

CO₂ and H₂O role as diluents in combustion chemical kinetics: an open issue

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Abstract

The definition of new combustion modes, under the requirements of high efficiency and low environmental impact, comes throughout the identification of new operating conditions in terms of pressures, working temperatures and mixture stoichiometry [1]. For instance, new technologies such as MILD or Oxy-fuel combustion envisage the use of pre-heated and/or diluted mixtures. Such operating conditions define oxidation processes with chemical/physical features different from traditional flames. In particular the oxidation chemistry is altered in several ways:

- 1) the high dilution levels imply that the oxidation reactions rates are slower with respect to flame conditions, and that the temperature increase, due to the heat released by exothermic reactions, is modest, thus kinetic pathways controlling the combustion process can be different with respect to flame conditions, where high adiabatic temperatures promote high branching reaction mechanisms.
- 2) the dilution of fresh reactants is realized throughout the recirculation of exhausted gases, thus the reactive mixture contains species as H₂O and CO₂ ab-initio, and not in the post-oxidation phase as in case of traditional deflagrative or diffusive flames. Such species are recognized to have thermal and kinetic effects on the combustion process, thus their roles in the oxidations process as a function of operating parameters should be properly identified and discussed [2].

Thus a huge effort should be devoted to the adaptation of detailed mechanisms to these operating conditions. As matter of fact, the uncertainties of reaction rate constants, under the constraints of high dilution levels and the presence of H₂O and CO₂ have drastic effects on the reliability of detailed kinetic schemes, that count for many species involved in hundred-thousand reactions that interact in a highly non-linear manner.

In this sense, the first step would consist in the construction of dedicate database in terms of species distribution and system working temperatures as a function of initial conditions in model reactors.

This approach would allow for the evaluation of the reliability of kinetic schemes available in literature to predict the features of these new combustion modes, and, at the same time, would realize a reference database to adapt kinetic schemes to these new operating conditions. The second approach, to run in parallel with the former, would consist in the identification of kinetic pathways involved in the oxidation process, throughout numerical tools, i.e. sensitivity analysis, flux diagram and rate of reactions. Once identified the controlling reactions, the Arrhenius constants should be re-discussed considering reaction rate uncertainty parameters.

In this framework, several experimental tests were realized for different simple hydrocarbons (methane, propane) and mixtures of hydrocarbons (C₁-C₂) in presence of

H₂O and CO₂ in simple reactors (TFR, JSFR). The results were simulated by means of the ChemKin software and updated kinetic schemes available in literature.

While in general good agreement between experimental and numerical results were obtained for ultra-lean mixtures of fuel/O₂/ diluted in N₂ at 90%, significant discrepancies occur for stoichiometric and fuel rich mixtures. Such a disagreement significantly increases enhancing the mixtures dilution levels and complexity.

In case of methane/O₂/N₂, the numerical analyses have suggested the oxidation process comes through two main pathways, namely the oxidation route CH₃->CH₂O->HCO->CO and a the one that involves C₂ species formation/hydrogenation starting from methyl radical recombination to ethane. Numerical results suggest that the methyl radical recombination reaction along with third molecular reactions are not well described under diluted.

In case of propane mixtures and simple hydrocarbon blends, similar discrepancies between experimental tests and numerical predictions were noticed. Sensitivity analyses suggested the same controlling set of reactions as in the case of methane, and in case of propane mixtures, also fuel dehydrogenation reactions by radicals species.

When nitrogen was substituted with H₂O or CO₂, the roles of the identified reactions was stressed by the high third molecular efficiencies of such species in third body reactions. Such results suggest to revise the Arrhenius constants of such reactions and the third molecular efficiencies of H₂O and CO₂ species in third molecular reactions.

In particular the reactions to be considered under these operating conditions are the following:

- 1 H₂O₂ (+M) = OH + OH (+M)
- 2 CH₃ + CH₃ + M = C₂H₆ + M
- 3 H + O₂ = OH + O
- 4 H + O₂ + M = HO₂ + M

The third body efficiencies of H₂O or CO₂ are not un-ambiguously defined in literature, and the definition of such values is a mandatory target to improve the prediction performances of kinetic schemes. Furthermore H₂O and CO₂ strongly interact with the high temperature H₂/O₂ branching mechanism altering the radical pool production and distribution of OH, H and HO₂ radical species, thus condition the oxidation pathways. In case of CO₂ dilution, it is worth underlining that such a diluent strongly alter the CO/CO₂ equilibrium reaction (CO+OH=CO₂+H).

References

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