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Critical Issues of Chemical Kinetics in MILD Combustion

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Mild combustion processes occur with mixtures highly diluted and preheated by a strong recirculation of hot exhausted gases (thus mass and sensible enthalpy) within the combustion chamber. This strategy configures a process based on autoignition kernels outside or close to flammability limits transported by convection in the combustion chamber, thus defining a process with unique physical and chemical features drastically different from traditional deflagrative-diffusive flames. The article aims at analyzing the recent issues relative to kinetic aspects involved in moderate or intense low-oxygen dilution (MILD) combustion processes. First, the article comes through the identification of peculiar experimental features of simple hydrocarbons oxidation process induced by highly preheated and diluted conditions in model reactors typical of chemical engineering. Second, the effects of steam and carbon dioxides on fuel oxidation process, whose presence within the combustion chamber is imposed by high levels of hot gas recirculation, are addressed. Third, the article comes through a thorough analysis of recent scientific contributions on kinetic aspects of MILD combustion processes to identify the critical points in modeling activities.

Keywords: jet stirred flow reactor, tubular flow reactor, combustion regimes, temperature oscillations, NTC behavior, H_2O and CO_2 chemical effects, chemistry modeling queries

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INTRODUCTION

The attention of the scientific and industrial community involved in the identification and development of energy production systems has been devoted to new technologies under the keywords of high efficiency and reduced emissions. Given this background, clean combustion processes still can play an important role, but they are required to be flexible with respect to thermal loads, to respond to the fluctuation of energy produced (Luo et al., 2015) by renewable sources in virtue of their intrinsic intermittence (Lund and Kempton, 2008; Keyhani et al., 2010; Østergaard, 2012; Abdmouleh et al., 2015) and to be flexible with respect to fuel nature itself, given the high variability of fuels composition and smart "energy carriers" (Spliethoff et al., 1996; McKendry, 2002; Demirbas, 2004; Hosseini and Wahid, 2016; Van Vuuren et al., 2017; SMARTCATs COST[1]). Such a further requirement embitters the difficulties to develop advanced combustion technologies, because new processes [i.e., staged combustion, lean premixed, etc. (Zabetta et al., 2005; Huang and Yang, 2009; Dunn-Rankin, 2011; Cozzi and Coghe, 2012)] may work properly in restricted ranges of system parameters.

Among new combustion concepts, one promising candidate to simultaneously meet thermal efficiency needs and pollutant emission restrictions, while responding to fuel and thermal load flexibility, appears to be the moderate or intense low-oxygen dilution (MILD) combustion

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[1] SMARTCATs COST *Action CM1404*, http://www.smartcats.eu/.

(Wünning and Wünning, 1977; Weber et al., 2000, 2005; Cavaliere and de Joannon, 2004; Dally et al., 2004; Milani and Wünning, 2007). This combustion is also renewed as flameless oxidation (or FLOX) (Wünning and Wünning, 1977; Milani and Wünning, 2007), high-temperature air combustion (Katsuki and Hasegawa, 1998; Tsuji et al., 2003), and low-temperature combustion for engine applications (Saxena and Bedoya, 2013).

The MILD combustion has been successfully employed in furnaces and boilers, and it could be potentially used into many other applications, such as gas turbines, biogas burners, burners for hydrogen reformers, or for combined heat and power (CHP) units and engines (Levy et al., 2004; Riccius et al., 2005; Lückerath et al., 2008; Khalil and Gupta, 2011; Li et al., 2011; Reddy et al., 2015; Ho et al., 2016). In addition, MILD-oxyfuel combustion for coal combustions represents a subcategory of MILD processes with high potentiality to overcome problems relative to oxycombustion systems (Li et al., 2011, 2013).

MILD combustion relies on a strong recirculation of mass and sensible enthalpy by recycling the exhausted gases to dilute and simultaneously preheat fresh reactants (Wünning and Wünning, 1977; Katsuki and Hasegawa, 1998; Weber et al., 2000, 2005; Tsuji et al., 2003; Cavaliere and de Joannon, 2004; Dally et al., 2004; Milani and Wünning, 2007; Khalil and Gupta, 2011; Saxena and Bedoya, 2013; Reddy et al., 2015). The intrinsic nature of the process is based on autoignition/fuel-ultra-lean kernels that increase in size while being transported by convection (Van Oijen, 2013; Minamoto and Swaminathan, 2015), imposed by high-turbulence exhausted gas recirculation fluid-dynamics patterns, thus defining a process with homogenous intensive parameters within the combustion chamber (Özdemir and Peters, 2001; Noor et al., 2013a; Sidey et al., 2014; Sidey and Mastorakos, 2015).

