



Propane oxidation in a Jet Stirred Flow Reactor. The effect of H₂O as diluent species

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ABSTRACT

Advanced combustion technologies, such as MILD, LTC (Low Temperature Combustion) reduce emission of pollutants by controlling system working temperatures to values not critical to promote the formation of several classes of pollutants. To access this temperature range, a significant dilution of reactants is required. At the same time, reactants have to be preheated to sustain the oxidation process. Such conditions are achieved by a strong recirculation of exhaust gases. Such a strategy implies that high contents of CO₂ and H₂O interact with reactants oxidation chemistry. In order to characterize this aspect of the combustion processes under diluted conditions, experimental tests were carried out for propane/oxygen/nitrogen mixtures in presence of variable amounts of H₂O in a quartz Jet Stirred Flow Reactor (JSFR). Experiments were carried out at atmospheric pressure, over the temperature range 720–1100 K, from fuel lean to rich conditions and at a residence time of 0.5 s. Temperature and species concentration measurements suggest that the oxidation of propane is significantly altered by H₂O in dependence of mixture inlet temperatures and equivalence ratios.

Numerical analyses were performed to explore the interaction of H₂O with the oxidation chemistry of propane. Results suggested that such a species alters the main radical branching mechanisms, i.e. in termolecular reactions as a third body species with high collisional efficiency or directly participating in bimolecular reactions.

1. Introduction

Innovative combustion technologies for power generation in the industrial, domestic, and transport sectors are required to meet the needs of high energetic efficiency and low pollutants emissions, and they have to be flexible with respect to the fuel nature.

Diluted combustion strategies (MILD, LTC, etc.) are receiving increased attention as means to reach such targets, as the resulting peak flame temperatures are low to promote the NO_x and soot formation. To access this temperature range, significant dilution as well as preheating of the reactant mixtures is required. In practical systems, dilution and preheating are usually achieved through internal or external exhaust gas recirculation [1,2].

Therefore, these combustion processes occur in presence of great amounts of carbon dioxide and water. Such species may have thermal and chemical effects [3–5].

Lubrano Lavadera et al. [6] provided a summary of the experimental and numerical studies to date, which have investigated the

effects of CO₂ on combustion properties. They studied the effects of significant additions of CO₂ on propane oxidation in a JSFR at atmospheric pressure. They found that propane oxidation is significantly altered by CO₂ in dependence of mixture inlet temperatures and equivalence ratios.

Recently, mixtures of fuels with H₂O have received attention. In the scientific literature, several works have been reported on the study of laminar flame speeds and extinction strain rates [7–9] for fuel mixtures partially diluted in H₂O because of the increasing interest in Low Calorific Value (LCV) fuels. The common statement is that the H₂O significantly reduces the burning velocities and the extinction strain rates of these mixtures. Indeed, H₂O decreases the flame temperature, thus the fuel oxidation reaction rate. For systems working at high temperatures, it has also been pointed out that H₂O is not inert but directly participates in chemical reactions. Water addition was found to dramatically reduce H and O mole fractions while increasing OH ones, mainly due to H₂O + O = 2OH [9].

Anderlhor et al. [10] numerically investigated the thermal and

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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 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. The authors suggested revising the efficiencies of the potential collision partners.

Abián et al. [11] 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, representing different exhaust-gas recirculation conditions. In contrast with other works, the authors found that H₂O enhances the CO conversion. They optimized the H₂O third-body efficiency in reaction $H + O_2 + M = HO_2 + M$ in the detailed kinetic mechanism that they used and multiplied its efficiency for a correction factor.

Sabia et al. [12] studied the effects of significant additions of CO₂ and H₂O on propane autoignition delay times for temperatures ranging from 850 K to 1250 K and atmospheric pressure. Significant changes of autoignition delay times were observed for the mixtures compared with N₂ measurements, which were not captured by available kinetic models. The disagreement between experiments and model predictions was found even more evident when studying, in the same conditions, the ignition of a model gas surrogating the gaseous fraction of biomass pyrolysis products [13].

In all the cited papers, the authors recommended further investigation of the effect of higher concentrations of H₂O in the reactive mixture, as models need additional validation in this parameter space. Several reasons have been proposed to explain these discrepancies, including the sensitivity of rate coefficients at low-temperature/diluted conditions [7].

There are two major distinctions about the low temperature reactions when compared with the higher temperature classifications. The degradation of the hydrocarbons (involving both abstraction and addition processes) tends to follow a sequential breakdown of the carbon backbone (such as $C_4 \rightarrow C_3 \rightarrow C_2 \rightarrow C_1$) rather than the easy fragmentation into smaller carbon-containing units that may occur at higher temperatures ($C_4 \rightarrow 2C_2$, for example). Thus, simplifications of the kind that are employed at higher temperatures, as a result of common structures within certain classes of reactions, are not so readily applicable. Also, the selectivity of reactions of different propagating free radicals (especially OH, HO₂, RO₂ or RO) is so much more marked, and also the reactivity at particular C–H bonds have an increased importance at low temperatures because the relative magnitudes of rate constants for individual reactions are so much dependent on the activation energies in the Arrhenius expression at lower temperatures [14]. Kinetic models require reaction rate, thermochemical, and transport data for the rapidly growing number of species and reactions present. Unfortunately, only a relatively small proportion of reactions now included in comprehensive kinetic schemes actually have been studied directly by experiments. Theoretical methods for calculating reaction pathways and rates of reaction have been developed, many of which now require supercomputer resources to solve the complex quantum mechanical systems involved. Thus, there is considerable recourse to estimation techniques for reaction rates and thermochemical quantities required by models [15].

Therefore, fundamental study is necessary to understand the mechanisms of non-conventional combustion phenomena. The understanding of such phenomena must rely on validated detailed reaction models established for non-conventional conditions than those conventionally addressed. To assist the development and validation of more reliable chemistry models, new experiments are required, spanning as many different types of practical systems and as wide a range of conditions as possible.

