Auto-ignition delay times of methane/air diluted mixtures. Numerical and experimental approaches.

A. Picarelli[1], P. Sabia[2], M. de Joannon[2], R. Ragucci[2]

1. *Dipartimento di Ingegneria Chimica - Università degli Studi di Napoli "Federico II", Naples, Italy*
2. *Istituto di Ricerche sulla Combustione - C.N.R., Naples, Italy*

1. Introduction

Non-conventional combustion requires a reconsideration of physical and chemical sub-processes occurring during the oxidation and requires a redefinition and quantification of main parameters that describe the evolution of fuel conversion to final products.

Among these extreme operating conditions it is relevant the high level of reactant dilution, characteristic, for instance, of Mild Combustion [1]. This infers high level of heat capacity of mixtures, which in turn leads to a modest temperature increase. Therefore all the kinetic characteristic times are relatively longer with respect to traditional system ones. Furthermore, dilution affects the kinetics also by lowering reactants concentration. In order to correctly define parameters and equations for system dimensioning is fundamental an evaluation of chemical kinetic times.

The choice of the experimental rig to be used to this aim stems from the need of ensuring simple and controllable reactive conditions over wide ranges of temperature and equivalence ratio. This implies the capability of characterizing ignition and combustion processes evolving with characteristic times from milliseconds down to microseconds.

Several facilities have been used to investigate mixture auto-ignition under strictly controlled experimental conditions, including flow reactors, shock tubes and rapid compression machines (RCM). While each of these facilities has its merits, their utility is restricted to certain ranges of pressure, temperature and ignition time. A shock tube is ideal for studying ignition phenomena with short characteristic times (order of tens of microseconds).

Furthermore, for high pressures and relatively low temperatures, namely long mixture reactive times, ignition measurements can be affected by fluid dynamic non-idealities as weel as of deflagrative process [2]. The RCM offers the advantage that temperature and pressure can be sustained for times longer than 10 ms [3]. Nevertheless, the time needed to compress the test gas mixtures limits the minimum characteristic time of investigation to 1 ms [3, 4, 5]. Both these reference devices (shock tubes and RCM) operate in elevated pressure condition. This point is relevant, for instance, in the case of furnaces operated in Flameless conditions and VOC oxidation systems that evolve in Hot Diluted Diffusive Ignition (HDDI) regimes [6]. As matter of facts available data falls in a restricted range of conditions typical of these systems. Simple atmospheric experimental reactors that could be evaluated in view of their use to better assess kinetic data relevant for HDDI based systems are the Well Stirred Reactor and the Plug Flow Reactor. The first one is not suitable because it yields mixed condition among unreacted and reacted species. The second one is useful to study turbulent deflagrative conditions but these are not properly auto-ignition conditions since also in this case oxidation is triggered by species that are diffused into the ignition region from the main oxidation region. Furthermore the only way to have nearly one-dimensional flow is to operate plug flow in turbulent regimes. This ensures a quasi-flat average velocity outside the boundary layer

and, as a consequence, a well defined correspondence between residence time and spatial position along the reactor, but hinders a precise knowledge of local auto-ignition conditions. In fact, the mixture, where auto-ignition occurs, undergoes stretching which can affect the mass-temperature-diffusive structure and whose rate can be determined only on average and not in the whole spectrum of spatial-temporal scales. A possible alternative to the turbulent condition is to operate in laminar and/or transitional and/or low-level-turbulent conditions. In this case combustible mixture can ignite inside the reactor in correspondence of times quite longer than in turbulent conditions since flow rate can suitably be lowered. Furthermore the axial and radial dispersion of scalar can be better evaluated in terms of assessable values of laminar or slightly turbulent diffusion. This is the reason why in this work a Tubular Reactor was used and a careful evaluation of parameters was performed to determine their implications on experimental results.

2. Experimental and Numerical Tools

The experimental rig layout is not shown herein for the lack of room [7]. Tubular Flow Reactor, manufactured using 310 AISI stainless steel, is the core of the system with an axial dimension of 140 cm and the inner diameter equal to 1 cm with 28 physical accesses for temperature measurements. Thermocouples are equally displaced any 5 cm along the axis of the reactor. The reactor is located inside cylindrical fiber ceramic heaters in order to reach a quasi-adiabatic condition. The mixing section configuration is based on a multipoint injection from plain orifices realized on the wall of the mixing section of the reactor. They realize a "jets in crossflow mixing" scheme that has been proven to be very efficient and scarcely sensitive to the flow conditions. A detailed description of the premixer and of its performance can be found in [8].

