CO₂ and H₂O effect on propane auto-ignition delay times under mild combustion operative conditions

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Abstract

The auto-ignition process of propane/oxygen mixtures was experimentally and numerically studied over a range of temperatures (850–1250 K) and mixture compositions (from fuel-ultra-lean to fuel-rich conditions) under MILD operative conditions. The mixtures were diluted in CO₂ or H₂O from 90 up to 97%. The experimental tests were realized in a Tubular Flow Reactor (TFR) at atmospheric pressure.

Several combustion regimes were identified as a function of the mixture composition and inlet temperature. The experimental results showed that CO₂ and H₂O significantly alter the ignition process. In particular, a significant slowing of the system reactivity was observed with respect to the mixtures that were diluted in nitrogen.

Numerical simulations were performed by commercial codes and detailed kinetic mechanisms. Comparisons between experimental and numerical results pointed out that kinetic models are not able to correctly reproduce system behaviors in all the experimental conditions.

For CO₂-diluted mixtures a good agreement between experimental and numerical analysis was obtained for fuel lean mixtures, whereas for stoichiometric and fuel-rich mixtures conditions the consistency of predicted data was less satisfactory.

In the case of steam-diluted systems, the discrepancy between the experimental data and the predictions is about one order of magnitude for any mixture composition, but the model can reproduce the slight dependence of the ignition data on the mixture compositions.

Further numerical analyses were performed to identify the reactions controlling the ignition process under MILD operative conditions in presence of CO₂ and H₂O. Results suggested that steam and carbon dioxide drastically alter the main branching mechanisms as third molecular species in termolecular reactions and/or by decomposition reactions.

1. Introduction

The identification of new combustion technologies for energy production under the constraints of high efficiency and low pollutant formation has promoted the development of new technologies that exploit different operative conditions in terms of pressure, temperature, mixture compositions with respect to conventional systems.

Among the new technologies, MILD combustion [1] is considered one of the most promising new concepts that respond to the imposed requirements of environmental constraints.

The proposed strategy is to burn highly diluted and pre-heated mixtures. The dilution level is the key stratagem to contain system-working temperatures below critical values to produce undesired pollutants [soot and NOₓ] [2–4]. Under highly diluted conditions (outside conventional flammability limits) the oxidation process occurs throughout a continuous auto-ignition mode. In industrial systems, exhausted gases are recycled to dilute and pre-heat the fresh reactants above temperatures higher than the mixture auto-ignition one. Such operative conditions feature a nearly homogeneous process with unique physical and chemical aspects [5,6]. The quasi-isothermal conditions, which are associated with high dilution levels, and strong pre-heating of reactants, determine a drastic change of kinetics that are involved in the fuel oxidation process [7].

A similar process, which is widely applied in coal-combustion technologies, is oxy-fuel [8] combustion. Essentially, fuel and pure
oxygen react in presence of recycled flue gases. They are necessary to restrain the adiabatic flame temperatures to values that are compatible with the material thermal resistance and not critical for pollutants formation. The nitrogen-free atmosphere results in final flue gases mainly composed by CO2 and H2O, that can be easily purified and processed in Carbon Capture and Storage (CCS) technologies [9].

These combustion processes occur in the presence of great amounts of carbon dioxide and steam that can alter the kinetic routes by thermal and chemical effects [10–12]. The former is related to a high heat capacity of such diluent species with respect to nitrogen, which implies a low adiabatic temperature, whereas the latter is mainly related to the possibility of such species to directly participate in bimolecular reactions or indirectly participate in termolecular reactions with higher third-body efficiencies with respect to nitrogen. The evaluation of these effects on fuel oxidation processes and the quantification of their relative weight require dedicated investigations.

Glarborg and Bentzen [12] experimentally and numerically studied the oxidation of methane in a flow reactor under atmospheric pressure from fuel-lean to fuel-rich mixtures that were highly diluted in N2 and CO2 at temperatures in the range of 1200–1800 K. Under oxy-fuel combustion conditions, they observed a strong increase of CO concentrations after the onset of the reactions. A numerical analysis suggested that such behavior occurs because of the CO2 decomposition reaction (1) CO2 + H = CO + OH. Yuan et al. [13] performed a numerical work on the methane/oxygen/carbon dioxide mixtures. They showed that the CO2 addition significantly decreased the H and O peak concentrations at high temperatures (>1200 K) because reaction (1) consumed the H atom when the CO2 concentration is high, which competed with the main branching reaction (2) H + O = OH + O for H atoms and inhibited the oxidation process. Le Cong and Dagaut [14] experimentally investigated the oxidation of hydrogen that was diluted in nitrogen in the presence of 30% CO2 in a jet-stirred reactor over the temperature range of 800–1050 K from fuel-lean to fuel-rich conditions at atmospheric pressure. They showed that CO2 inhibited the oxidation of H2 because reaction (1) also competes for H radicals with the H2O/O2 branching reactions in the intermediate temperature range.