Given this background, the objectives of the current work were to investigate the effect of H₂O dilution on the concentration profiles of chemical species and how it depends on process parameters, including data obtained in a JSFR, at conditions relevant to diluted combustion. The experiments were carried out for lean, stoichiometric, and rich mixtures, diluted with N₂ and two mixtures of N₂ and H₂O, at atmospheric pressure. The study bridges the region between low and intermediate temperature conditions of practical interest to diluted combustion applications. Propane was chosen as the reference fuel because its chemical kinetics is fundamentally important for all combustion processes of hydrocarbons, is well known, and is sufficiently simple. Moreover, propane reflects the thermochemical and combustion properties of larger hydrocarbons.

Obtaining such measurements was the primary objective of the present study. They provide validation targets for detailed kinetic mechanisms development.

In addition, the performance of updated kinetic models in predicting the experimental data was tested. The experiments do not only provide data for models validation, but also contain information in itself. Therefore, numerical analyses were performed to gain an understanding of the contribution of these non-conventional conditions on the combustion chemical kinetics. Finally, possible sources of disagreement between the model predictions and experimental data were outlined.

2. Experimental and numerical tools

The oxidation of propane was studied in a JSFR; it approaches the behavior of an ideal Perfectly Stirred Reactor (PSR). The JSFR is an important experimental tool in kinetic studies because it allows for an accurate monitoring of the extent of reaction, focusing only on chemical kinetics phenomena. The apparatus consists basically of a gas feeding system, a JSFR reactor and a chemical gas analysis system.

The reactor [16] consists of a sphere of 113 cm³. It is made in quartz to prevent catalytic reactions. The main flow is composed by oxygen and diluent. It passes through a quartz tube located within two cylindrical electrically heated ceramic fiber ovens. The main flow residence time within the quartz tube and the installed electric power are designed to reach pre-heating temperatures up to 1250 K. It subsequently mixes with the secondary flow, composed by fuel and diluent, in a premixing chamber. Then the pre-mixed mixture enters the reactor through four nozzles of 1 mm diameter located at its center. The well mixing of the reactor was verified in the past by means of pulse tracer experiments following a procedure described by Levenspiel [17]. The results suggested that the reactor behaves as a PSR for residence times lower than 0.6 s. The residence time used in the present experiments was thus fixed to 0.5 s. Under these conditions, the mean residence time differs from the ideal PSR residence time of about 3%. The residence time of the fuel mixture in the injector is more than 100 times lower than the mean residence time in the reactor. Thus, oxidation of the fuel inside the injector is prevented. The products of combustion were exhausted through a 3 mm diameter tube located at the bottom of the reactor. The reactor is located within other two electrical fiber ovens to minimize heat loss to the surroundings. A recirculation air system provides a homogeneous temperature distribution in the oven. The homogeneity of the reactor wall temperature is monitored with movable thermocouples. The temperatures of the reactor wall and of the gases upstream are measured by type N thermocouples and regulated by PID controllers.

The flow rates of gases from cylinders are measured and regulated by digital thermal mass flow controllers supplied by BronkHors High-Tech with a high accuracy ($\pm 0.5\%$). The controllers are connected to a PC and managed by sub-routines developed in Labview. The pressure is kept constant at 1.1 atm in the apparatus by means of a needle valve on the exhaust gas line.

Gases were provided with high purities: 99.999% for nitrogen,

99.995% for oxygen, and 99.5% for propane.

The water feeding system consisted of a stainless steel cylinder, pressurized with dry nitrogen in order to feed the distilled water through a calibrated liquid mass flow meter into a Controlled Evaporator Mixer (CEM) supplied by BronkHorst High-Tech. It consisted of a control valve, a mixing device and a heat exchanger. A carrier gas (nitrogen), controlled by a dedicated mass flow controller, is used to transport the evaporating fuel until the reactor inlet to a pre-heated line to prevent water condensation.

To provide a detailed chemical analysis, the outlet stable species were analyzed by gas chromatography. The exit gases were cooled down efficiently by means of a heat exchanger installed at the reactor outlet to quench the oxidation reactions in the sampling line. Then, gases passed through a silica gel trap to eliminate the moisture content before gas analyses. Therefore all the results are reported on a dry basis. The system exit was connected to a gas chromatograph (Agilent 3000) that was used for the quantification of different species. It was equipped with two specific capillary columns: a column Plot U to detect online carbon dioxide, ethylene, ethane and acetylene and a column Molsieve 5A equipped with a pre-column Plot U to separate hydrogen, nitrogen, oxygen, methane and carbon monoxide. Species concentrations were quantified by means of a Thermal Conductivity Detector (TCD). Stable species were identified by the determination of their individual retention times and calibrations were made directly using cold-gas mixtures. Maximum relative errors in mole fractions are estimated to be $\pm 10\%$ when the concentrations approach the detection threshold, which is about 10 ppm.

It should be stated that, in the case of mixture diluted in water vapor, since water is condensed prior to analysis, the measured concentrations are higher than the real ones. Hence, in order to compare the results obtained in the case of mixtures diluted in water with the other case the species concentrations are recalculated on the basis of the nitrogen concentration, in the following way:

$$X_{\text{real}}^{\text{species}} = \frac{X_{\text{measured}}^{\text{species}}}{100 + \left(X_{\text{measured}}^{N_2} \left(\frac{X_{\text{in}}^{H_2O}}{X_{\text{in}}^{N_2}} \right) \right)}$$

where the subscripts “in”, “measured” and “real” refer to the molar fractions fed, measured and calculated, while the superscript “species” refers to any measured species. Then, the term in the brackets at the denominator is the condensed water, without however taking into account the water produced by the reaction, which is also condensed using nitrogen. This allows comparing the results obtained with different diluents, but adds a higher uncertainty in the data relating to H₂O-diluted mixtures due to the uncertainty of the measured nitrogen concentration ($\pm 1\%$).

Experiments were performed at least twice under all test conditions to ensure measurement reproducibility. The test repeatability was excellent under all conditions with differences among the various tests well within the reported experimental uncertainties.