Characteristic working temperatures are modest ($T <$ 1,500 K) and below critical values for the production of pollutants (i.e., NO_x, particulate matter; Wünning and Wünning, 1977; Weber et al., 2000; Cavaliere and de Joannon, 2004; Milani and Wünning, 2007), while complete fuel conversion, high thermal efficiencies, and process stability are ensured by the high recirculated sensible enthalpy. Because the stability of the oxidation process does not rely on heat feedback mechanisms from the flame front, as in conventional diffusion/deflagrative flames, but on the recycled sensible heat, the process is intrinsically highly flexible with respect to fuels chemical/physical properties and quality (Weber et al., 2005; Colorado et al., 2010; Derudi and Rota, 2011; Hosseini and Wahid, 2013; Noor et al., 2013a), given that the mixture temperature after the mixing process between fresh reactants and recirculated gas is higher than mixtures autoignition one.

MILD combustion processes present unique physical/chemical features, drastically different from traditional combustion systems, which should be discussed at basic levels for the fine comprehension of the process itself. The structure of the reactive region (Özdemir and Peters, 2001; de Joannon et al., 2012a,b; Van Oijen, 2013; Minamoto et al., 2014; Minamoto and Swaminathan, 2015; Sorrentino et al., 2019), the chemistry (de Joannon et al., 2005; Zhukov et al., 2005; Li et al., 2014; Sabia et al., 2014; Lubrano Lavadera et al., 2018b), and the interaction between chemistry–turbulence (Dally et al., 2004; Parente et al., 2008, 2016; Isaac et al., 2013; Noor et al., 2013b) represent key points to address, with strong implications also on modeling activities (Dally et al., 2004; Parente et al., 2008, 2016; Isaac et al., 2013; Noor et al., 2013b).

Among the issues to consider, the chemical aspect of the oxidation process represents a fundamental one. In fact, the high levels of dilution coupled with moderate working temperatures imply a drastic change of the kinetics involved during the fuel oxidation process with respect to flame chemistry, with relatively lower chemical characteristic times and heat release rates (Dally et al., 2004; de Joannon et al., 2005; Zhukov et al., 2005; Parente et al., 2008, 2016; Isaac et al., 2013; Noor et al., 2013b; Li et al., 2014; Sabia et al., 2014; Lubrano Lavadera et al., 2018b). Furthermore, it occurs in presence of great amounts of non-inert species, such as carbon dioxide and steam, which can alter the kinetic routes by means of several effects, here reported:

1) Thermal: higher heat capacities with respect to N_2, thus lower adiabatic flame temperature;
2) Kinetic: they participate directly in bimolecular reactions and enhance the role of third-molecular reactions because of higher third-body efficiencies with respect to N_2. For these effects, a huge literature has been produced in the last decade, as reported in the next paragraphs (Fedyaeva et al., 2018; Lubrano Lavadera et al., 2018a).

In addition, these species can modify the structure of the reactive region because of the variation of the transport properties of the mixture (Dally et al., 2004; Mardani et al., 2010, 2013) and lowering local temperatures by enhancing heat radiation transfer (Dally et al., 2004; Mardani et al., 2013; Sorrentino et al., 2018; Zhang et al., 2019) mechanisms, because of their high radiative properties.

In this article, the chemical issues of MILD combustion processes are discussed. They will be analyzed throughout the implication on simple hydrocarbons oxidation chemistry, but the discussion could be extended to higher pressures (Gurentsov et al., 2002; Zhukov et al., 2005; Sjöberg et al., 2007; Le Cong and Dagaut, 2008, 2009a,b; Anderlohr et al., 2010; Xie et al., 2014b; Donohoe et al., 2015), to H_2 and syngas (Mueller et al., 1999; Park et al., 2003; Wang et al., 2003; Zabetta et al., 2005; Le Cong and Dagaut, 2008; Lee et al., 2012; Xie et al., 2014a), or to high-molecular-weight paraffins at elevated pressures (Sjöberg et al., 2007; Anderlohr et al., 2010).

OXIDATION PROCESS OF SIMPLE HYDROCARBONS UNDER DILUTED CONDITION

MILD oxidation configures as a chemically controlled process with characteristic kinetic times relatively longer than the ones involved in traditional flames. Within this slow oxidation regime, system exchange phenomena can drastically endorse the establishment of instabilities if coupled with complex heat reaction release rates, given the high non-linearity of exothermic/endothermic reactions. The direct experimental evidence is the insurgence of peculiar oxidation phenomena, as reported in the following.