Anderlohr et al. [15] numerically investigated the thermal and kinetic impact of the residual species CO, CO2 and H2O on the oxidation chemistry of n-heptane/iso-octane/toluene blends at high dilution ratio (97%) from low to medium temperatures (650–1100 K) at atmospheric pressure. These operative conditions are relevant for the post-oxidation zone in IC engines. They found that the CO2 and H2O thermal effects inhibited the oxidation process instead of the kinetic one mainly because of the third-body reactions. They showed the importance of H2O2 dissociation at low and intermediate temperatures. Its reaction rate depends on the efficiencies of its collision partners. The authors suggested to revise the efficiencies of the potential collision partners. The authors suggested to revise the efficiencies of the potential collision partners.

Abián et al. [16] investigated the oxidation of CO in a quartz flow reactor that operated at atmospheric pressure over the temperature range of 700–1800 K from fuel-rich to fuel-lean conditions in the presence of various amounts of CO2 and H2O, which represent different exhaust-gas recirculation conditions. They found that CO2 inhibited the CO oxidation because the H concentration is diminished by reaction (1), which competed with reaction (2) for H radicals. Furthermore, CO2 inhibits reaction (2) by promoting reaction (3) H + O2 + M = HO2 + M because of its high third-body collisional efficiency, which diminishes the system reactivity. In contrast with other works [17,18], the authors found that H2O enhances the CO conversion. They optimized the CO2 and H2O third-body efficiencies in reaction (3) in the detailed kinetic mechanism that they used and multiplied their efficiency for a correction factor.

Recently, Wang et al. [19] numerically studied the flame structure of CH4–O2/N2/CO2/H2O counterflow diffusion flames with various mole fractions of CO2 and H2O under oxy-fuel conditions. They mainly argued that both CO2 thermal and chemical effects reduced the flame temperature, whereas the H2O thermal and chemical effects compensate resulting in a weak effect on the flame temperature. They found that CO2 enhances the CO concentration throughout the reactions CO2 + H = CO + OH and CH2(S) + CO2 = CH2O + CO. The mass diffusion property of CO2 affects the distribution of the temperatures and the major species with negligible effects on the maximum flame temperature and the CO emissions. On the contrary, H2O addiction to the mixture induces a decrease of H radicals and decreases CO concentration limiting the reaction CO2 + H = CO + OH.

Furthermore, under oxy-fuel conditions the conversion of methane occurs mainly through C1 routes while the C2 formation-oxidation pathways are depressed. Recently, Schönborn et al. [20] experimentally investigated the influence of CO2 on the propane ignition delay times for mole fractions of 0 < xCO2 < 0.1 at 870 K, 0.5 MPa and φ = 0.4. They showed that the auto-ignition delay increased when the mole fraction of CO2 increased. The chemical kinetic computations failed to accurately predict this behavior. They suggested that such discrepancy mainly occurred because of the high collisional efficiency of CO2 in third-body reactions.

Chinnici et al. [21] performed numerical simulations in a perfectly stirred flow reactor for methane/O2/CO2 mixtures under MILD operative conditions, and they identify temperature oscillations induced by the CO2 decomposition reaction for fuel rich mixtures at working temperature higher than 1500 K.

Mardani et al. [22] studied the mechanism of CO and CO2 formation for a CH4/H2 fuel mixture under MILD combustion conditions of a jet in hot co-flow (JHC) burner using computational fluid dynamics and zero dimensional well-stirred reactor analyses. They suggest that under MILD conditions, the high concentration of CO is due to the strong activation of the ethane formation/decomposition route to acetaldehyde that is oxidized to CO by means of O radicals. Furthermore, for temperatures higher than 1500 K, the CO2 decomposes increasing CO levels.

The common statement in the cited papers is that CO2 alters the equilibrium reaction CO + OH + CO2 + H, which modifies the concentration of key radicals that compete with the high-temperature H2O/O2 branching reactions, whereas H2O mainly acts as a third-body species in termolecular reactions. In particular, it modifies the role of the H2O2 decomposition reaction and promotes the reaction H + O2 + M = H2O2 + M, which inhibits the competitive branching reaction H + O2 = OH + O. The relative weight and the promotion of peculiar kinetic routes by such diluent species depend on the system operative conditions.

In most of these works, the effects of CO2 and H2O are analyzed in oxy-fuel conditions, namely relatively high temperatures and dilution degrees, where high-temperature branching reactions are notably fast. However, it is not yet clear what effect CO2 and H2O can have under MILD operative conditions, where very high diluted mixtures and intermediate temperature are considered. Earlier works [6,11] showed that these operating conditions led to drastic change of kinetic routes with respect to conventional flames, and a strong competition among the oxidation and pyrolysis/recombination channels was identified. The influence of the diluent nature can be stressed under such operative conditions.

In this framework, the paper aims at investigating the effect of H2O and CO2 on fuel oxidation under MILD operative conditions. In particular, the auto-ignition delay times of propane/oxygen mixtures diluted up to 90, 95 and 97% in CO2 or H2O were characterized. The auto-ignition time has a practical relevance because it is one of the essential parameters to combustion design and
Experimental and numerical tools

Experimental tests were realized in a laboratory-scale stainless-steel tubular flow reactor, which was 140 cm long with an inner diameter of 1 cm, as described elsewhere [6,23,24]. The main flow, which was composed of oxygen and diluent, was pre-heated to the desired temperature using electric fiber heaters and was subsequently mixed with the fuel flow using jets in a cross-flow configuration; then, the premixed charge entered the reactor.