To detect and follow accurately the temperature changes during gaseous reactions, a homemade unshielded thermocouple type R (0.1 mm bead size) was used. The thermocouple response time is less than 30 ms with a precision of ± 2 K. The thermocouple wires were housed in thin-wall double-core covers of Al₂O₃ in order to prevent catalytic reactions on the platinum wire.

The experimental results obtained in the JSFR were simulated using the PSR code of the Chemkin PRO package [18]. It predicts the time-dependent and the steady-state properties of an open well-mixed reactor. This zero-dimensional model also allows for heat loss from the reactor to the surroundings.

Specifications of the reactor were the same as those of the experimental apparatus, i.e., a volume of 113 cm³ and an internal surface area of 113 cm². The wall of the reactor is assumed to be infinitely thin, and there is no temperature gradient in the wall. The linear heat convection

equation was used, with constant coefficient, to calculate the heat loss term in the gas energy equation. The wall temperature was set equal to the inlet one. A heat loss occurs only with a temperature increase caused by chemical reactions. There is no additional heat flux from the wall. The reactor overall heat transfer coefficient in the JSFR was calculated by means of an empirical correlation available in the literature [19]. It was fixed at 1.3×10^{-3} cal/cm² s K.

A recently updated detailed gas-phase chemical kinetic model was used, namely the “CRECK-2014” [20]. It was developed by Ranzi et al. for the pyrolysis and combustion of a large variety of fuels. It includes 107 species involved in 2642 elementary chemical reactions. In recent papers, authors showed that it was one of the most reliable scheme in predicting auto-ignition delay times [12,21] and speciation measurements [6] for propane mixtures under MILD operating conditions.

3. Results and discussion

Experiments were performed at constant pressure of 1.1 atm, a constant residence time of 0.5 s, over the temperature range 720–1100 K. Three equivalence ratios ($\Phi = 1.5, 1, 0.5$) were considered and mixtures were diluted with N₂ (reference case), 75% N₂–25% H₂O and 55% N₂–45% H₂O, keeping a fixed overall dilution (d) of 90%. In particular, d is the overall percentage molar fraction of the diluent species in the mixture and Φ is defined as:

$$\Phi = \frac{C/O}{C/O_{\text{stoichiometric}}}$$

where in this expression C/O indicates 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, whereas C/O_{stoichiometric} represents the stoichiometric carbon to oxygen ratio. When H₂O is present in the reactant mixture, given the definition of C/O, oxygen atoms in the H₂O are not included in the C/O ratio calculation.

The experimental conditions are summarized in Table 1.

The influence of diluent type, inlet temperature, and the equivalence ratio were studied by measuring the outlet concentrations of chemical species and the temperature inside the reactor.

Fig. 1 reports the experimental ΔT obtained under stoichiometric conditions for the three cases studied. Squares symbols represent experimental results for the N₂-diluted system; triangles are relative to the 75% N₂–25% H₂O-diluted system, while circles represent the results for the 55% N₂–45% H₂O system, as a function of T_{in}.

The ΔT reported as a function of T_{in} reveal an interesting behavior. At low temperatures (around 800 K), mixtures start reacting. As the inlet temperature is increased, two different regimes with two different ΔT are identifiable (at T_{in} = 850 K) for the same inlet conditions. Both of the steady states are stable from an experimental point of view. In fact, the response of the system to an induced temporary displacement in terms of pressure or mixture composition perturbation slightly shifts it from the steady state for a while before it then returns once again to

Table 1

Experimental conditions studied in the JSFR for C₃H₈ mixtures. 720 K < T_{in} < 1100 K, P = 1.1 atm, d = 90%, τ = 0.5 s.

Φ	C ₃ H ₈ (vol%)	O ₂ (vol%)	N ₂ (vol%)	H ₂ O (vol%)	Number of experiments
0.5	0.91	9.09	90	0	46
0.5	0.91	9.09	67.5	22.5	25
0.5	0.91	9.09	49.5	40.5	23
1	1.67	8.33	90	0	49
1	1.67	8.33	67.5	22.5	25
1	1.67	8.33	49.5	40.5	23
1.5	2.31	7.69	90	0	41
1.5	2.31	7.69	67.5	22.5	24
1.5	2.31	7.69	49.5	40.5	22

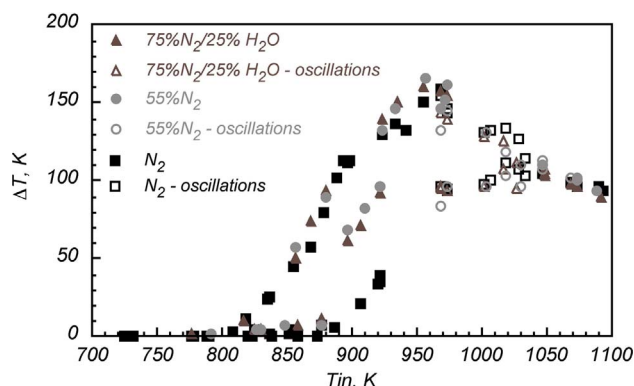


Fig. 1. Experimental ΔT profiles versus T_{in} . $\Phi = 1$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, N_2 (square symbols), 75% N_2 –25% H_2O (triangle symbols), 55% N_2 –45% H_2O (circle symbols). Full symbols represents steady states, empty symbols oscillatory regimes.

the same steady state. Bistability is an already observed phenomenon for propane oxidation [22]. Increasing T_{in} , the two regimes collapse into a single one at T_{in} equal to about 970 K, characterized by temperature oscillations in time. For this oxidation regime, two ΔT are reported for the same T_{in} in Fig. 1. They correspond respectively to the maximum and minimum values detected during the oscillatory behavior. To better identify this condition in Fig. 1, the full symbols are substituted with empty ones. In general, increasing T_{in} , the temperature oscillation amplitude decreases while the frequency increases.

The overall temperature trend is quite similar for the three investigated cases. In particular the figure shows that the results for the mixture diluted in 75% N_2 –25% H_2O lie in-between the N_2 and 55% N_2 –45% H_2O -diluted cases.