Figure 1 is relative to the experimental combustion regimes detected for methane/oxygen mixtures diluted in nitrogen at $d =$ 90% at environmental pressure in a jet stirred flow reactor (JSFR) (de Joannon et al., 2005) and in a tubular flow reactor (TFR) (Sabia et al., 2014).

Figures 1A,B are relative to the JSFR. The mixture averaged residence time (τ) is 0.5 s. The characteristic combustion regimes were summarized in a carbon/oxygen feed ratio/mixture inlet temperature (C/O-T_{in}) map. Steady combustion and dynamic behaviors were identified. The widest region corresponds to steady stationary combustion conditions. For C/O $<$ 0.55 and for 1,150 $< T_{\text{in}} <$ 1,200 K, the system shows more complex behaviors with the establishment of temperature oscillations in time. As it can be seen from **Figure 1A**, this area is divided into several zones on the basis of different temperature waveforms (**Figure 1B**). This range of behavior reflects the richness of oxidation kinetics promoted under MILD conditions.

Numerical investigations devoted to the delineation of the controlling kinetics of these phenomenologies revealed that methane oxidation at low temperatures (<1,000 K) is sustained by this set of reactions $H + O_2 + M = HO_2 + M$, $HO_2 + HO_2 = H_2O_2 + O_2$, and $H_2O_2 + M = OH + OH + M$ coupled with $HCO + O_2 = CO + HO_2$ for HO_2 production, whereas methane converts to CO through the following chemical

