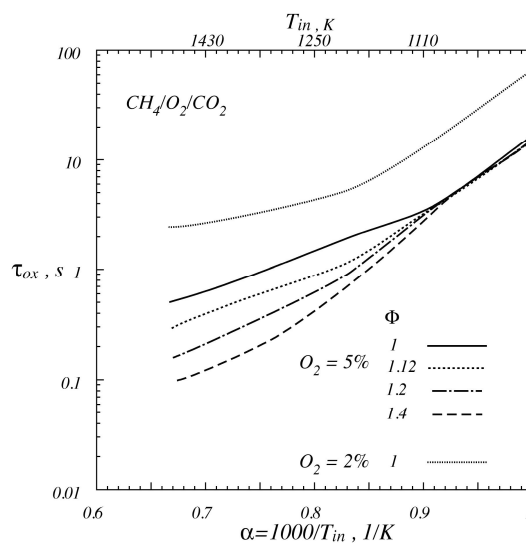**Fig. 2** *Oxidation times computed for different equivalence ratio and different residual oxygen mole fraction.*

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In general, the oxidation time decreases as the inlet temperature system is increased and it is sensitive to the equivalence ratio. Curves relative to a residual oxygen molar fraction of 5%, are coincident for $0.9 < \alpha < 1$, while for $\alpha < 0.9$ they spread showing that the oxidation time decreases as much as the mixture enriches in fuel.

For instance, for $\alpha = 0.67$ τ_{ox} obtained for $\sqrt{} = 1.4$ is about one order of magnitude smaller with respect to the one computed at the stoichiometric condition ($\sqrt{} = 1$).

Decreasing the residual molar fraction down to 2%, the oxidation times, as well as auto-ignition delay times, increase with respect to the previous ones in all the temperature range considered.
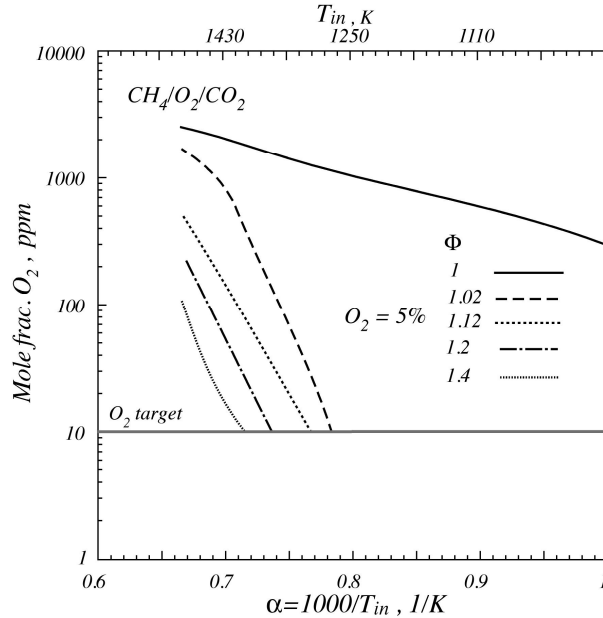

Fig. 3 Oxygen mole fraction evaluated at τox for the system $CH_4/O_2/CO_2$

The O_2 molar fraction (on dry basis) relative to the oxidation time is reported in Figure 3 as function of α, for the system $CH_4/O_2/CO_2$ with an oxygen molar fraction equal to 5% on curves parametric in the equivalence ratio $\sqrt{}$ (from 1 to 1.4). In the figure, also the oxygen threshold value (10ppm) acceptable in the treated CO_2-rich stream is indicated.

For the stoichiometric condition, the O_2 mole fraction is greater than 10 ppm for any inlet temperature. This result implies that the post-oxidation process is not realizable with such mixture composition.

For $\sqrt{} > 1$ (even slightly greater than the stoichiometric condition) and for $\alpha > 0.77$ (corresponding to T_{in} equal to 1300 K) the target is reachable for all the $\sqrt{}$ values analyzed while, at higher temperatures, the O_2 mole fractions result higher than 10 ppm.

Figure 4 shows the production of CO_2 (in terms of g/s) at τ_{ox} as function of α for the systems described previously.