The ΔT for the two mixtures diluted in H_2O are similar to the ones relative to the N_2 -diluted mixture. Nonetheless, Fig. 1 shows that for such mixtures the oxidation onset occurs for lower T_{in} with respect to the N_2 -diluted system. For $T_{in} = 970$ K, ΔT becomes lower for the H_2O -diluted systems.

The chemical species profiles of C_3H_8/O_2 mixtures of equivalence ratios 1, 0.5, and 1.5 diluted in N_2 and H_2O with ratios 100/0, 75/25, 55/25 are plotted in Figs. 2–4. The overall dilution is kept constant at 90%.

Fig. 2 depicts the experimental and numerical concentrations of some chemical species as a function of T_{in} for stoichiometric propane/oxygen mixtures diluted at 90% in N_2 , or in N_2 and H_2O .

As can be seen in Fig. 2, all the experimental intermediate species start to form in correspondence of oxygen consumption onset. Intermediate species mole fraction maxima are in the range of 10^{-2} – 10^{-6} . C_2H_6 , C_2H_4 and C_2H_2 are formed, involving CH_3 recombination, and their maxima appear sequentially shifted to slightly higher temperatures, consistently with detailed propane oxidation schemes.

In correspondence of the onset of the oscillatory behavior (empty symbols), the measured concentrations show a discontinuity with an abrupt decrease of concentration (an increase for the CO_2). In such a case, the concentration values are averaged in time. With increasing the inlet temperature, the concentrations again increase, or at least reach a plateau level. For higher T_{in} , species concentrations further decrease, with the exception of CO_2 concentration that increases.

This was observed in all the considered mixtures. Fig. 2 confirms that H_2O slightly anticipates the reactivity with respect to the N_2 -diluted system, as the chemical species for the N_2 - H_2O -diluted systems start producing at slightly lower T_{in} with respect to the N_2 reference case. Afterwards, there is an inversion point and the effect of H_2O is to slow down the reactivity. This inversion point occurs for T_{in} around 970 K. For $970\text{ K} < T_{in} < 1070\text{ K}$, the periodic dynamic behavior is also experimentally detected for the systems diluted in N_2 and H_2O . Therefore, the dynamic behavior occurs at the same T_{in} but the oscillatory behavior extends in a wider T_{in} range for the mixtures partially

diluted in H_2O with respect to the one diluted in N_2 . For higher T_{in} , the species amounts are higher than the ones detected for the N_2 dilution case, with differences up to one order of magnitude (or higher) for $T_{in} = 1100\text{ K}$.

Along with the experimental data, Fig. 2 also reports the numerical simulations obtained with the chosen kinetic mechanism. It should be noted that, by simulating the reactive system, oscillatory regimes have been identified (dashed lines), but multiple solutions at low temperature do not.

The CRECK-2014 scheme predicts the onset of the oxidation reactions for $T_{in} = 830\text{ K}$ and at $T_{in} = 1000\text{ K}$ the insurgence of temperature oscillations in time that persist up to $T_{in} = 1100\text{ K}$. For $T_{in} > 1100\text{ K}$ the propane oxidation occurs through a stationary steady state. The kinetic mechanism anticipates the consumption of the reactants with respect to test results. For $T_{in} > 1000\text{ K}$, a good agreement between numerical and experimental data is observable. However, C_2H_2 concentration is relatively overestimated.

For the N_2 - H_2O -diluted systems, the kinetic mechanism predicts the onset of the oxidation reactions for inlet temperatures lower than the one obtained for the N_2 -diluted system.

Thus the scheme well predicts the anticipating effect of H_2O on the reactivity of the system at low temperatures observed during experimental tests. Furthermore the model shifts the inversion point for the systems diluted in N_2 and H_2O to slightly lower temperatures respect to the experimental observations. For the systems diluted in N_2 and H_2O the oscillatory regime is predicted for $1020\text{ K} < T_{in} < 1200\text{ K}$. Thus, the model well predicts the wider T_{in} range in which the oscillations are detected when adding water to the system.

In general, simulations do capture the H_2O effect on the reference species, but overestimate it at low T_{in} .

Fig. 3 shows the measured chemical species concentrations as a function of T_{in} for fuel rich ($\Phi = 1.5$) propane/oxygen mixtures diluted in N_2 , 75% N_2 –25% H_2O and 55% N_2 –45% H_2O at 90%.

For $\Phi = 1.5$, the experimental onset of the oxidation reactions is identified for $T_{in} > 800\text{ K}$ for the N_2 -diluted system. As for the stoichiometric condition, bistabilities are identified at low temperatures.

For $970\text{ K} < T_{in} < 1050\text{ K}$, the propane oxidation process occurs throughout a periodic oscillatory behavior while at $T_{in} > 1050\text{ K}$ through a stationary steady state. Reactants are quickly consumed in the range $880\text{ K} < T_{in} < 920\text{ K}$, then with a slower rate during the temperature oscillation range.

At low T_{in} , H_2O slightly anticipates the reactivity of the mixture with higher conversion with respect to the N_2 -diluted system. At $T_{in} > 970\text{ K}$, the conversion becomes higher for the mixture diluted in N_2 . Thus, the inversion point for the fuel rich mixtures considered occurs at $T_{in} = 970\text{ K}$ for both the 75% N_2 –25% H_2O - and the 55% N_2 –45% H_2O -diluted systems.

For the system 55% N_2 –45% H_2O no periodic regime is experimentally detected, while for the 75% N_2 –25% H_2O -diluted system the periodic dynamic regime is experimentally observed in the T_{in} range 1000–1050 K.

CO is formed through the entire investigated T_{in} range with a lower rate where temperature oscillations occur. At higher T_{in} , the CO concentrations are greater for the N_2 -diluted mixture with respect to the other cases.