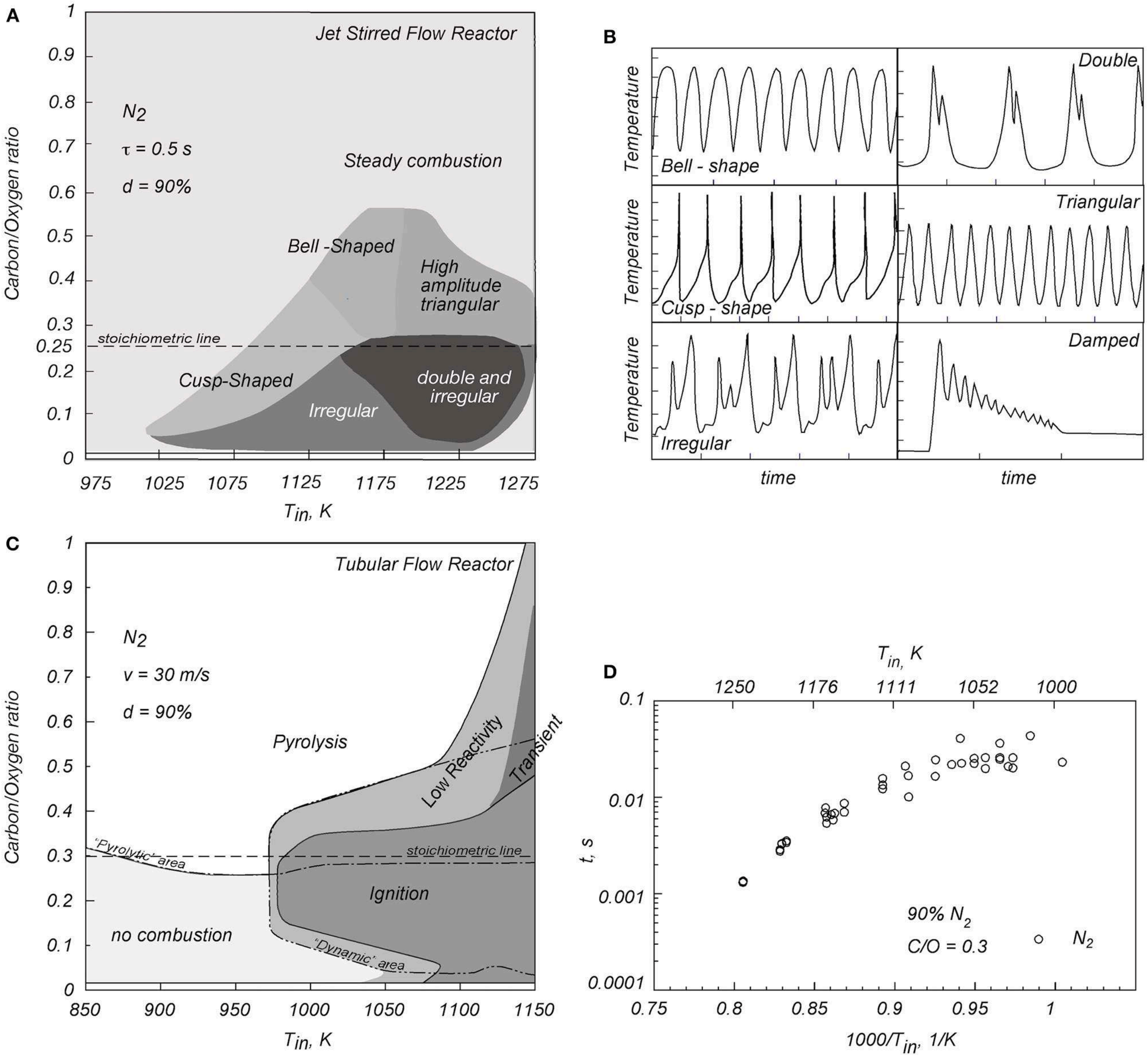

FIGURE 1 | (A,B) Dynamic behaviors and temperature oscillation shapes for a methane/oxygen mixture in a JSFR, from de Joannon et al. (2005). **(C,D)** Combustion regimes, and NTC-like behavior of autoignition delay times for propane/oxygen mixtures in a TFR, from Sabia et al. (2014).

route $CH_3 + HO_2 \rightarrow CH_3O \rightarrow CH_2O \rightarrow HCO \rightarrow CO$) (de Joannon et al., 2005; Glarborg and Bentzen, 2007; Le Cong and Dagaut, 2008, 2009a,b; Mendiara and Glarborg, 2009; Wang et al., 2013; Sabia et al., 2014, 2015; Xie et al., 2014a; Song et al., 2015; Lubrano Lavadera et al., 2016, 2018a). For the conditions where temperature oscillations were detected, methyl radicals are directly oxidized to CH_2O ($CH_3 + OH \rightarrow CH_2O + H_2$) by OH radicals produced by the high-temperature branching mechanism of the subsystem H_2/O_2. At the same time, methyl radicals recombine to ethane ($CH_3 + CH_3 + M = C_2H_6 + M$), followed by C_2 dehydrogenation/pyrolytic routes. The competition between oxidation/recombination–pyrolytic routes, coupled with system heat exchange phenomena, promotes instabilities (de Joannon et al., 2005; Sabia et al., 2014; Lubrano Lavadera et al., 2018b). The enhanced role of the methyl recombination routes for these temperatures is emphasized also in other works (Zhukov et al., 2005; Li et al., 2014).

For higher T_{in} (>1,250 K), the activation of further oxidative routes ($CH_3 + OH + M \rightarrow CH_3OH \rightarrow CH_2OH \rightarrow CH_2O$) followed by $CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2$, or $CH_3 + OH \rightarrow CH_2(s) \rightarrow CH_2 \rightarrow CH \rightarrow CO$, relieves the system from the inhibiting effect of methyl radicals conversion to ethane; thus, the system reaches a steady stationary state (Lubrano Lavadera et al., 2018b).

Figures 1C,D are relative to experimental tests in a TFR (Sabia et al., 2014). It is equipped with thermocouples equi-displaced along the axial coordinate of the system, to detect ignition/oxidation states. Following the same methodology used for the JSFR data, the characteristic combustion regimes were summarized in a C/O-T_{in} map.

For low T_{in} (850–975 K), no combustion was detected for C/O <0.3 (stoichiometric condition), whereas for rich mixtures, a pyrolytic behavior was identified (temperature values lower than the isothermal inlet profiles). As T_{in} is increased, for C/O = 0.3, the operative conditions lead to ignition, defined as a temperature increase of 10 K (Mardani et al., 2010, 2013) with respect to the inlet axial one (T_{in}). When T_{in} is increased up to 1,080 K, the ignition region extends to fuel leaner conditions, while remaining almost constant for the fuel-rich side. For T_{in} >1,120 K, the ignition region extends up to C/O = 0.5. Between the ignition and the pyrolysis–no combustion regions, a low reactivity behavior occurs with a temperature increase lower than 10 K with respect to T_{in}, thus not satisfying the ignition criterion (de Joannon et al., 2002; Evans et al., 2017).

Conditions included within the dynamic line show oscillatory behaviors, for which two temperature profiles are recorded, downstream of a steady ignition point, periodically switching from one to the other in time. The last region, indicated as transient (enclosed by the dotted line), identifies conditions where mixtures temporarily ignite, leading to a temporarily first steady state, followed by a second final one.