Such results highlight that the production of CO_2 is strongly affected by the equivalence ratio and the inlet temperature system. In particular it decreases as $\sqrt{}$ and the inlet system temperature are increased. For $\sqrt{} = 1.4$ the production of CO_2 at τ_{ox} becomes negative. In such condition, the post-oxidation process is useless because a certain amount of the CO_2 to be treated is converted into undesired species, such as CO, negatively affecting the sequestration process.
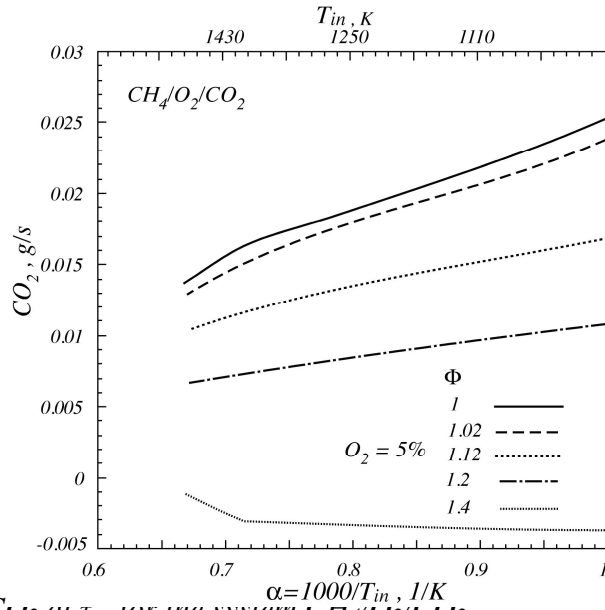
Fig. 4 Production of CO₂ at τₒₓ for the system CH₄/O₂/CO₂

Figure 5 and 6 report the CO and H_2 molar fraction (on dry basis) in the treated CO_2-rich stream as function of α for the system $CH_4/O_2/CO_2$ at τ_{ox}, for a residual oxygen molar fraction equal to 5% and different equivalence ratios (from 1 to 1.2). According to literature, CO and H_2 targets were set to 1000 and 100 ppm respectively [14].

In general H_2 molar fraction evaluated at τ_{ox}, decreases as system inlet temperature increases, while the CO molar fraction exhibits the opposite trend. Moreover both of them increase as equivalence ratio increases.

Results obtained for values of equivalence ratio near stoichiometric conditions ($\sqrt{}$ = 1.02, 1.04) show that in such conditions the H_2 molar fractions evaluated at τ_{ox} are smaller respect to the target of 100 ppm. Similar considerations can apply for the CO molar fraction except to higher temperature (T_{in} > 1300) where it is higher than 1000 ppm.
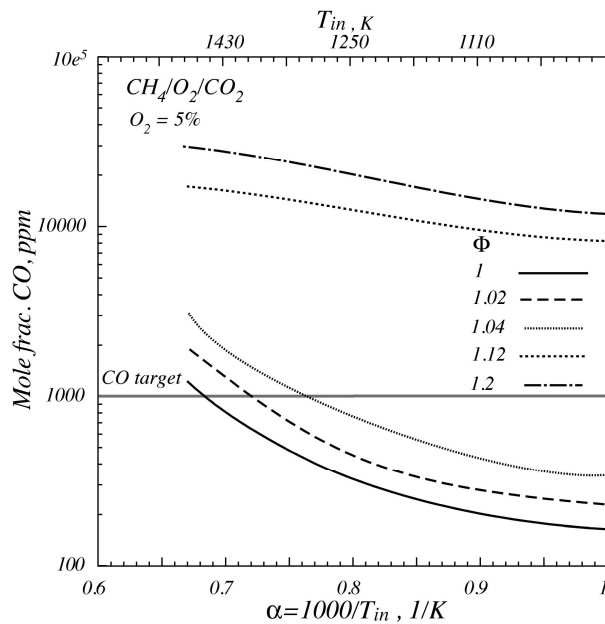