Thermocouples (type N) were located along the axial direction of the reactor and allowed to measure the temperature profiles over this coordinate. They were used to evaluate the oxidation regimes that occur during the mixture oxidation and to evaluate the ignition delay times (t). In particular, t was defined on the basis of axial steady temperature profiles. When the oxidation reactions occurred, the temperature profile stabilized after a transient period. Then, the ignition time was calculated by dividing the axial distance, where a temperature increase of 10 K [25] was measured, by the flow velocity (defined as \( v = \text{flow rate/reactor cross area} \)).

The experimental tests were performed by varying the carbon/oxygen (C/O) ratio from approximately 0–1 and the inlet temperature \( (T_{in}) \) from 850 to 1250 K.

Table 1 reassumes the operative conditions in which experiments have been carried on.

The (C/O) ratio is defined as the ratio between the molar fraction of carbon atoms in fuel and the molar fraction of oxygen atoms in the oxidant flow, taking into account only the O2 species. Thus, \((\text{C/O})_{\text{stoich}} = 0.3\) is the mixture stoichiometric value. Reactants were fully diluted in CO2 or H2O from 90% to 97%. The mixture dilution level is the percentage molar fraction of the diluent species in the mixture. Given the definition of (C/O), oxygen atoms in the CO2 or H2O are not included in the (C/O) ratio calculation.

All the inlet operative conditions experimentally explored in the paper fulfill the necessary conditions reported in Ref. [1] to be ascribed as MILD Combustion. In fact, reactants were highly diluted (up to 90–97%) while inlet temperatures were higher than the nominal auto-ignition temperature.

Numerical simulations were performed to study the evolution of the propane oxidation process in diluted and highly preheated conditions in a tubular flow reactor using the PLUG module of the ChemKin 3.7 [26].

Several kinetic simulations were performed using a chosen kinetic mechanism to highlight the crucial aspects of the auto-ignition delay-time trend as a function of the temperature for mixtures with different dilution levels and compositions. The “C4H9” [27] mechanism was chosen after the evaluation of its performance in predicting main features of the oxidation process under MILD conditions in previous works [6,24].

3. Experimental results

The system behavior was evaluated based on the systematic analysis of the axial-temperature profiles as a function of the inlet pre-heating temperature \( (T_{in}) \), mixture composition and dilution levels. Several main typologies of the axial-temperature profiles were recognized and associated with the characteristic combustion regimes.

The typical temperature profiles were reported and thoroughly explained in Sabia et al. [6,24]. Briefly, it was possible to recognize the following combustion regimes:

- “no combustion”: no temperature increase occurs, and \( T \) maintains its inlet value.
- “pyrolysis”: the recorded temperature values are lower than the isothermal inlet profiles, which suggests the onset of endothermic/pyrolytic reactions.
- “low reactivity”: the temperature profiles show a modest temperature increase that does not exceed 10 K.
- “ignition”: the working temperatures are at least 10 K higher than \( T_{in} \).
- “dynamic”: for the same inlet conditions, temperature profiles are recorded downstream a steady ignition point, which periodically switch from one to the other in time.
- “transient”: the mixture ignites and leads the system to a first reactive state. Afterwards, the temperature profiles spontaneously shift towards a second final stationary state.

3.1. Mixtures diluted in CO2

Each acquired temperature profile corresponds to a point on a map of behavior in the C/O-\( T_{in} \) plane, as reported in Fig. 1. Experimental tests were carried out by varying the inlet temperature stepwise any 20 K, for thirteen C/O ratios, keeping constant the CO2 concentration and the inlet flow velocity. For the \( T_{in} – C/O \) values for which transitions among regimes were observed, the step was tightened. The map reported in Fig. 1 was drawn up on the basis of about 200 experimental tests. Figure 1 allows to identify the combustion regimes in the C/O-\( T_{in} \) plane. The \( T_{in} \) (850–1170 K) and C/O (0.035–1) ranges in Fig. 1 identify the analyzed conditions for a flow velocity of 30 m/s and a mixture dilution level of 90%. The experimental analysis covers both fuel-lean (C/O < 0.3) and fuel-rich (C/O > 0.3) mixtures (C/O = 0.3 is the stoichiometric condition).

For temperatures below 1030 K and ultra-lean/lean conditions, the “no combustion” regime is identified. As soon as the fuel molar fraction is increased, this area extends to slightly higher temperatures. The “no combustion” regime converts into the “pyrolytic regime” when the C/O ratio becomes higher than 0.3. A richer mixture corresponds to a wider “pyrolytic” temperature range in the map.

Both “pyrolytic” and “no combustion” behaviors border with the “low reactivity” region. For mixtures that are characterized by a C/O feed ratio of 0.035, this region extends from 1040 K to 1090 K. As soon as the C/O feed ratio is increased, the “low reactivity” area borders move towards higher temperatures, which slightly reduces the difference between their edge temperatures.

For \( T_{in} \) above 1090 K and ultra-lean conditions, the ignition process occurs. When the C/O ratio is increased, the ignition temperature increases.

In the map, the “pyrolytic” (dashed dot) and the “dynamic” lines (double dotted) are drawn. All operative conditions on the map above the “pyrolytic line” show a temperature decrease relative to the first thermocouples, which indicates the onset of
When the transitional regimes occur, two ignition delay values are reported (case I in the map).