For N_2 - and 55% N_2 –45% H_2O -diluted mixtures, H_2 is monotonically produced, while, for the 75% N_2 –25% H_2O -diluted system, it is produced monotonically up to 1020 K, then the values remain almost constant and reach a plateau, later on they further increase for $T_{in} > 1050\text{ K}$. The H_2 volumetric percentages for the two N_2 - H_2O -diluted mixtures are higher than those observed in the other cases.

CH_4 concentrations reach a maximum value, subsequently they decrease H_2O increases the methane concentration and shifts the maximum value of CH_4 concentration towards higher T_{in} .

The CRECK-2014 mechanism correctly reproduces the general trend of species production/consumption as well as it predicts the effect of

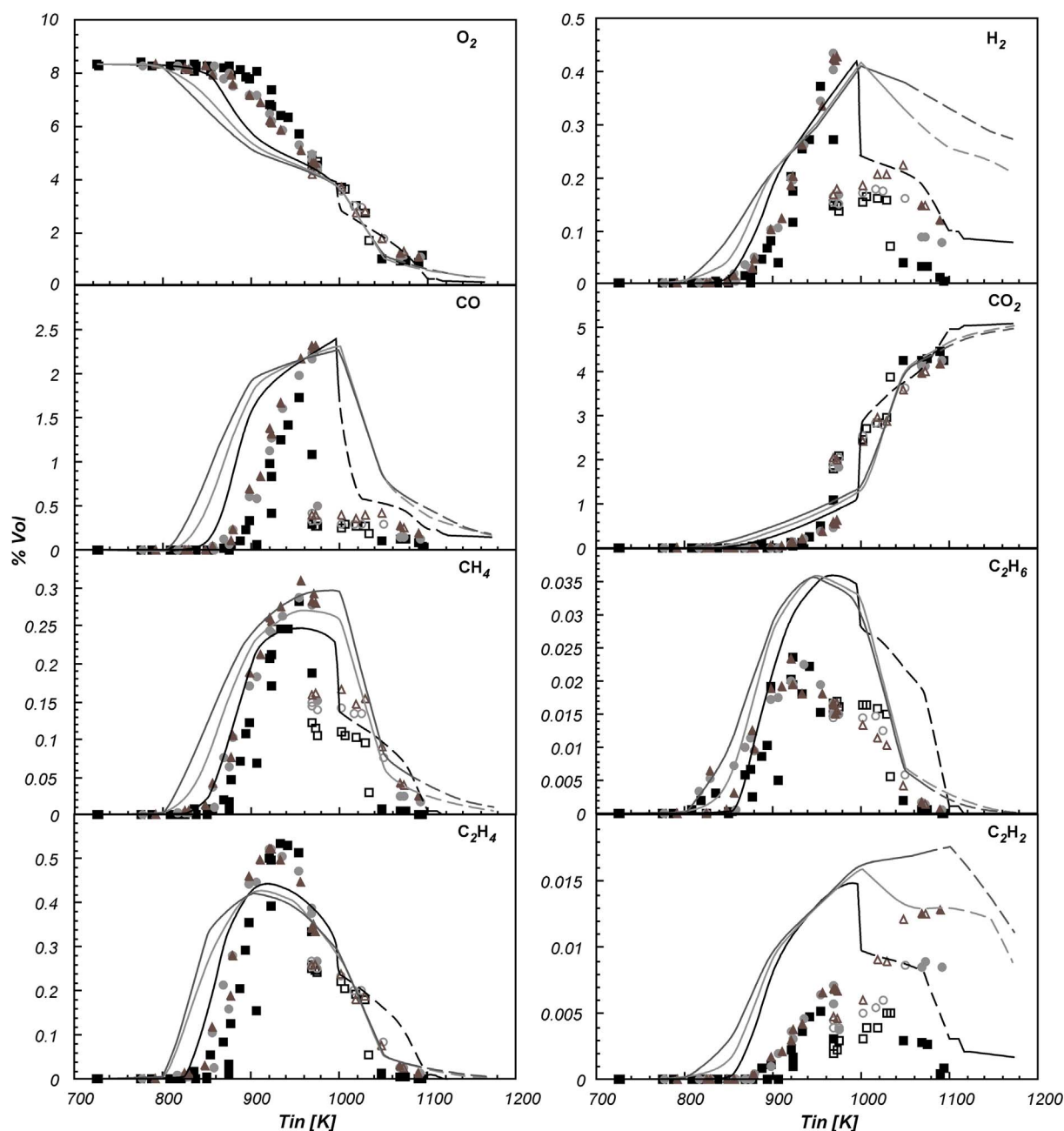


Fig. 2. Experimental (symbols) and numerical (lines) species profiles versus T_{in} . $\Phi = 1$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, N_2 (square symbols), 75% N_2 –25% H_2O (triangle symbols), 55% N_2 –45% H_2O (circle symbols). Full symbols and solid lines represent steady states, empty symbols and dashed lines oscillatory regimes.

H_2O at low and high temperatures. Nonetheless, the onset of the oxidation reactions occurs for a lower T_{in} with respect to the experimental results. The relative difference in species concentration between the N_2 - and the N_2 - H_2O -diluted systems is overestimated at low temperatures and well predicted at high ones.

The model does not properly reproduce the T_{in} range where temperature oscillations are experimentally detected. In particular, for the N_2 -diluted system, the dynamic behavior is not predicted, while experimentally it occurs for $970\text{ K} < T_{in} < 1050\text{ K}$. However, the mechanism correctly predicts the absence of oscillatory regimes for the mixture with H_2O .

Fig. 4 shows the experimental and numerical species concentrations versus T_{in} for fuel lean ($\Phi = 0.5$) propane/oxygen mixtures.

For this equivalence ratio, experimental results indicate that the reaction onset occurs for T_{in} equal to about 830 K for the mixture diluted in nitrogen. For $T_{in} > 970\text{ K}$, periodic temperature oscillations

occur. As for the stoichiometric and rich conditions, bistability are identified at low temperatures.

The oxygen concentration diminishes from 9% to 7% at $T_{in} = 970\text{ K}$. For higher T_{in} , it reaches an almost constant value equal to 6%, and then it slightly diminishes for $T_{in} = 1100\text{ K}$.