CFD package software FLUENT 6 [9] has been used to perform analyses of the velocity profile inside the duct for different mixture inlet temperatures. Simulations were run using a 3D geometry that reproduces the reactor geometry. The energy equation, the species model, and the turbulence standard model k-ω were enabled. Fig.1 shows velocity profile along a reactor diameter at 2cm from the entrance for a mixture composed by CH_4-O_2 diluted in nitrogen up to 85%. The C/O feed ratio is 0.2 and two reference temperatures were considered.
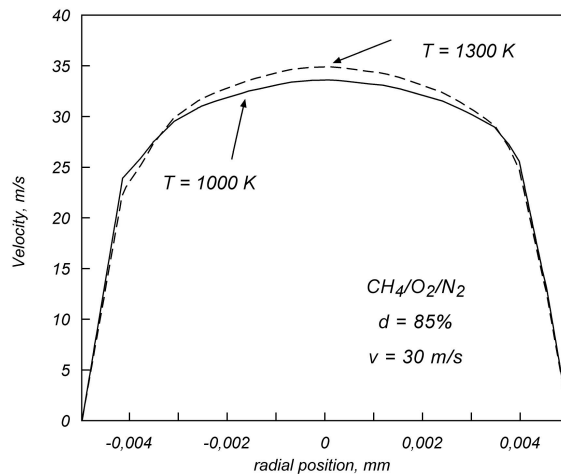

Fig.1   Numerical radial velocity profile.

After the main and the lateral flows mix, they enter the reactor with a velocity equal to 30 m/s. They respectively correspond to a Reynolds number equal to 2300 and 1500. Lines identify a boundary layer of about 1 mm and a parabolic shape of the radial velocity. The velocity goes from 0 to about 25 m/s at 1 mm from the wall. Then it increases slowly and, in both cases, at 2 mm from the wall it is about 30 m/s. Later on, it reaches its maximum values respectively equal to 33 m/s and 35 m/s.

An analysis of axial and radial dispersion of mass and enthalpy is mandatory in order to evaluate the reliability of experimental results. A detailed analysis based on local scale consideration is synthetically reported in the following. The first kind of dispersion (the axial) has to be analyzed in terms of the largest and smallest possible length and temporal scales. The largest scales, even in a more conservative case of transitional or low-level-turbulent flow, are related to macro-stirring effect and they do not affect the auto-ignition determination significantly. In fact the largest possible scale is fraction of the tube diameter, which in turns is fraction of the measurement interval in the set up. In other words this means that the auto-ignition can take place inside the error measurements range fixed by the apparatus, i.e. at maximum in an interval of 1cm, whereas the measurements point are placed every 5 cm. On the other side, the smallest scale are related to the micro mixing effect, which is relevant in order to evaluate the presence of product species in the auto-ignition kernel. The analysis is straight in terms of comparison of convective velocity and diffusive isothermal (iso-concentration) propagation. The first one is the local axial velocity at the radial position where the analysis is performed. In the present case this is approximately 30m/s. The second one is in the order of square root of D/t, which is maximized by the highest value of the diffusivity, D, and minimum value of time, t. The first is maximized taking into account the maximum temperature of the system and it has been evaluated at maximum as 10^{-4} m^2s^{-1}. The second one, the time t, has to be minimized among the possible kinetic times in which the iso-concentration front evolves toward oxidation. At temperature higher than those used in the present experiment this can be evaluated in the order of tens of microsecond. Therefore the maximum propagation velocity of a diffusive (thermal or mass) layer is in the order of meter per second which is much lower that tens of meters evaluated for convective times. In synthesis the axial dispersion could be a factor for the following oxidation time but not in the evaluation of auto-ignition time delay. The radial dispersion has to be evaluated in terms of auto-ignition that takes place in region flowing at velocity slower than that at the measuring point since, if the auto-ignition takes place in point at higher velocity, this has to be evaluated in terms of axial dispersion, which has just been evaluated. On the contrary the error due to the auto-ignition delay at slower velocity affects this measurement taking into account the ratio of the velocities where auto-ignitions take place and where the temperature profiles are detected. In fact, under the hypothesis of infinite thermal and mass conductivity the temperature and concentration profile are flat, but the velocity profiles determine, in any case, the residence time of the mixture. In other words the error is not significant if the velocity in the auto-ignition point is higher that tens of meters. Very low average velocity occurs only near the reactor wall, where thermal quenching and catalytic effect can alter the evaluation of the auto-ignition delay time in opposite "direction". In fact this is the reason of the displacement of the measure control volume at 2 mm from the wall. Thermocouples placed on the wall and at 1 mm far from the wall yield measured longer auto-ignition delay. This supports the hypothesis that quenching due to enthalpy flux outward the reactor is effective at least in the first millimeter. Possible catalytic reaction enhancements are depressed by the