Figure 1D reports the autoignition delay times (t) with respect to mixture inlet temperature (T_{in}) for the stoichiometric condition in the Arrhenius plot diagram. The autoignition delay time is defined as the ratio between the axial positions where the temperature increase is equal to 10 K and the flow mean velocity (Sabia et al., 2014). The autoignition delay time curve shows two different slopes with respect to T_{in}: for T_{in} lower than about 1,100 K, t is almost independent from T_{in}, whereas for 1,000/T_{in} <0.9, t linearly diminishes with temperature. Such a trend was identified for 0.15 < C/O < 0.3. Congruently with the methane dynamic behavior in the JSFR, the negative temperature coefficient (NTC)-like phenomenology and the oscillatory regimes detected in the TFR emerge from the competing methyl radicals oxidative/recombination–pyrolytic routes at intermediate temperatures (1,000 < T < 1,100 K), whereas the H_2/O_2 system is passing from the low- to the high-temperature branching mechanism.

In similar operative conditions, NTC-like and oscillatory behaviors were detected in other systems for simple hydrocarbons (Cadman et al., 2000; Penyazkov et al., 2005; Zhukov et al., 2005; Gallagher et al., 2008; Sabia et al., 2013; Lubrano Lavadera et al., 2016, 2018a; Hashemi et al., 2017).

As evident, the nature of such behaviors is very different from conventional "cool" flame or "NTC" phenomena observed for low-molecular-weight paraffins at high pressures (Herzler et al., 2004; Gallagher et al., 2008; Hashemi et al., 2016, 2017, 2019) or high-molecular-weight paraffins (Sokolov et al., 1996; Basevich and Frolov, 2007; Ju et al., 2019; Wang et al., 2019), where the oxidation chemistry of alkyl-peroxide radicals is fundamental. In particular, for high-molecular-weight paraffins, a double O_2 addition to alkyl-radicals and internal isomerization to ketohydroperoxy radicals, ruled by equilibrium reactions, determine temperature oscillations in time or the NTC behavior (if referred to ignition delay times), coupled with heat exchange mechanisms.

OXIDATION PROCESS OF SIMPLE HYDROCARBONS UNDER DILUTED CONDITION IN PRESENCE OF H_2O AND CO_2

As examples of the chemical effects of H_2O and CO_2 on combustion processes, **Figure 2** reports some recent experimental data, adapted from Sabia et al. (2015), Lubrano Lavadera et al. (2016, 2018a). In **Figure 2**, round symbols are relative to the N_2- diluted mixtures, triangles to the CO_2-diluted mixtures, and squares to the H_2O–partially diluted one. **Figure 2A** shows the experimental $\Delta T = (T_{reactor} - T_{inlet})$ obtained for the stoichiometric condition obtained in a JSFR (de Joannon et al., 2005; Sabia et al., 2014) for these three cases. The residence time (τ) is equal to 0.5 s, and the overall mixture dilution level (d) is 90%.

For the N_2-diluted mixture, the oxidation onset occurs for T_{in} = 880 K. The system temperature increases monotonously up to T_{in} = 940 K, and then the oxidation occurs throughout temperature oscillatory regimes, likewise the methane (**Figures 1A,B**). For this oxidation regime, the maximum and minimum values detected during the oscillatory behavior (full symbols) are reported. Afterward, for T_{in} = 1,100 K, a stationary steady condition is identified.

The experimental ΔT for the CO_2-diluted mixture and the system partially diluted in H_2O (45% H_2O—55% N_2) are similar to the ones relative to the N_2-diluted one. Nonetheless, the