For the N_2 - H_2O -diluted systems, the concentrations profiles are similar to the N_2 -diluted system. In particular for low T_{in} , the conversion is slightly higher than the one obtained for the reference system, while at $T_{in} > 970\text{ K}$ (inversion point), it becomes lower. It is interesting to note that for the N_2 - H_2O -diluted mixtures the periodic dynamic behavior is not detected in the whole investigated temperature range.

All the intermediate species profiles reach a maximum value, and then their concentrations diminish. It is possible to note that also for $\Phi = 0.5$, H_2O accelerates the oxidation process up to T_{in} corresponding to the inversion point, then it decreases the system reactivity.

The chosen model predicts the general trend of the considered

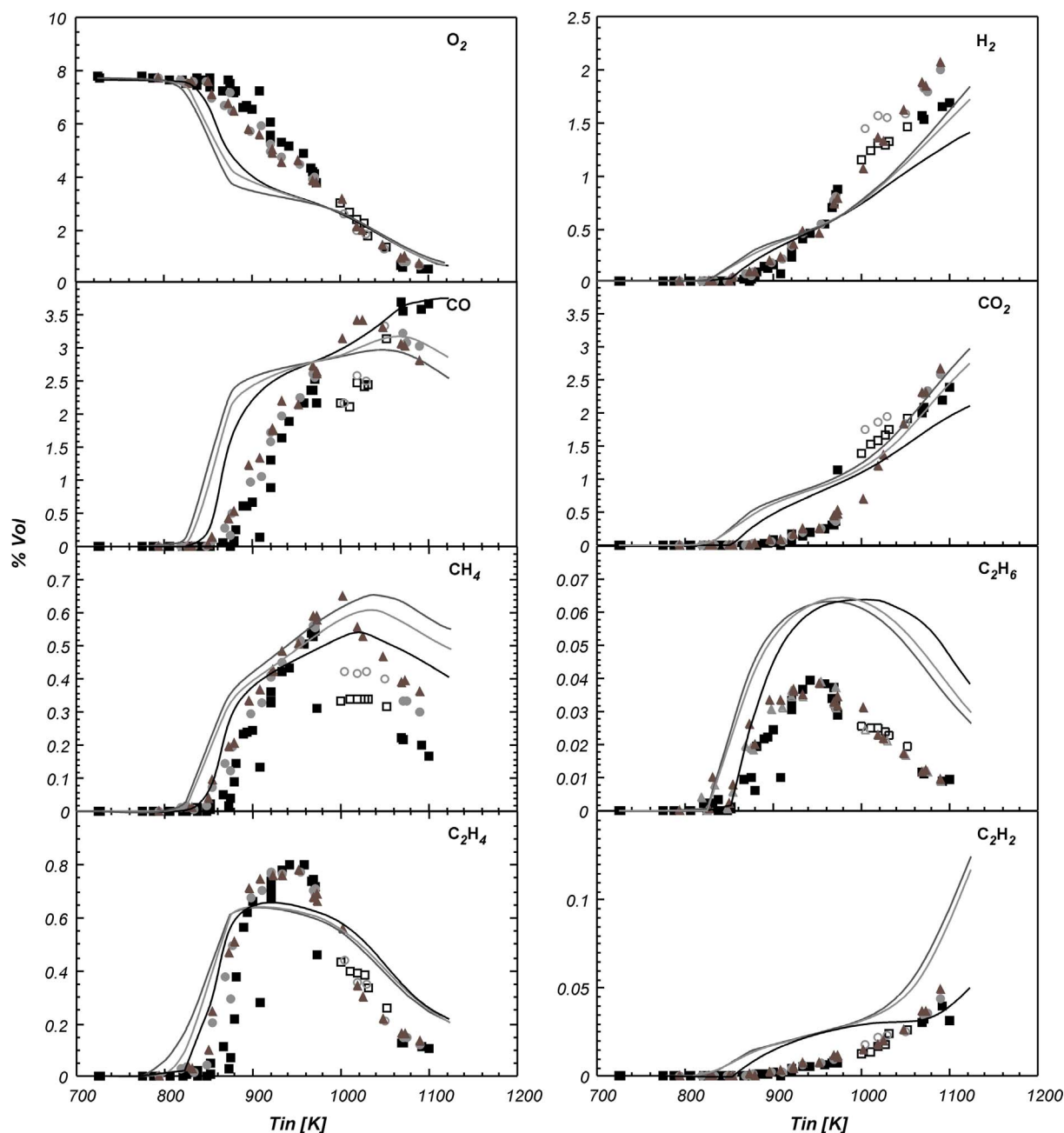


Fig. 3. Experimental (symbols) and numerical (lines) species profiles versus inlet temperature. $\Phi = 1.5$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, N_2 (square symbols), 75% N_2 –25% H_2O (triangle symbols), 55% N_2 –45% H_2O (circle symbols). Full symbols and solid lines represent steady states, empty symbols and dashed lines represent oscillatory regimes.

measurements along with the effect of H_2O on system reactivity. Under fuel lean conditions, the agreement between numerical and experimental species concentration is satisfactory. Nonetheless, the model does not properly reproduce the T_{in} range where oscillations are experimentally recognized.

The experimental results suggest that the oxidation process onset occurs for lower T_{in} for fuel rich conditions with respect to the stoichiometric and the lean cases.

In general, H_2O accelerates the reactivity at low T_{in} , while it slows down it at higher temperatures, compared to N_2 -diluted mixtures for any equivalence ratio considered in this work. Also, H_2O has an effect on the onset of the oscillatory behavior with respect to the N_2 system. Furthermore, it is worth noting that at high T_{in} the H_2 concentration is higher for systems diluted in N_2 – H_2O . In particular, for fuel rich conditions, the impact of the H_2O on C_3H_8 oxidation is less pronounced with respect to stoichiometric and lean conditions.