thermal quenching and in any case do not affect the early thermal auto-ignition. It is also worth mentioning that similar results have been obtained for a reactor with the same design and different material confinement (alumina), which have been used in the first part of experimental characterization for a limited range of input parameters. This confirms that wall material properties are not a factor and that, also for this reason, catalytic kinetics enhancement can be disregarded.

The evolution of methane oxidation process in diluted and highly preheated conditions in a Tubular Flow Reactor was studied by means of the PLUG [10] application of the Chemkin 3.7 [11] software and several oxidation kinetic mechanisms available on internet, c1-c3 [12], GRI [13], SanDiego [14] and finally the Warnatz mechanism [15]. Kinetic mechanisms were opportunely validated for several operative conditions and different reactor configurations, as well described in literature [16].

3. Experimental Results

Experimental analyses were carried out on CH_4/O_2 system diluted at 85% by N_2 at atmospheric pressure in the TFR described previously, over a wide inlet temperature (T_{in}) range (up to 1300K) and carbon/oxygen ratios (C/O) from values very close to zero up to 1. Flow inlet velocity was set equal to 30 m/s. Fig. 2 shows the temperature profiles as function of the axial coordinate of the system at three different inlet temperatures and C/O = 0.1. They represent typical profiles obtained during experimental campaigns and show possible combustion regimes reachable in such operative conditions.
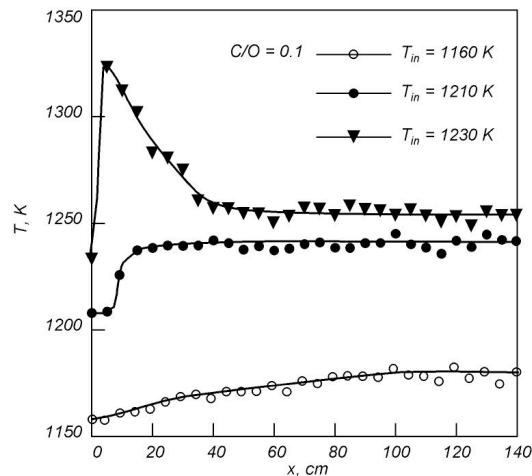

Fig.2   T profiles at C/O = 0.1 for several T_{in}.

For T_{in} = 1160 K the temperature trend is typical of slow combustion regimes since temperature increases slowly up to 1172 K and reaches a constant value at an axial distance longer than 100 cm. In the second case, at T_{in} = 1210 K, the same trend is recognizable but the temperature increase is higher (T_{max} = 1241 K) and occurs at an axial distance smaller than the previous case, so that also the corresponding auto-ignition delay time is smaller. At T_{in} = 1235 K the temperature profile exhibits a trend typical of high temperature combustion. As soon as the mixture is introduced in the reactor, after mixing, it reacts. The temperature profile shows a first abrupt jump, up to a maximum value (1325 K), followed by a relatively slow temperature decrease due to the heat exchange transfer to external environment, down to a