For any C/O feed ratio, the auto-ignition delay times exhibit a linear trend as a function of the inlet temperature on an Arrhenius diagram. For the fuel-rich mixtures, fewer points are reported because the required temperatures to achieve ignition are higher, as shown in Fig. 1.

A thorough comparison among the auto-ignition values that were obtained at several C/O ratios is provided in the next paragraph, where the experimental data are also compared to the numerical results.

Further experimental tests were realized for mixtures that were diluted at 95% and 97% in CO2 to evaluate the influence of the dilution degree on the process features. The results suggested that higher dilution levels imply the achievement of lower temperature increase inside the reactor, but the oxidation regimes were identical; therefore, the C/O-T_in maps are omitted. Nevertheless, a comparison among the ignition delay times at different dilution degrees is provided.

### 3.2. Mixtures diluted in H2O

Applying the same regime classification that was used to comment on the obtained results for C3H8/O2 mixtures diluted in CO2, the map was drawn relative to the mixtures diluted in H2O. For a dilution level of 90% and a flow velocity of 30 m/s, the explored temperature range was 850–1180 K, whereas the C/O feed ratio range was 0.035–1. The map is shown in Fig. 3.

The “no combustion” region extends from 850 K to 1060 K for C/O = 0.025. This area slightly widens in the inlet temperature range when C/O increases toward the stoichiometric condition. For C/O above 0.3, the temperature profiles show the typical trend of the “pyrolytic” case. The “pyrolytic” and “no combustion” behaviors change to the “low reactivity” case, which increases the inlet temperature. This region extends from 1060 K to 1130 K for C/O = 0.025 and from 1140 K to 1180 K for C/O = 1.

A further increase of the temperature makes the system move to reactive conditions. In particular, for C/O = 0.1 and 0.025, the “ignition” case is recognizable at approximately 1100 K and 1130 K, respectively. This region extends to 0.55 for T_in = 1170 K. In addition, in this map, as illustrated in Fig. 1, the “pyrolytic” and “dynamic” lines were shown. In particular, the dynamic-behavior region in the map is more extended than that in the case of mixtures that were diluted in CO2, and it includes the “low reactivity” conditions. It extends for T_in higher than 1090 K and C/O lean conditions; then, when the temperature increases, it is also established for richer conditions. In case of fuel-rich mixtures, the propane oxidation evolves through the “transient” regimes. For T_in = 1180 K, it is recognized up to C/O = 0.85–0.9. This region is subdivided into “transient I” and “transient II” areas following the previously reported classification.

In this case, experimental measurements were also performed at higher velocities and temperatures (up to 50 m/s and 1235 K), but the maps do not show substantial differences compared to the one in Fig. 3.

It was possible to evaluate the auto-ignition times for all analyzed operative conditions that satisfied the criterion of ignition. Figure 4 shows the ignition delay times for several C/O values from lean to rich reactive conditions on a typical Arrhenius plot. The mixtures were diluted to 90% in H2O, and the flow velocity was changed from 30 to 50 m/s.

When the transitional regimes occur, two ignition delay values are reported for the C/O-T_in values in the “transient I” case. In any case, the auto-ignition delay times show a linear trend as a function of the inlet temperature on the Arrhenius diagram. For rich mixtures, fewer points are reported because the
required temperatures to achieve ignition are higher, as shown in Fig. 3.

In addition, the comparison among the obtained auto-ignition values at several C/O values is provided in the next paragraph.

It was not possible to collect sufficient data to build C/O-T_in maps for dilution levels above 90% because the system reactivity was low.

4. Comparison between experimental and numerical results

4.1. Effect of diluent

Numerical simulations were performed using the PLUG application of the ChemKin 3.7 [25] with the “C1-C3” kinetic mechanism [26].

To evaluate the effect of CO₂ and H₂O on the propane ignition process, it is useful to compare the obtained results (experimental and numerical) with those of mixtures that were diluted in inert environments, as reported by Sabia et al. [24].

Figure 5 shows the auto-ignition delay times for a stoichiometric propane/oxygen mixture that was diluted up to 90% in N₂, CO₂, and H₂O. The numerical predictions are reported with lines. Experimental data show that the ignition occurs for lower inlet temperatures in the case of N₂, whereas for CO₂ and H₂O it starts at nearly the same high T_in. In both cases, the ignition times are longer by almost one order of magnitude than those obtained for the mixture diluted in nitrogen. All three sets of data show an Arrhenius trend in the range of high temperature, whereas for lower temperatures, the obtained data for nitrogen show a change in activation energy of the ignition process that passes from intermediate to high inlet temperature, as widely discussed by Sabia et al. [24].

It is possible to note that although the auto-ignition data obtained for N₂ are predicted with a good approximation using the chosen kinetic mechanism, the consistency was not good for the other two diluent species. Furthermore, in contrast to the experimental data, the numerical predictions suggest that in the considered temperature range, carbon dioxide is the most effective in delaying the auto-ignition times.

