

EXPERIMENTAL STUDY OF THE EFFECT OF CO₂ ON PROPANE OXIDATION IN A JET STIRRED FLOW REACTOR

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Abstract

The influence of CO₂ on the combustion chemistry of hydrocarbons is important in several advanced technologies (MILD combustion, oxy-fuel combustion, combustion with exhaust gas recirculation in diesel). It has been assessed that the presence of diluents, required for temperature control and pollutant mitigation, leads to failure of the consolidated kinetic models in predicting the fundamental combustion features. In order to better understand and characterize the effect of CO₂ on the oxidation kinetics of simple hydrocarbons, experimental tests were carried out on propane oxidation in presence of variable amounts of CO₂ in a quartz jet stirred flow reactor (JSFR) at atmospheric pressure, over the temperature range 720-1080 K and at a residence time of 0.5 s. Three equivalence ratios (0.5, 1, 1.5) and three CO₂ dilution (90% N₂, 45% CO₂-45% N₂, 90% CO₂) were considered. Sampling and GC-TCD/FID analyses of exhaust gases allowed the measurement of the concentration of the stable species. Temperature and concentration measurement results obtained varying the inlet CO₂ concentration suggests that the oxidation of propane is significantly altered by CO₂ depending on temperature and equivalence ratio.

Comparison between experimental and numerical results pointed out that the adaptation of detailed kinetic mechanisms when CO₂ dilutes reactant mixtures is mandatory.

1. Introduction

In an effort to improve energy efficiency and reduce pollutant emissions, substantial investments have been made in research related to the development and implementation of advanced combustion technologies.

Diluted combustion systems (MILD [1], oxy-fuel [2]) using exhaust gases recirculation have proved to be an effective way of improving combustion efficiency and reducing emissions of pollutants such as NO_x and soot [3].

These combustion processes occur in the presence of great amounts of water vapor and carbon dioxide. It is well established that adding a diluent in a reactive mixture leads to significant changes in oxidation properties [4]. Although it has been

established that addition of CO₂ and H₂O has thermal and chemical effects, the mechanism of the effects of these species addition on combustion chemistry remains unclear.

Sabia et al. [5] provided a summary of experimental and numerical studies to date, which have investigated the effects of CO₂ and H₂O on combustion chemistry. They studied the effects of significant additions of CO₂ and H₂O on propane autoignition delay for temperatures ranging from 850 K to 1250 K and atmospheric pressure. Significant changes in autoignition delay times were observed for the mixtures compared with N₂ measurements, which were not captured by available kinetic models. They recommend further investigation of the effect of higher concentrations of CO₂ and H₂O in the reactive mixture, as models need further validation in this parameter space.

In the present work, as part of a continuing effort to improve the knowledge on the CO₂ effect on the combustion chemistry of simple hydrocarbons, the range of the study presented in [5] was extended to include data recorded in a Jet Stirred Flow Reactor (JSFR) to lower temperatures (720 K-1080 K). These data complement the results of the plug flow reactor tests, and serve to further test and validate the detailed kinetic models.

2. Experimental and numerical tools

The oxidation of propane was studied in a Jet Stirred Flow Reactor (JSFR) that can be modeled as a perfectly stirred reactor. The reaction system is described in detail elsewhere [6]. Experiments were performed at a steady state, at a constant pressure of 1.3 bar, at a fixed residence time of 0.5 s, at temperatures ranging from 720 to 1080 K, at three equivalence ratios ($\varphi = 1.5$, C/O = 0.45; $\varphi = 1$, C/O = 0.3 and $\varphi = 0.5$, C/O = 0.15). The proportions of the diluent gases (N₂, CO₂) were varied. Experiments were carried out using as diluents a) N₂, b) CO₂ and c) 50% N₂-50% CO₂. To provide a detailed chemical analysis, the outlet stable species were analyzed online and offline by gas chromatography, enabled by a transfer line connecting the reactor outlet and the chromatograph sampling gate (online) or a sampling valve (offline).

Two gas chromatographs were used for the quantification of CO₂, ethylene, ethane, acetylene, hydrogen, nitrogen, oxygen, methane, CO, methyl acetylene, propylene and propane. The O₂ concentration was also analyzed by means of a continuous O₂ analyzer equipped with two electrochemical cells.

Experiments were completed by simulations of a transient, open well mixed reactor using the AURORA code of the Chemkin package. The experimental results on C₃H₈ oxidation in an O₂/N₂/CO₂ atmosphere were analyzed in terms of a detailed gas-phase chemical kinetic model. The comprehensive reaction mechanism (C1C3) used for the simulations was developed by Ranzi et al. [7] for the pyrolysis and combustion of a large variety of fuels. It includes 107 species involved in 2642 elementary chemical reactions.