constant value. The analysis of experimental data was carried on considering the mixture auto-ignition delay times (τ). It was defined as the time needed by the system to increase its temperature of 10 K with respect to the inlet one, following a criterion discussed elsewhere [17, 18]. The auto-ignition delay times were assessed dividing the axial position, where the condition $\Delta T = T_{reactor} - T_{in} = 10K$ was respected, by the velocity at 2 mm from the reactor wall, since at such a radial distance velocity is almost independent on mixture inlet temperature, as Fig. 1 shows. Temperature data between two thermocouples were linearly interpolated. System resolution time is equal to 0.0015 since thermocouples spacing is 5 cm. Fig. 3 shows the auto-ignition time in an Arrhenius plot versus the parameter $\alpha = 1000/T_{in}$ (K^{-1}) for several mixture compositions. The light-grey area identifies auto-ignition delay times below the measurement resolution time. It is possible to recognize a qualitative trend for all the reported data. In the lower and upper α ranges the ignition delays decrease for all the considered C/O as it is expected. It is worth noting that at high temperatures, although auto-ignition delay times are not valuable, they are significantly lower than the ones corresponding to other temperatures. In the range $0.82 < \alpha < 0.86$ the ignition delay is substantially constant and around stoichiometric C/O values a clear negative temperature coefficient behavior can be observed. Although such behaviour is well known in literature for paraffins at high molecular weight [19, 20], few experimental evidence are present in literature for methane oxidation [21-23]. In particular, shock-tube experiments on methane ignition under engine-relevant conditions were carried out by Huang et al. Experimental and numerical analysis, by means of their kinetic mechanism, detected NTC phenomenology for mixtures of methane diluted in nitrogen and argon at moderate temperatures (1000 to 1350 K) and elevated pressure (16-40 atm). Ignition delay time evaluated, were in the order of thousand of microseconds and are similar with our measurements.
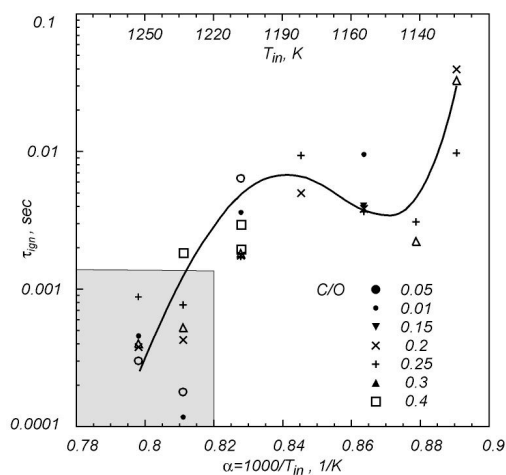

Fig. 3   Experimental $\tau_{ign.}$ vs α for several C/O.

4. Numerical Results

In order to see whether the methane negative temperature coefficient was predictable by means of numerical tools, preliminary simulations were run using the four kinetic mechanisms previously cited, and the application PLUG of the ChemKin software. Simulations were carried out in the same operating conditions of experimental tests and auto-ignition delay time was computed following the same criterion.
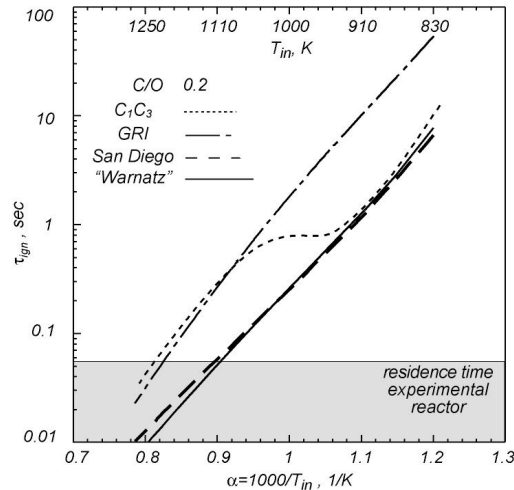
Fig. 4   Numerical τ_{ign} vs α for C/O =0.1 for different kinetic mechanisms.

Fig. 4 shows the Arrhenius plot of numerical auto-ignition times versus α for C/O = 0.2. The light-grey area identifies τ lower than the experimental residence time. The prediction of τ is very different among all the considered kinetic mechanisms. "Warnatz", SanDiego and GRI mechanisms show a linear dependence of the auto-ignition delay time as function of T_{in}. In particular the GRI mechanism overestimates the auto-ignition times with respect to the cited ones. Results obtained using the c1-c3 mechanism are close to those of "Warnatz" and SanDiego mechanisms for α >1.1, and close to the GRI results for α < 0.92. In the intermediate range the c1-c3 mechanism predicts a curve slope change. Since it was the only kinetic mechanism able to predict approximately an NTC behavior, further simulations were carried on extending the numerical analysis for several C/O feed ratios (0.05, 0.1 and 0.3). The peculiar behavior of the results obtained with c1-c3 mechanism cannot be interpreted as a clear indication of a "classical" NTC zone typical of heavier paraffins. More probably it can be explained by a change of the kinetic pathways (for instance oxidation ad recombination channels) involved during methane oxidation [24].