Figure 6 shows the experimental ignition delay times for an ultra-lean (C/O = 0.05) mixture and a rich mixture (C/O = 0.6) and the numerical predictions. The experimental auto-ignition data for CO₂-diluted mixtures are near the nitrogen values for fuel ultra-lean (Fig. 6a), whereas the ignition delay times of the H₂O-diluted system

![Fig. 2. Auto-ignition delay times for C₃H₈/O₂ mixtures from lean to rich conditions, which were diluted to 90% in CO₂.](image-url)
are longer and show a different slope in the Arrhenius plot with respect to the \( N_2 \) and \( CO_2 \) times.

Numerical simulations perform well in predicting \( N_2 \) and \( CO_2 \) test data, but a significant discrepancy occurs between the experimental and the numerical data for \( H_2 O \).

For fuel-rich mixtures (Fig. 6b), the difference among the obtained experimental data for the three reference fuels becomes less pronounced, and noticeable differences occur between numerical and experimental results, particularly for \( H_2 O \).

4.2. Effect of carbon/oxygen feed ratio

Figure 7 shows the ignition delay times for propane/oxygen mixtures that were diluted up to 90% in \( CO_2 \) for fuel-lean (\( C/O = 0.05 \)), stoichiometric (\( C/O = 0.3 \)) and fuel-rich (\( C/O = 0.6 \)) conditions.

It is evident that in the high-temperature range, the kinetic mechanism well predicts the increase of the delay times with increasing \( C/O \), but the experimental and numerical results are only consistent for the lean conditions. Under rich and stoichiometric conditions, the model underestimates the experimental data.

Figure 8 shows the same comparison for propane/oxygen mixtures that were diluted to 90% in \( H_2 O \). The disagreement between experimental and numerical data is even more pronounced in this case, and the kinetic mechanism cannot predict the experimental results. It should be noted that for any \( C/O \) feed ratio, the experimental ignition delay times are notably close to the data of \( N_2 \).

In Fig. 9, the ignition delay times for a stoichiometric mixture propane/oxygen that was diluted to 90%, 95% and 97% in \( CO_2 \) are compared. The figure shows a clear slowing of the ignition process when the dilution level of the mixture increases. The disagreement between experimental and numerical results increases with the dilution degree.

5. Discussions

The numerical simulations do not properly reproduce the experimental data when \( CO_2 \) dilutes the propane mixtures, particularly for fuel-rich mixtures, whereas the results are consistent for fuel-lean/ultra-lean mixtures, which resembles the behavior of \( N_2 \)-diluted mixtures [24]. When the mixtures are diluted in steam, all experimental data are longer than the numerical predictions, although the model reproduces the small variation of ignition data as a function of the \( C/O \) values.

Based on the obtained numerical analysis for nitrogen-diluted systems [24], further simulations were performed to understand the role of \( CO_2 \) and \( H_2 O \) in the ignition process. They were extended to a wider range of \( T_{in} \) (from 800 K to 1400 K) to highlight the effects of such diluent species on the ignition chemistry at low, intermediate and high temperatures. Figure 10 shows the auto-ignition data that were numerically obtained for a stoichiometric mixture that was diluted with the three reference diluents.

In any case, the ignition process presents a complex behavior. For low temperatures, on the Arrhenius plot, the trend is linear with \( T_{in} \); for intermediate temperatures, the curves present a less pronounced slope, which increases again at high temperatures. As reported by Sabia et al. [24], the change of the auto-ignition process activation energy that passes from low to high inlet temperatures was experimentally recognized in the tubular flow reactor for nitrogen-diluted propane/oxygen mixtures. Figure 10 shows that this peculiar behavior is more evident in case of \( CO_2 \) and \( H_2 O \) mixture dilution.

For \( T_{in} < 1000 \text{ K} \), the shortest numerical auto-ignition data are comparable to that of \( H_2 O \)-diluted system, whereas the longest one is comparable to that of \( N_2 \)-diluted system. The data of \( CO_2 \) dilution lie between and are notably close to the data of \( N_2 \). For \( T_{in} > 1200 \text{ K} \), the situation is reversed, and the \( N_2 \)-diluted system presents shorter numerical ignition delay than the other two mixtures. In particular, for intermediate temperatures, the \( CO_2 \)-diluted system has the longest auto-ignition times, whereas for \( T_{in} > 1300 \text{ K} \), the curves suggest a lower reactivity for the \( H_2 O \)-diluted system.

The description of the figure suggests that the oxidation paths are significantly modified by the presence of the considered diluent species with complex interactions that depend on \( T_{in} \).

In particular, \( CO_2 \) and \( H_2 O \) have a thermal effect and a chemical effect. The former concerns the greater heat capacity of \( CO_2 \) and \( H_2 O \) with respect to \( N_2 \), which decreases the adiabatic flame temperature and alters the kinetic pathways that are promoted by the temperature.

The latter effect concerns the possibility of \( CO_2 \) and \( H_2 O \) interactions with the reaction kinetics. They can:

- directly participate in the elementary reactions as reactants;
- decompose to release/consume radical species;
- participate in termolecular reactions as a third body with third-body efficiencies that are significantly higher than that of \( N_2 \).

Furthermore, \( CO_2 \) and \( H_2 O \) are the main products of the combustion process of hydrocarbons; consequently, their high initial concentrations can alter the thermodynamic equilibria of the reactions in which they are involved.

Further numerical simulations were performed to separate these contributions. In particular, a fictitious species \( X \) with identical thermodynamic properties to either \( CO_2 \) or \( H_2 O \) was defined.