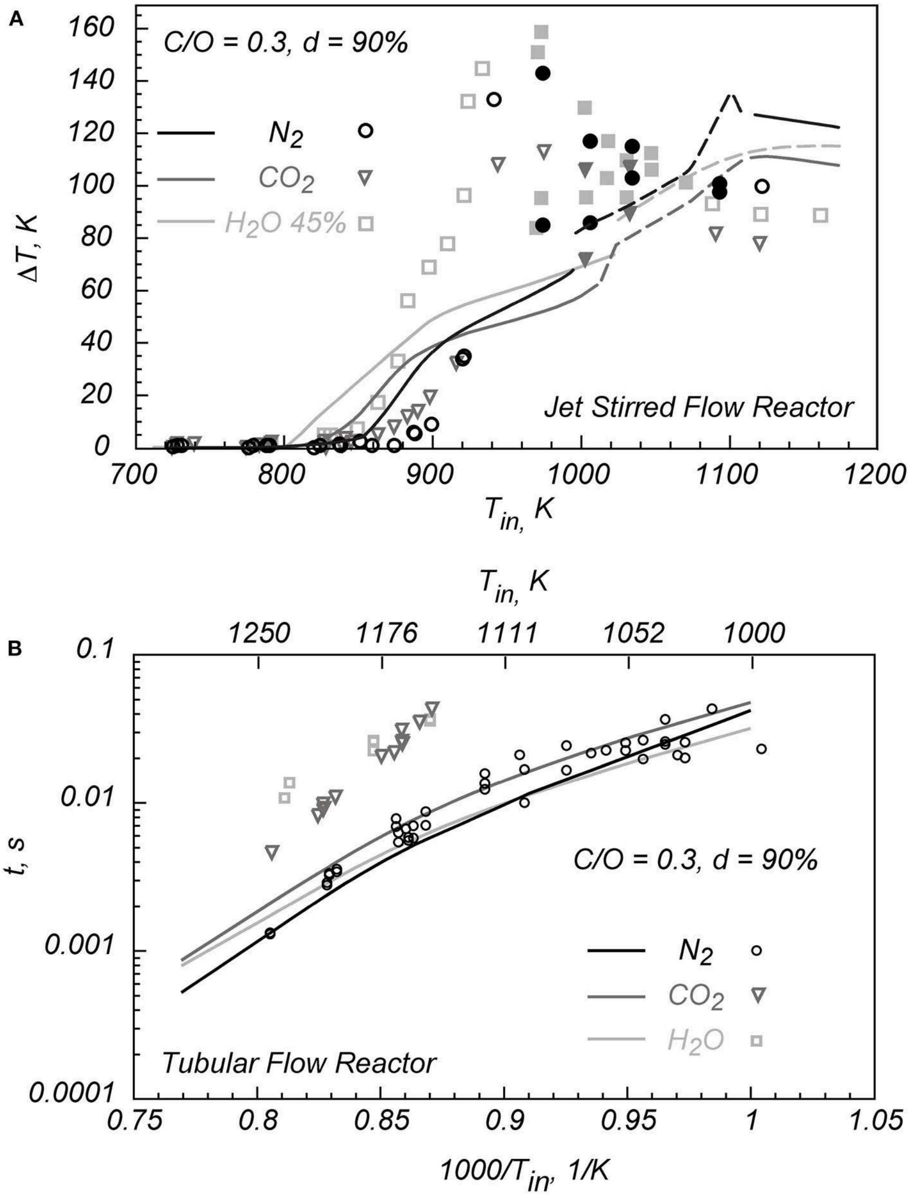

FIGURE 2 | Effects of H_2O and CO_2 on the oxidation process of stoichiometric C_3H_8/O_2 mixtures in a JSFR **(A)**, adapted from Lubrano Lavadera et al. (2018a) and Lubrano Lavadera et al. (2016), and the autoignition delay times of stoichiometric C_3H_8/O_2 mixtures in a TFR **(B)**, adapted from Sabia et al. (2015).

oxidation onset occurs, respectively, for $T_{in} = 820$ K and for $T_{in} = 850$ K, thus slightly anticipating the reactivity with respect to the reference system. For CO_2, oscillation occurs for $1{,}030\text{ K} < T_{in} < 1{,}100\text{ K}$, whereas for the system diluted in H_2O for $980\text{ K} < T_{in} < 1{,}100\text{ K}$. Afterward, a stationary steady state regime is detected for both the mixtures. At high temperatures, the system diluted in N_2 shows a higher temperature increment.

Along with the experimental data, **Figure 2A** reports the numerical simulations obtained with a detailed kinetic model PoliMi (Cadman et al., 2000; Faravelli et al., 2003; Frassoldati et al., 2003), as reported in Lubrano Lavadera et al. (2018a) and Lubrano Lavadera et al. (2016). In general, it well-predicts both the anticipating effect of CO_2 and H_2O at low temperatures and the temperature oscillatory behaviors (dashed lines), even though overestimates system reactivities at low temperatures, considering ΔT as the reference parameter.

Figure 2B shows the experimental autoignition delay times (t) for a stoichiometric propane/oxygen mixture diluted at $d = 90\%$ in N_2, CO_2, and H_2O along with numerical predictions (lines) (Sabia et al., 2015).

For the system diluted in CO_2 and H_2O, the experimental autoignition delay times (t) are longer of almost one order of magnitude with respect to the ones obtained for the N_2-diluted mixture.

The autoignition delay times obtained for N_2 are predicted with a good approximation, but this consistency fails for the other two diluents. Because MILD combustion configures as a continuous autoignition states, the fine comprehension of the chemical effect of CO_2 and H_2O is mandatory.

DISCUSSION AND CONCLUSION

There are different main aspects that should be considered in the development of detailed oxidation chemistry for MILD combustion processes.