3. Results and discussion

Intermediate species concentration profiles were measured quantitatively and recorded versus inlet temperature. The results include the C_3H_8 and O_2 behavior and the output concentrations of the main product gases found in quantitative amounts during C_3H_8 oxidation, i.e. H_2 , CO , CH_4 , C_2H_6 , C_2H_4 , C_3H_6 , C_2H_2 and C_3H_4 , for different temperatures. Also temperature increase (ΔT) were measured. The dependence of the species concentration on CO_2 addition is investigated. The C1C3 chemical detailed kinetic mechanism was used to simulate these experiments and the results of this analysis are depicted in Figs. 1-3.

Fig. 1 shows the results obtained under stoichiometric conditions ($\varphi = 1$). Solid rhombus represent experimental results in N_2 dilution, solid triangles represent results obtained in N_2 - CO_2 dilution and squares denote CO_2 dilution. The results of the experiments are compared to the predictions of the detailed mechanism (lines).

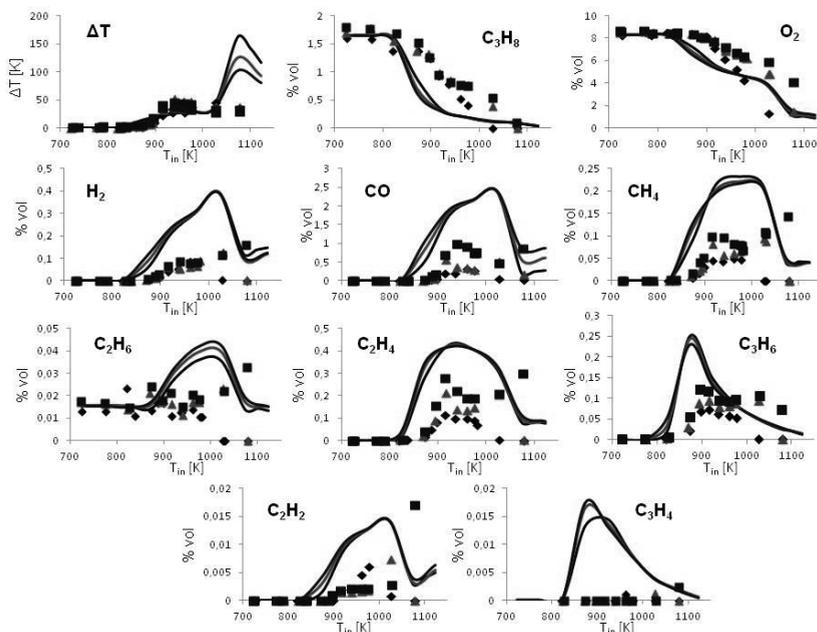


Figure 1. ΔT and mole fraction profiles versus inlet temperature. $\varphi = 1$, $\tau = 0.5$ s, $p = 1.3$ atm, 90% N_2 (rhombus), 90% CO_2 (squares), 45% N_2 -45% CO_2 (triangles).

As can be seen in Fig. 1, the effect of CO_2 addition is to slow down the reactivity. This appears from observing the C_3H_8 and O_2 profile.

The onset of intermediates formation occurs in parallel with the decrease in C_3H_8 and O_2 concentration. Nevertheless, the concentrations and the trends of these compounds are very different using CO_2 . In particular the concentrations increase

with CO_2 dilution. This increase is found to be non linear when the CO_2 molar fraction is varied between 0 and 0.9.

Simulations do capture the global features of the fuel mixtures reactivity but tend to be faster compared to experimental measurements. The discrepancy between the predictions and the measurements increases as the CO_2 percentage increases.