Simulations were performed for both \( CO_2 \) and \( H_2 O \) dilution according to the following steps:

Case (1) diluting the mixtures with \( X \) instead of \( CO_2 \) or \( H_2 O \) to single out the thermal effect from the kinetic effect.

Case (2) diluting the mixtures with \( X \) and setting the third-body efficiencies of \( X \) equal to those of \( CO_2 \) or \( H_2 O \) to highlight the effects on the termolecular reactions.

Case (3) diluting the mixtures with the real species \( CO_2 \) or \( H_2 O \) and deleting their third-body efficiencies in the third molecular reactions from the kinetic mechanism to analyze the chemical effect.
Starting from the computed data, the percent variation of the auto-ignition delay times was evaluated case by case with respect to a reference case. In general, negative percent variations indicate that the ignition delay time is accelerated, whereas positive values imply that the process is decelerated.

On the left axis of Fig. 11, the percent variations of CO₂ dilution are shown. The dashed-dotted line represents the percent variation of the auto-ignition delay times that were obtained for N₂-diluted mixtures and case (1). It considers the thermal effect of CO₂ with respect to N₂, which varies from 15\% to 25\% in the entire considered temperature range. With this almost constant thermal contribution, case (1) was chosen as the reference case to evaluate the direct kinetic and third-body efficiency effect. Thus, the solid black line is the percent variation between case (2) and case (1) and represents the contribution of the third-body efficiencies of CO₂ to the auto-ignition delay times, whereas the percent variation between case (3) and case (1) represents the chemical effect of these species on the auto-ignition delay time values.

For low temperatures, the main effect is given by termolecular reactions that diminish the auto-ignition times by up to 30\% with respect to the X species. This effect is partially counterbalanced by
the thermal effect. At low temperature, the kinetic effect is negligible, which suggests that the CO₂ contribution as a reactant in bimolecular reactions is negligible. When \( T_{\text{in}} \) increases, the third-body efficiency effect diminishes, which suggests that the termolecular reactions are less active in the ignition process, which becomes 0 for \( 1000/T_{\text{in}} = 0.98 \) and positive for higher temperatures. This trend indicates that in this temperature range, the termolecular reactions inhibit the ignition process.

The kinetic effect becomes important for \( 1000/T_{\text{in}} < 0.8 \) with positive values, which determine a delay in the auto-ignition process with respect to the X case. For high temperatures, it becomes the most important effect.

Similar considerations apply to the H₂O-diluted system. Figure 12 shows the third-body efficiency effect and the species direct kinetic effect, and the thermal contribution with respect to N₂ for a stoichiometric propane/oxygen mixture was similarly evaluated as in the previous case.

For the H₂O-diluted system, the thermal effect is less pronounced than that for the CO₂-diluted system because H₂O has a lower heat capacity than CO₂, which slightly decelerates the ignition process with respect to the N₂ case.

At low temperatures, the most effective contribution to alter the auto-ignition process is related to the third-body reactions. They diminish the auto-ignition time values by approximately 60% with respect to the X species. This contribution diminishes when \( T_{\text{in}} \) increases, first rapidly for \( 1.1 < 1000/T_{\text{in}} < 0.95 \), then slowly up to \( 1000/T_{\text{in}} < 0.8 \), where it becomes positive.

The kinetic effect is negligible up to 1.05. At higher temperatures, it becomes slightly negative, which accelerates the oxidation process. Afterwards, it becomes positive and drastically delays the auto-ignition times at high temperatures.

In case of propane mixtures that were diluted in N₂, the authors thoroughly analyzed the propane ignition chemistry to identify the key reactions that control the auto-ignition times using the
sensitivity, rate of production analyses and flux diagrams at low, intermediate and high temperatures [24].

The results suggest that at low temperatures, propane is dehydrogenated to isopropyl and normal-propyl by OH and HO2 radicals. These C3 radicals mainly undergo dehydrogenation reactions to react with molecular oxygen and produce HO2 radicals. These radicals react through the reaction HO2 + HO2 = H2O2 + O2 and H2O2 (+M) = OH + O, O + H2 = HO + H, OH + H2 = H2O + H). It significantly increases the system reactivity, thus the slope of the auto-ignition delay time curve increases in the Arrhenius plot diagram with respect to one at intermediate temperatures.

In summary, at low temperatures, the decomposition of HO2 sustains the ignition process. At intermediate temperatures, the activation of the methyl recombination channel inhibits system reactivity. At high temperatures, the ignition process is sustained and accelerated by the high-temperature branching reactions of the system H2/O2.

Given these kinetic pathways, several numerical analyses were realized to identify the reactions altered by CO2 and H2O at the ignition time as a function of system inlet temperature. Figure 13 shows the Rate Of Production (ROP) analysis for a stoichiometric propane/oxygen mixture diluted up to 90% in CO2. Figure 13a is relative to radicals productions, while Fig. 13b to CH3 to consider the competitions between oxidation and recombination route.

At low temperature, CO2 mainly affects the ignition process accelerating the reaction H2O2 + M = OH + OH + M because it has a higher third molecular efficiency than N2. Thus the HO2 radicals, formed by H abstractions from n- and i-propyl radicals by O2, recombine in H2O2 that promotes OH radicals formation by thermal decomposition. As matter of fact, in the “C3:C2” kinetic scheme, the CO2 third-body efficiency for this reaction is 2.4, whereas that of N2 is 1.26.