The first point concerns the complexity of the oxidation process at low ($T < 1{,}000$ K) to intermediate ($1{,}000\,\mathrm{K} < T < 1{,}200\,\mathrm{K}$) temperatures. In fact, under these operative conditions, the numbers of species and consequently of elementary reactions are meaningfully larger with respect to the ones necessary to describe the high-temperature flame oxidation processes. This implies high computational cost for computational fluid dynamics (CFD) calculations, because detailed chemistries are required. As previously shown, the light hydrocarbons chemistry under these operating conditions is governed by a delicate balance between slow oxidation and recombination/pyrolytic channels. Uncertainties of the Arrhenius parameters (Konnov, 2008; Varga et al., 2015) of elementary reactions and of thermodynamic data have a stronger impact on the predictive performance of kinetic models with respect to conventional flame conditions. In fact, at high temperatures, the performance of kinetic schemes relies on the proper description of the high-temperature branching reactions of the subsystem H_2/O_2. The fast chemistry promoted by such reactions may hide the elementary reaction constants uncertainties of slow reactions, reducing the impact of their relative weight in the prediction of combustion features.

The presence of H_2O and CO_2 *ab initio* poses several problems. First, their interaction on fuel oxidation kinetics process is an aspect not contemplated for traditional systems, where H_2O and CO_2 are present as combustion products in the postoxidation phase, thus acting only on a subset of kinetic reactions that involve few species close to equilibrium conditions. On the contrary, CO_2 and H_2O can drastically alter the ignition process in dependence of operating conditions with a twofold interaction. They increase system reactivity at low temperatures (Sabia et al., 2007, 2015; Sjöberg et al., 2007; Anderlohr et al., 2010; Lubrano Lavadera et al., 2016), but delay it at intermediate–high temperatures (Mueller et al., 1999; Cadman et al., 2000; de Joannon et al., 2002; Park et al., 2003; Wang et al., 2003, 2013; Herzler et al., 2004; Penyazkov et al., 2005; Zabetta et al., 2005; Basevich and Frolov, 2007; Glarborg and Bentzen, 2007; Sjöberg et al., 2007; Gallagher et al., 2008; Le Cong and Dagaut, 2009a,b; Mendiara and Glarborg, 2009; Mardani et al., 2010, 2013; Lee et al., 2012; Sabia et al., 2013, 2015; Chen and Ghoniem, 2014; Xie et al., 2014a; Song et al., 2015; Zou et al., 2015; Hashemi et al., 2016, 2017, 2019; Lubrano Lavadera et al., 2016, 2018a; Evans et al., 2017; He et al., 2017; Fedyaeva et al., 2018; Sorrentino et al., 2018; Zhang et al., 2019).

These effects mainly depend on the interaction that such species have on the branching mechanisms, related to the H_2/O_2 subsystem. At low temperatures, the ignition–oxidation chemistry is sustained by hydrogen peroxides molecule formation and decomposition to OH radicals, namely, $H + O_2 + M = HO_2 + M$, $HO_2 + HO_2 = H_2O_2 + O_2$, and $H_2O_2 + M = OH + OH + M$. At intermediate–high temperatures, the branching mechanism relies on the following set of reaction $H + O_2 = OH + O$, $O + H_2 = OH + H$, and $OH + H_2 = H_2O + H$.

Literature works, relative to H_2O and CO_2 effects on H_2 oxidation (Mueller et al., 1999; Park et al., 2003; Wang et al., 2003; Lee et al., 2012; Xie et al., 2014b), suggest that they act on the low-temperature mechanism due to their high third-body collisional efficiencies, enhancing the reaction $H + O_2 + M = HO_2 + M$ to the detriment of $H + O_2 = OH + O_2$ at low temperatures. At high temperatures, H_2O delays reaction $H_2 + OH = H_2O + H$, by shifting its equilibrium state, and $O + H_2 = OH + H$ as O radicals is consumed by reaction $O + H_2O = OH + OH$. In general, H_2O leads to a change of radicals distribution, decreasing H and O while promoting OH concentration. At high temperatures, CO_2 further inhibits reaction $H + O_2 = OH + O$ by consuming H radicals throughout decomposition reactions ($CO_2 + H = CO + OH$) (Glarborg and Bentzen, 2007; Le Cong and Dagaut, 2008, 2009a,b; Mendiara and Glarborg, 2009; Song et al., 2015).

Fuel oxidation chemistry in presence of H_2O and CO_2 is further complicated by their possibility to interact with the C_1-C_2 reactions directly in bimolecular reactions or indirectly as third-body species in third-molecular reactions.