The CRECK-2014 mechanism correctly reproduces the dependence of the onset of C_3H_8 oxidation reactions on the mixture equivalence ratio with T_{in} . Actually both the numerical and the experimental results suggest that the oxidation process occurs for lower T_{in} in the case of fuel rich mixtures. Nonetheless, numerical predictions predict the insurge of oxidation reactions for T_{in} lower with respect to the experimental results for any equivalence ratio considered.

Furthermore, the kinetic model predicts the H_2O effects at low T_{in} and at high T_{in} experimentally identified. The relative differences among reactivities of the N_2 - and the N_2 – H_2O -diluted systems are overestimated at low inlet temperatures.

The very rich variety of phenomena that accompany the diluted combustion processes provides a rigorous foundation against which a kinetic model may be tested qualitatively as well as quantitatively in certain circumstances. The main features are the bistability, oscillatory regimes, and the influence of diluent and/or equivalence ratio on

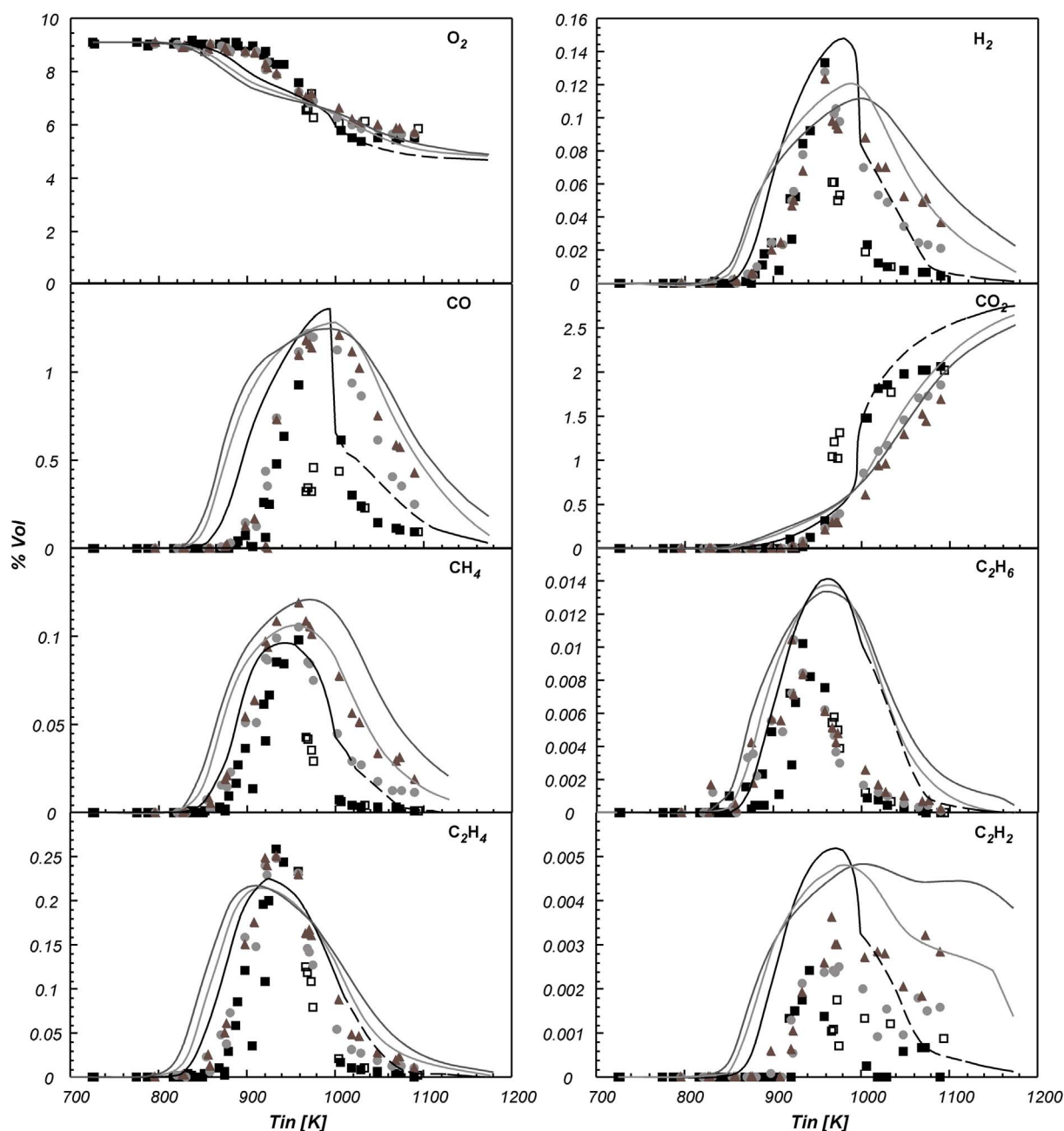


Fig. 4. Experimental (symbols) and numerical (lines) species profiles versus T_{in} . $\Phi = 0.5$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, N_2 (square symbols), 75% N_2 –25% H_2O (triangle symbols), 55% N_2 –45% H_2O (circle symbols). Full symbols and solid lines represent steady states, empty symbols and dashed lines oscillatory regimes.

species concentrations.

Numerical studies form the link between experimental observations and fundamental interpretations. Since the used numerical model was able to reproduce the observed phenomena, although not in all the explored conditions, this model can help us to gain valuable insights into the nature of the phenomena being explored.

Therefore, it has been attempted to identify the rate-controlling processes to focus attention on what controls the chemistry of the observed phenomena in the attempt to unravel the nature of these effects.

It has been verified that the specific selection of the chosen mechanism does not alter the generality of this discussion: while elementary reactions in the other kinetic mechanisms have different kinetic parameters, the predominant reaction pathways are identical in the mechanisms.

It should be pointed out that the experiments also evidenced the presence of a bistability at low temperatures. However, this

phenomenon was not predicted by the kinetic model. Therefore, a numerical analysis on this feature was not possible and we leave it as a question mark for future experimental and theoretical research.

Several kinetic analyses were performed with the aim to understand the main oxidation reactions at the stationary conditions for all the operating conditions considered in the JSFR experiments.