5. Comparisons between experimental and numerical results

Experimental results are resumed in an ignition map, reported in Fig. 5, in the plane T_{in} - C/O ratio. Below C/O = 0.02 it was not possible to perform experiments, since the mass flow meters/controllers sensitivity was not high enough to regulate so minute methane flow rate.
Two main zones can be identified: a "no ignition" zone, where it was not possible to detect any significant temperature increase, and an "ignition" zone where temperature enhancement was higher than 10K. The latter area covers a T_{in} range comprised between 1125 K and 1275 K, while C/O ranging from values very close to 0 up to 0.55.
In the range 1125< T_{in} <1150 K ignition can be observed only for C/O comprised between 0.1 and 0.3. Later on, for 1200< T_{in} <1225 K the C/O range where mixtures ignite extends both toward lean and rich sides, down to values very close to zero and, up to C/O = 0.55, respectively. At higher temperature the ignition zone restricts toward lower C/O values.
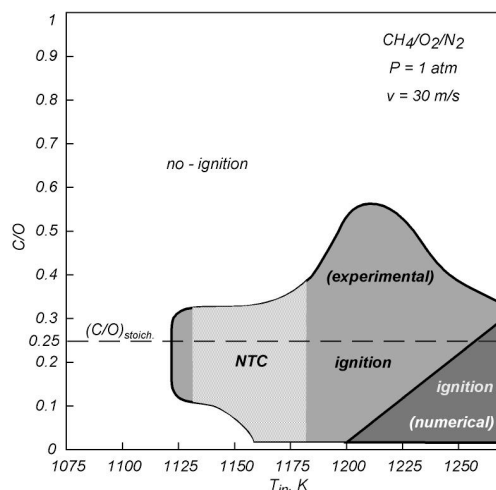
Fig. 5   Experimental and Numerical ignition maps.

In the map, also the area where the NTC behavior was detected is reported. Such region interests a temperature range between 1140 K up to 1180 K. Numerical ignition map obtained from the abovementioned simulations are also reported for comparison. The shape and the extension of this region are significantly narrower with respect to experimental results. Such area interest an inlet temperature range comprised between 1200 K and 1270 K, and goes for very lean conditions (C/O = 0.02) up to fuel rich mixtures (C/O = 0.3).

6. Discussion and Conclusion

Comments on the relevance of the results are worth of note. For T_{in} comprised between 1140 K and 1190 K, the auto-ignition delay time, as reported in Fig. 3, shows a peculiar NTC region. The attempts to predict such a behavior by means of simulations resulted inconclusive. As matter of fact, among the kinetic mechanisms here considered, only one was able to predict a similar behavior, but with longer ignition delay times and in a higher inlet temperature range (910 - 1000 K) than those of experimental data. This is also evident from the numerical ignition map where numerical ignition zone results to be much narrower in both T_{in} and C/O with respect to experimental results and it is shifted towards higher T_{in}. The lack of reliable and robust chemical kinetics schemes is mainly due to the scarcity of experimental data at atmospheric pressure. As matter of fact, extreme operative conditions at so high temperatures and\or so short mixing time to obtain homogeneous mixture make quite difficult design, manufacture, set up and control of lab-scale facilities.

Finally, it is worth noting some conclusive points:

1)   The paper shows the occurrence of two auto-ignition regimes for methane oxidation at atmospheric pressure and for moderate level of dilution. In particular it is relevant the fact that auto-ignition takes place also along the low temperature branch of auto-ignition for residence times of interest for practical application without the need for catalytic support.

2)   The ignition diagram reported in the paper shows that ignition dominions are placed around the stoichiometric mixture fraction or in lean side of the mixture fraction. This is also of practical interest because it shows that the pyrolytic channel, present in combustion in presence of intermediate/complete oxidation product (as in Well Stirred Reactor) disappear for this pure auto-ignitive conditions suppressing heavy carbonaceous pollutant products.

Furthermore the rich mixtures in diluted conditions do not favor the auto-ignition, as it is the case of undiluted mixtures.

3)   The set of the auto-ignition data reported in the paper supports the inconsistency of the kinetic data reported in the literature for temperature lower than 1300 K at atmospheric pressure. It is a preliminary data base to validate kinetic schemes in this temperature range, but need to be extended in a wider dilution range taking into account also different wall properties.

4)   Finally the experimental set-up, used in this work, has its intrinsic merit, because it allows reaching very high temperature without use of compression devices. This is relevant in terms of possibility to measure "long" auto-ignition delay times.

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