Fig. 5 Carbon monoxide mole fraction evaluated at τox for the system CH₄/O₂/CO₂

Increasing the equivalence ratio value ($\sqrt{}$ = 1.12, 1.2), the H_2 and CO molar fractions result higher than their targets in all the temperature range considered.
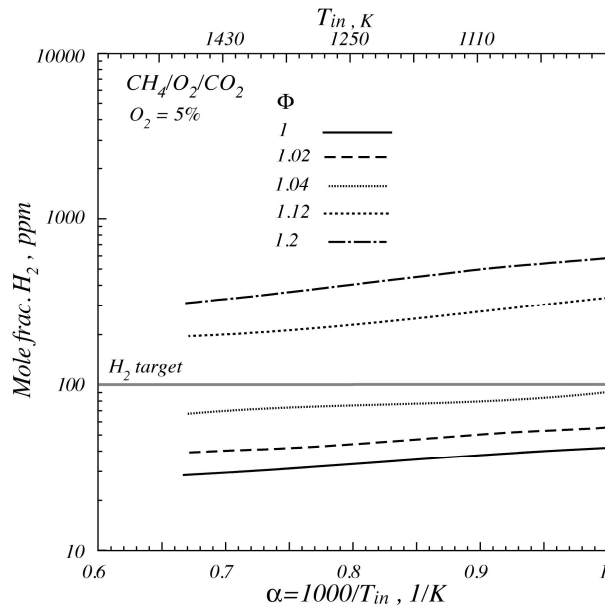

Fig. 6 Hydrogen mole fraction evaluated at τ_{ox} for the system $CH_4/O_2/CO_2$

Figures 7 and 8 show the effect of the presence of H_2O in the CO_2-rich exhaust stream to be treated on the characteristic kinetic times. Such effect was considered because water is always present in different amount in the CO_2-rich flue gas streams of real combustion systems.
The system considered is $CH_4/O_2/CO_2/H_2O$ for a residual O_2 molar fraction equal to 5% and $\sqrt{}$ = 1.02. The H_2O molar fraction was varied from 0 up to 35%.
The trend of auto-ignition delay time curves is similar for all the cases analyzed (H_2O molar fraction equal to 0, 15, and 35 %). At low temperatures the shortest τ_{ign} competes to system with 35% of H_2O, while the longer τ_{ign} to system diluted totally in CO_2. In the NTC region the trend is inverted. Finally, for $\alpha < 1$ the curves are very close to each other.
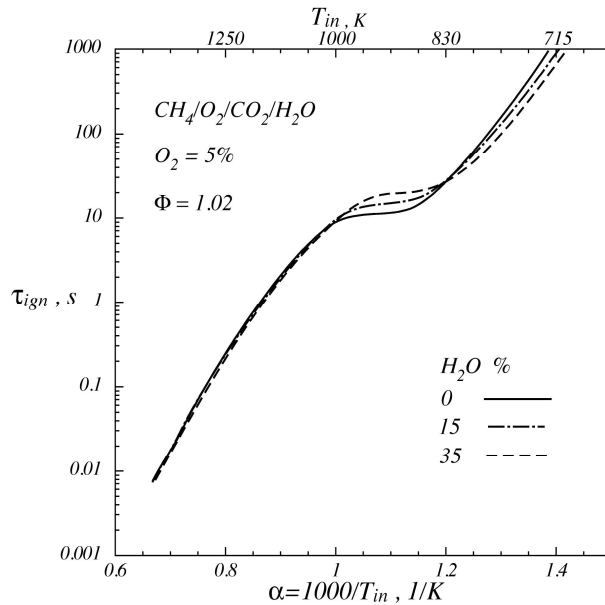

Fig. 7 Auto-ignition delay times computed for different H_2O mole fraction.

The effect of H_2O on auto-ignition delay times of CH_4/O_2 systems highly diluted has been exploited numerically in a previous work [15].
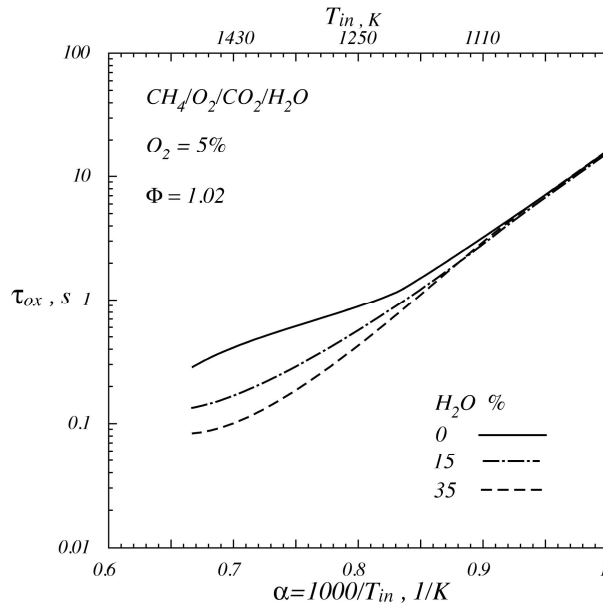

Fig. 8 Oxidation times computed for different H_2O mole fraction.