At intermediate temperatures, CO2 enhances the methyl recombination reactions because its efficiency is three times higher than that of N2 and system reactivity slows down. Figure 13b that for Tth > 975 K this channel becomes faster than the methyl oxidation route, represented by the reaction CH3 + HO2 = CH3O + OH for the considered temperatures.

A proof of this effect is given in Fig. 7 by the closeness of the curves of the stoichiometric and rich conditions, for which the recombination reactions have a greater effect. Both curves differ from the lean curve by approximately one order of magnitude. For N2-diluted mixtures, this effect is less evident [24].

Figure 13a shows that for Tth > 1200 K, the reaction H + O2 = OH + O becomes dominant with respect to H2O2 decomposition and sustain the ignition process. For Tth higher than 1300 K, the CO2 decomposition reaction (dashed line) consumes H radicals. At Tth = 1400 K it is just 4 times lower than the high temperature branching reaction. Such reaction inhibits the ignition chemistry for two reasons: it is endothermic and competes with the high-temperature branching reactions for H radicals.

The ROP analyses at the ignition times as a function of Tth, for a stoichiometric propane/oxygen mixture diluted up to 90% in steam are reported in Fig. 14a and b. The former is relative to radicals production while the latter to the CH3 fate.

At low temperatures, H2O mainly participates as a third body in the peroxide decomposition reaction H2O2 + M = OH + OH + M because its third-body efficiency is six times higher than that of N2. Such action reduces the auto-ignition delay times with respect to N2.

At intermediate temperatures, H2O promotes the inhibiting effect of the methyl recombination reactions because its efficiency is five times higher than that of N2. The ROP analysis (Fig. 14b) shows that the methyl recombination reaction overcomes the
methyl oxidation through HO2 species for $T_{in}$ higher than 1000 K. Simultaneously steam interacts with methyl radicals to convert them to methane and produces OH radicals (CH$_3$ + H$_2$O = CH$_4$ + OH). Such reaction strongly interacts with the oxidation/recombination-pyrolytic routes of methyl radicals, and for $T_{in} > 1000$ K its reaction rate is comparable to the methyl recombination rate (Fig. 14b). Furthermore, this reaction plays an important role also in OH production, as Fig. 14a shows, resulting as the fastest reaction in OH production between 1200 and 1350 K.

For intermediate temperature, the reaction H + O$_2$ + M = HO$_2$ + M becomes important because the H$_2$O third-body efficiency is approximately 15 times higher than that of nitrogen. This reaction assures HO$_2$ radical to oxidize methyl radicals to CH$_3$O and feed the oxidation channel with a large production of H radicals from CH$_3$O and HCO decomposition reactions.

At high temperature reaction H + O$_2$ = OH + O becomes faster than H + O$_2$ = HO + H, and sustain the ignition process. Numerical analyses suggest that H$_2$O can also participate in the reactions O + H$_2$O = 2 OH and H$_2$O + H = H + OH. Figure 14a shows that the contribution of such reactions to the radical production/consumption is marginal at low-intermediate temperatures, but at high temperatures their reaction rates are comparable with the branching mechanism. They consume O and H radicals that are necessary to sustain the high-temperature branching reactions in this set of reactions:

\[
\begin{align*}
H + O_2 &= OH + O \\
O + H_2 &= OH + H \\
H_2 + OH &= H_2O + H
\end{align*}
\]

lowering system reactivity and delaying the ignition process.

The determination of the key reactions in the propane/oxygen mixture oxidation under MILD operative conditions can explain the oxidation regimes that are encountered during the experimental tests and the auto-ignition trend as a function of the inlet temperature and the mixture composition.

In general, as discussed in the previous works [5,6,11,24], for fuel-rich/stoichiometric mixtures and high inlet temperatures, a delicate competition among oxidation, pyrolysis and recombination reactions is established. This condition and the heat exchange to the surroundings determine the onset of dynamic/transient regimes.

At high temperatures, the oxidation/recombination-pyrolytic competition in the presence of CO$_2$ is altered because this diluent mainly promotes the recombination channel as an effective third-body species and decreases the H radical concentration, which depresses the high-temperature branching mechanism through its decomposition. This effect determines the onset of instabilities in the neighborhood of the stoichiometric mixture.

For H$_2$O-diluted mixtures, the oxidation/recombination-pyrolytic balance is altered because of its high efficiency in the third molecular reactions that damp the oxidation routes, which promotes the recombination channel, decreases the high-temperature branching routes (H + O$_2$ = OH + O) and boosts the productions of HO$_2$ (H + O$_2$ + M = HO$_2$ + M) radicals. Therefore, when H$_2$O dilutes the system, a double-competition mechanism establishes, the former is relative to C$_1$ and C$_2$ chemistry, the latter occurs between H + O$_2$ + M = HO$_2$ + M and H + O$_2$ = OH + O reactions. Although the C$_1$/C$_2$ route competition is promoted at high temperatures for fuel-rich mixtures, the latter occurs for lean/ultra-lean mixtures, where H radicals miss. In fact, the behavior maps that were realized for H$_2$O- and CO$_2$-diluted mixtures show that steam promotes instabilities in a wide range of C/O feed ratios.