Peculiar attention was devoted to the interference of H_2O on the oxidation kinetics at stationary conditions.

In case of propane mixtures that were diluted in N_2 , in [6] it has been thoroughly analyzed the propane chemistry to identify the key reactions that control the oxidation process using the sensitivity, rate of production analyses and flux diagrams at low, intermediate and high temperatures. Given these kinetic pathways, several numerical analyses were realized to identify the reactions altered by H_2O as a function of system inlet temperature.

At low temperatures, H_2O mainly participates as a third body in the

peroxide decomposition reaction (1) $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$ because its third-body efficiency is six times higher than that of N_2 in the CRECK-2014 model. Such action increases the reactivity with respect to N_2 . This is consistent with the experimental ΔT and species trends showed in the previous section.

At intermediate temperatures, H_2O promotes the inhibiting effect of the methyl recombination reaction (2) $\text{CH}_3 + \text{CH}_3 + \text{M} = \text{C}_2\text{H}_6 + \text{M}$ because its efficiency is five times higher than that of N_2 . The ROP analysis shows that the methyl recombination reaction overcomes the methyl oxidation (3) $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$ for T_{in} higher than 1000 K.

Simultaneously H_2O interacts with methyl radicals to convert them to methane and produces OH radicals: (4) $\text{CH}_3 + \text{H}_2\text{O} = \text{CH}_4 + \text{OH}$. Such reaction strongly interacts with the oxidation/recombination-pyrolytic routes of methyl radicals, and for $T_{\text{in}} > 1000$ K its reaction rate is comparable to the methyl recombination rate. Furthermore, this reaction plays an important role also in OH production.

For intermediate temperature, the reaction (5) $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ becomes important because the H_2O third-body efficiency is approximately 15 times higher than that of nitrogen in the used detailed kinetic model. This reaction assures HO_2 radical to oxidize methyl radicals to CH_3O and feed the oxidation channel with a large production of H radicals from CH_3O and HCO decomposition reactions.

At high temperature reaction (6) $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ becomes faster than reaction 5, and sustain the process.

Numerical analyses suggest that H_2O can also participate in the reactions (7) $\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$ and (8) $\text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{OH}$. 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 the set of reaction 6 and (9) $\text{O} + \text{H}_2 = \text{OH} + \text{H}$, lowering system reactivity. The observed strong effect of H_2O on H_2 concentration was found to be due to reaction 8.

Given the efforts put in developing of kinetic models to date, our fundamental understanding of combustion processes is significantly improved. The thermochemistry and elementary rate coefficients for many reactions have also been significantly revised during the last few years. Also, there have been tremendous methodological advances for computing the pressure-dependence of rate-coefficients.

However, the observed discrepancies between model predictions and experimental data presented in this work suggest that some additional effort should be dedicated to the development of detailed kinetic schemes to correctly describe the oxidation process under diluted combustion conditions.

The reason for some of the bad performances of kinetic mechanisms is due to lack of validation for certain types of measurements. There is a very substantial foundation to the validation of high temperature chemistry components of comprehensive models. All of this inspires considerable confidence in the understanding of the kinetic foundation of alkane flames and in the kinetic models that describe them. However, although several examples have already been cited, the extent to which comprehensive models for lower temperature oxidation have been tested against experimental chemical measurements is less satisfactory. The rather limited extent to which comprehensive schemes have been put to a test under low- and intermediate-temperature conditions is a weakness at present.

However, the majority of users of reaction mechanisms are interested in robust, general-purpose mechanisms. Therefore, in order to improve the model predictive ability, model parameters should be adjusted in a systematic manner on the basis of as many different types of practical systems and as wide a range of conditions as possible. The present work has provided important additions to the experimental database for kinetic model validation, in presence of water at atmospheric pressure.

From this analysis, it was found that the rate parameters of several reactions might need to be studied further. The numerical results here reported give clear indications on the set of reactions to tune to improve the reliability of kinetic mechanisms to properly predict combustion features of small hydrocarbons for non-conventional conditions.

4. Conclusion

The present work experimentally characterized the oxidation process of diluted and pre-heated propane mixtures, at atmospheric pressure, in a Jet Stirred Flow Reactor under a wide range of operating conditions involving temperatures and mixture compositions. The diluent gases used were N_2 and H_2O . The attention was focused on oxidation characteristics and their dependences on the operating parameters, such as temperature, diluent and equivalence ratio.

The influence of these parameters was analyzed on temperature and stable species concentrations profiles.

The exploitation of the oxidation process of propane mixtures under diluted conditions at intermediate temperatures has led to the identification of different phenomena and combustion regimes as functions of the inlet temperature and mixture composition. The very rich variety of phenomena observed provides a rigorous foundation against which a kinetic model may be tested qualitatively as well as quantitatively.

In particular, the differences detected in relation to the presence of a different diluent atmosphere on propane oxidation highlight the importance of this study.

As matter of fact, it was observed that, compared to pure N_2 , the presence of H_2O accelerates the reactivity at intermediate temperatures while slows down it at high temperatures. The relative importance of the effect of H_2O on species concentrations also depends upon the equivalence ratio.

In addition, the measurements were also compared to simulations based on a kinetic mechanism available in the literature to verify its validity under diluted combustion conditions. Numerical predictions showed that kinetic model was capable of only partially quantitatively reproducing the observed experimental data. This demonstrates the need for further investigations concerning the oxidation studies, especially in the intermediate temperature regime at high dilution.

Numerical analyses were performed to understand the main effects on the combustion chemistry of the H_2O . It mainly acts as a third-body species. It boosts the intermediate-temperature branching reactions. At higher temperatures, it inhibits the combustion process depressing the C_1 oxidation channel chemistry and the high-temperature branching reactions, promoting the methyl recombination channel and the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$, respectively. This effect is strengthened at high temperatures, where H_2O decomposes through reactions ($\text{H}_2\text{O} + \text{H} = \text{H}_2 + \text{OH}$) and competes for H atoms with the high-temperature branching reactions.

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