The presence of H_2O in the system shows an effect on the oxidation time similar to that of equivalence ratio described previously. In particular for $0.9 < \alpha < 1$ the τ_{ox} is not affected significantly by the presence of H_2O in the system while for $\alpha < 0.9$ it decreases as H_2O molar fraction increases.

For evaluating the effect of the nature of fuel used in the post-oxidation process on kinetic characteristic times and species production numerical simulations were performed considering mixtures of methane/ethylene and methane/propane and different mixture compositions as fuels,, while considering the same equivalence ratios used in previous integrations

The systems analyzed are fuels/O_2/CO_2/H_2O with a residual O_2 molar fraction equal to 5%, H_2O molar fraction equal to 15% and $\sqrt{} = 1.02$. The CH_4/auxiliary fuel volume ratio (R) has been set equal to 4 and 9. The trend of O_2, H_2 and CO mole fractions at τ_{ox} as function of $\sqrt{}$ for the systems considered, are not reported for the lack of the room, but, for such an equivalence ratio and for $\alpha > 0.77$, their concentrations in the treated CO_2-rich stream are below target thresholds.

Figures 9 and 10 show the effect of the nature of fuel used on the characteristic kinetic times.

In particular curves in figure 9 represent the ratio between auto-ignition delay times evaluated for $CH_4/O_2/CO_2/H_2O$ system and those obtained for fuels/O_2/CO_2/H_2O systems ($\tau_{ignCH4}/\tau_{ignMIX}$), as function of α for parametric values of CH_4/C_2H_4-C_3H_8 ratios.

The values of auto-ignition delay times ratios are higher than 1 for CH_4/C_2H_4 and CH_4/ C_3H_8 mixtures considered in all the temperature range investigated. Such a result implies that ethylene or propane strongly increases the system reactivity during the auto-ignition process.

For the CH_4/C_2H_4 mixture with R=9 the $\tau_{ignCH4}/\tau_{ignMIX}$ curve exhibits a nearly bell-shaped trend. In particular for $1.4 <\alpha< 1.2$ it shows a linear trend in a logarithmic scale, later on, decreasing α the ratio $\tau_{ignCH4}/\tau_{ignMIX}$ increases reaching a maximum value at $\alpha = 1$ ($\tau_{ignCH4}/\tau_{ignMIX} =20$), then it decreases. At the extreme of the inlet temperature range investigated the ignition time are comparable ($\tau_{ignCH4}/\tau_{ignMIX} =2.5$). Increasing the amount of ethylene in the fuel mixture (R=4), $\tau_{ignCH4}/\tau_{ignMIX}$ curve shows a similar behavior with respect

to the case just described, but $\tau_{ignCH4}/\tau_{ignMIX}$ is higher. In particular for $\alpha = 1$ the auto-ignition delay time ratio becomes 100.
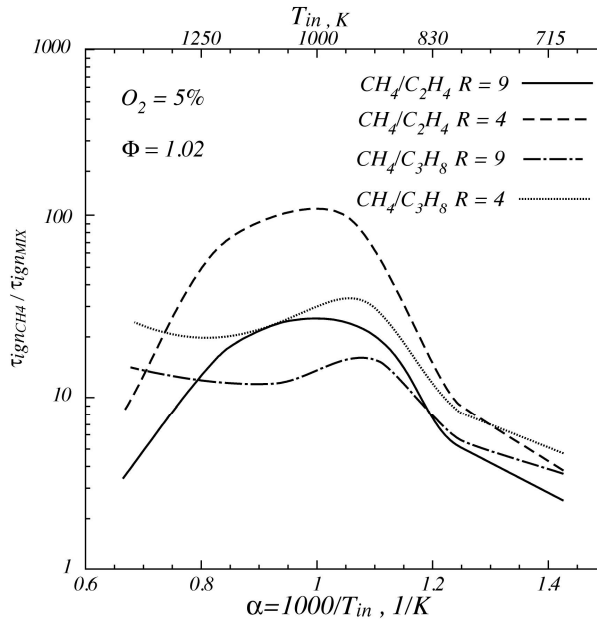

Fig. 9 Auto-ignition delay times computed for different fuels.

For the CH_4/C_3H_8 fuels mixture with R=9 and for 1.4 $<\alpha<$ 1.2, the $\tau_{ignCH4}/\tau_{ignMIX}$ shows a linear trend in a logarithmic scale. For $\alpha = 1.1$ it reaches a maximum, then it slightly decreases down to a constant value of 10.
Decreasing R down to 4, $\tau_{ignCH4}/\tau_{ignMIX}$ is similar respect to the case described above with a shift toward higher α values.