The analysis of the ignition delay times shows that the data obtained for CO$_2$-diluted systems are notably sensitive to the mixture composition, which resembles the behavior of N$_2$-diluted systems [24], whereas the H$_2$O-diluted systems are almost independent. Furthermore, the CO$_2$ ignition data are similar to the N$_2$ data for ultra-lean and rich conditions, whereas in H$_2$O, the strong discrepancy among the data for the three reference systems only reduced for the rich mixtures. These behaviors suggest that CO$_2$ mainly alter the ignition process for mixtures with composition close to the stoichiometric value, whereas steam delays the ignition process at high temperatures almost independently on mixture composition. The ignition data that were obtained
under fuel-rich conditions for the three reference bath gases suggest that the effects of H₂O and CO₂ are less pronounced when the recombination/pyrolytic reactions prevail.

6. Conclusion

The present work experimentally characterized the ignition process and oxidation regimes of diluted and pre-heated propane/oxygen mixtures in a tubular flow reactor under a wide range of operative conditions involving various temperatures, mixture compositions and dilution levels. In particular, the attention was focused on the H₂O and CO₂ effects, which were used as diluent agents.

Several combustion regimes were identified as functions of the inlet temperature and mixture composition based on the characteristic temperature axial profiles. In particular, the dynamic behaviors were identified. These phenomenologies occur under operative conditions where a delicate competition among oxidation, pyrolysis and recombination reactions is established.

In particular, the results suggest that the steam-diluted systems present a dynamic behavior area in the C/O-Tm plane wider than the CO₂-diluted one.

Analysis of the auto-ignition delay times suggests that H₂O and CO₂ sensibly reduce the system reactivity with respect to N₂.

In the case of CO₂ dilution, the discrepancy between N₂ and CO₂ experimental data is less pronounced for ultra-lean and ultra-rich conditions, whereas for steam-diluted mixtures, the discrepancy is less important only for ultra-rich conditions. This aspect suggests that when the recombination/pyrolytic reactions control the ignition process, the effect of H₂O and CO₂ become less significant with respect to nitrogen.

Furthermore, in the case of CO₂ dilution, the ignition delay data are notably sensitive to the C/O feed ratio, whereas in the case of H₂O dilution, they are almost independent of this parameter.

The simulations, which were performed to evaluate the robustness and reliability of the detailed kinetic models, produce significant discrepancies between the experimental and the numerical ignition delay time values when the systems are diluted in H₂O and CO₂. Consistently with a previous work [24], numerical results in fuel-rich mixtures conditions are not in good agreement with the experimental data. Furthermore, in the case of steam-diluted systems, the discrepancy between the test data and the predictions is one order of magnitude, but the model can reproduce the slight dependence of the ignition data on the mixture compositions.

Based on the previous kinetic analyses [24], which aimed to identify the key reactions that controlled the ignition process in the kinetic model, further analyses were performed to understand the main effects on the ignition chemistry of these used diluents. It should be again clarified that the main issue of the numerical analysis is to identify the controlling kinetic steps in the mechanism. They represent the steps on which it is needed to act to modify the prediction ability of the kinetic model.

In particular, at low temperatures, CO₂ incentivizes low-temperature branching reactions (H₂O + OH + M = H₂O₂ + M, H₂O₂ + M = 2OH + M) because of its third-body efficiency that promotes the ignition process. This effect is partially contrasted by its high heat capacity, which damps the temperature increase. At intermediate temperatures, CO₂ promotes C₂ chemistry, which inhibits the ignition process. This effect is strengthened at high temperatures (Tm > 1200 K), where CO₂ decomposes through endothermic reactions (CO₂ + H = CO + OH) and competes for H atoms with the high-temperature branching reactions.

In the case of steam dilution, H₂O mainly acts as a third-body species. At low temperatures, it boosts the low-temperature branching reactions (H + O₂ + M = HO₂ + M, H₂O₂ + M = 2OH + M) and decreases the ignition times. At intermediate and high temperatures, it inhibits the ignition process that depresses the C₁ oxidation channel chemistry and the high-temperature branching reactions, which promotes the methyl recombination channel and the reaction H + O₂ + M = HO₂ + M, respectively.

In the case of steam, the double competition between the C₁ and C₂ chemistry, which is established at high temperatures in the neighborhood of stoichiometric mixtures, and between the H + O₂ + M = HO₂ + M and H + O₂ + OH + O reactions occurred for lean/ultra-lean mixtures, which makes the system prone to instabilities in a wide range of carbon/oxygen feed ratios with respect to CO₂, as shown in the behavior maps.

The comparison between the experimental and numerical results suggests that the kinetic models cannot correctly reproduce the system behaviors when MILD operative conditions are simulated. Thus, the adoption of kinetic mechanisms to such conditions is mandatory. This consideration becomes stricter when carbon dioxide and/or steam dilute the reactant mixtures.

In this perspective, the rich database of propane auto-ignition times in this work provides necessary information to update the detailed kinetic mechanisms.

The key reactions that were identified in this work must be considered because a further tuning of kinetic schemes is needed for a good description of the ignition delay times in MILD operative conditions.

References