Such species can sensibly alter the intermediate temperature consumption of CH_3 rates by promoting methyl recombination routes to C_2 species, as high collisional efficiency third-body species. Steam can partially reconvert methyl radicals back to methane ($CH_3 + H_2O = CH_4 + OH$), thus inhibiting system reactivity (Sabia et al., 2015). At the same time, CO_2 can strongly interact in the C_1 high-temperature chemistry through the reaction $CH_2(S)/CH_2 + CO_2 = CH_2O + CO$ (Glarborg and Bentzen, 2007; Le Cong and Dagaut, 2009a,b; Mendiara and Glarborg, 2009; Sabia et al., 2015; He et al., 2017). Recently, He et al. (He et al., 2017) have introduced a new methyl radical conversion channel ($CH_3 \rightarrow CH_3OCO \rightarrow CH_2O$ and $CH_3 \rightarrow CH_3OCO \rightarrow CO$) exclusive in O_2/CO_2 atmospheres for methane oxidation chemistry at high temperatures.

As it has emerged within this brief description, kinetic mechanisms involve a set of third-molecular reactions whose role is emphasized by third-molecular species with high collisional efficiencies (such CO_2 and H_2O). In this context, the reaction $H + O_2 + M = HO_2 + M$ plays a crucial role for HO_2 radical production. In this regard, it is worth mentioning that big uncertainties on kinetic parameters still remain (Konnov, 2008; Varga et al., 2015). All these works highlight that for such a reaction there are considerable scattered data especially for the low-pressure limit with big uncertainties for third-bodies collisional efficiencies. Some recent efforts to calculate these values were made by Jasper et al. (2015) for monoatomic and biatomic species, whereas Shao et al. (2019) have recently proposed new values for H_2O and CO_2.

The problem relative to third-body collisional efficiency uncertainties is even more relevant if it is considered that they may exhibit temperature dependence. For instance, Baulch et al. (1988) suggested a temperature dependence $k(H_2O)/k(N_2) = 1.36T^{0.4}$ for water in the reaction $H + O_2 + M = HO_2 + M$, whereas Davis et al. (2005) suggested a temperature dependence $k(H_2O)/k(MN_2) = 60T^{0.25}$ for water in the elementary reaction $H + H + M = H_2 + M$. Also, for the reaction $CH_4 + H = CH_3 + H_2$, Jasper et al. (2013) suggested $(H_2O)/k(Ar_r)$ should be 3 at 300 K and 7 at 2,000 K.

The definition itself of third-body species with third-molecular efficiencies different from 1 is ambiguous. Several authors have proposed third-body collisional efficiencies also for H_2O_2 and HO_2, with collisional efficiencies similar to the ones declared for steam (Gerasimov and Shatalov, 2013).

In addition, the basic chemistry of the H_2/O_2 mechanism would require a right description of $H + HO_2$ reactions (i.e., $H + HO_2 = OH + OH$, $H + HO_2 = H_2 + O_2$, and $HO_2 + OH = H_2O + O_2$, $H + HO_2 = H_2O + O$) (Conaire et al., 2004; Mousavipour and Saheb, 2007; Burke et al., 2010, 2012; Shimizu et al., 2011), whereas for high-pressure conditions, the inclusion of reaction $H + OH + M = H_2O + M$ would be fundamental for the description of laminar flame speeds (Conaire et al., 2004; Konnov, 2008; Burke et al., 2012). Konnov (2008) also suggested the inclusion of the termolecular reaction $HO_2 + HO_2 + M = H_2O_2 + O_2 + M$ for laminar flame speed prediction.

Burke et al. (2010) have recently suggested that the pressure dependence description should be described separately for different bath gases, with center broadening factors from 0.5 to 0.7 for Ar, 0.5 to 0.7 for N_2, and 0.6 to 0.8 for H_2O. Burke et al. (2010) have also discussed the necessity to include "non-linear mixing rules" for the reaction $H + O_2 + M = HO_2 + M$ in presence of multicomponent bath gases, in agreement with Li et al. (2004).

In this perspective, at low–intermediate temperatures and in presence of conspicuous amount of non-inert species, the chemical kinetic validation procedure suffers the lack of experimental results in simple and controlled facilities.

AUTHOR CONTRIBUTIONS

MJ and PS have synergistically contributed to the research concept and design and equally contributed to the manuscript through fruitful discussions and data analyses. The work represents a summary of their joint research activities. PS has assembled the data and written the first release of the manuscript. MJ has critically revised the paper up to the final version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.