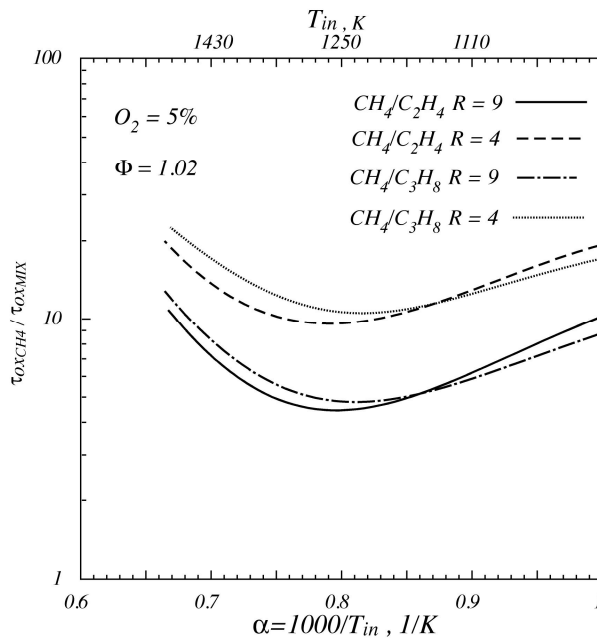*Fig. 10 Oxidation times computed for different fuels.*

At low temperatures (1.4 $<\alpha<$ 1.2) and for a fixed value of R, the $\tau_{ignCH4}/\tau_{ignMIX}$ curves relative to CH_4/C_2H_4 and CH_4/C_3H_8 fuels mixture are very similar while in the intermediate

temperature region the $\tau_{ignCH4}/\tau_{ignMIX}$ values relative to CH_4/C_2H_4 mixture are higher than those obtained for CH_4/C_3H_8 systems. At high temperature ($\alpha < 0.8$) the trend is inverted.

Figure 10 shows the ratio between oxidation times evaluated for $CH_4/O_2/CO_2/H_2O$ system and those obtained for fuels/$O_2/CO_2/H_2O$ systems ($\tau_{oxCH4}/\tau_{oxMIX}$), as function of α for parametric values of R.

Results reported in figure 10 suggest that, as well as for auto-ignition delay time, the addiction of C_2H_4 or C_3H_8 in the system, leads to a faster oxidation process respect to CH_4 system.

For the CH_4/C_2H_4 fuels mixture with R=9 the $\tau_{oxCH4}/\tau_{oxMIX}$ value decreases as inlet temperature increases reaching a minimum for $\alpha = 0.8$ ($\tau_{oxCH4}/\tau_{oxMIX}$ =5), then it increases with T_{in}. Decreasing R,down to 4, oxidation time ratio curve shifts to higher values. In such case the minimum value of $\tau_{oxCH4}/\tau_{oxMIX}$ is about 10.

For a fixed value of R, the $\tau_{oxCH4}/\tau_{oxMIX}$ curves relative to CH_4/C_2H_4 and CH_4/C_3H_8 mixture are very similar in all the temperature range investigated.

Conclusions

The paper shows that a post-combustion process in MILD conditions is highly efficient for the elimination of oxygen and incondensable species from CO_2 streams to be sequestered. Starting from a flue gas stream deriving from an oxy-fuel combustion process, i.e. with a typical composition at the exit of combustion chamber, the evolution of cleaning reactive process has been followed as a function of inlet temperature and fuel/oxygen ratio, with the aim of identifying the optimal range of working conditions.

Three main parameters have been taken into account during such a recognition. A first edging of potential working conditions has been made by fixing the target concentration values of undesired species to be reached, on the basis of market requirement.

Among the potential favorable conditions with respect to target concentrations, an evaluation of corresponding characteristic time of the process has been carried out in order to identify the working parameters that allow for ignition and oxidation time compatible with residence time of real burners. In such analysis, it has been shown that both methane and mixtures of methane with C_2 or C_3 species, are effective both in reduction of oxygen and in promoting the oxidation of other incondensable species present in CO_2 stream, even though the presence of higher molecular weight paraffins strongly reduce ignition and oxidation time. As a consequence, the choice of fuel is related to the design, logistic and economic evaluation in the overall assessment of the sequestration plant. In both cases, the needed initial temperature of CO_2 enriched streams to be treated are congruent with characteristic temperatures at the exit of the main combustion chamber.

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