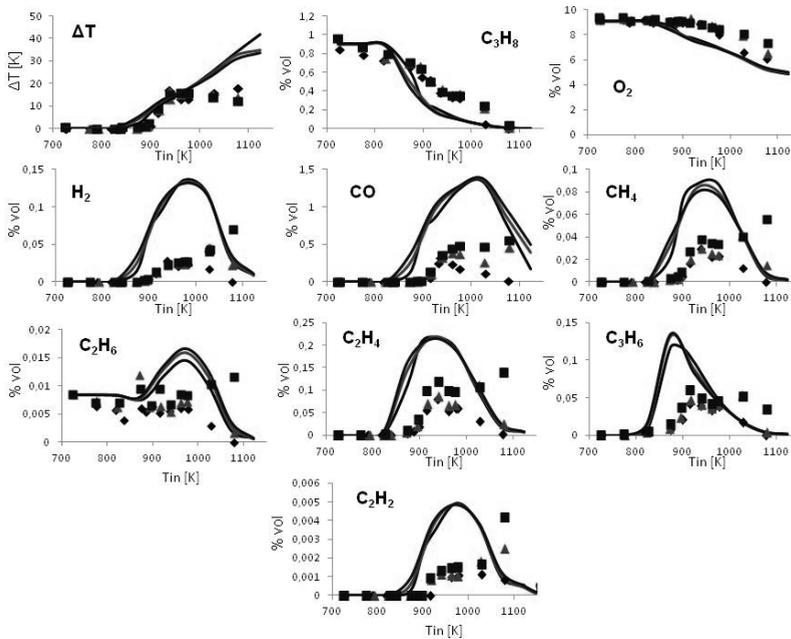


Figure 2. ΔT and mole fraction profiles versus inlet temperature. $\phi = 0.5$, $\tau = 0.5$ s, $p = 1.3$ atm, 90% N_2 (rhombus), 90% CO_2 (squares), 45% N_2 -45% CO_2 (triangles).

Fig. 2 presents the results of the experiments in comparison to the predictions of the detailed mechanism under lean conditions ($\phi = 0.5$). The trends of the measured compounds are similar to the profiles explained above. The concentrations of intermediates from propane oxidation diluted in N_2 are lower and showed a strong dependence upon the CO_2 concentration with their peak value increasing strongly as the CO_2 mole fraction increases. Overall, the applied mechanism provides quite good agreement between model predictions and experimental results for N_2 dilution, even though the computed profiles are shifted to lower temperatures for all the compounds analyzed. The model is able to reproduce the experimental trends, except for the results at N_2 - CO_2 and CO_2 conditions, where significant discrepancies are found. While concentrations of intermediates appear to be higher in the model compared to the experimental data for all temperatures and dilution analyzed, the model calculations of the reactants concentration are under-predicted.

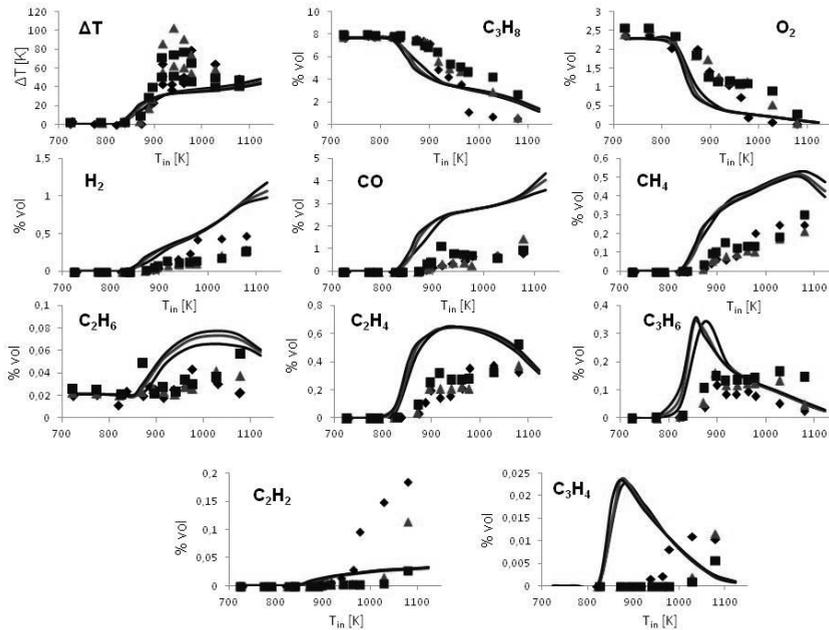


Figure 3. ΔT and mole fraction profiles versus inlet temperature. $\phi = 1.5$, $\tau = 0.5$, $p = 1.3$ atm, 90% N_2 (rhombus), 90% CO_2 (squares), 45% N_2 -45% CO_2 (triangles).

Fig. 3 shows the evolution of the species concentration and ΔT of $C_3H_8/O_2/N_2/CO_2$ rich mixtures ($\phi = 1.5$) when the CO_2 molar fraction is increased from 0 to 0.9.

A two stage production of H_2 , CO , CH_4 and C_2H_4 can be observed. As higher temperatures enhance the consumption of fuel, more intermediates are produced, including C_2H_2 and C_3H_4 . C_2H_6 and C_3H_6 are also included among the main products originated during C_3H_8 oxidation. The trends of these compounds are similar to their profiles explained above, reaching a maximum and subsequently decreasing.

However, in rich conditions lower difference is found between the profiles obtained in the three cases than that obtained for stoichiometric and lean mixtures. This may indicate that chemical effects of CO_2 addition are reduced for rich conditions compared to lean and stoichiometric conditions, as reported in [5].

The mechanism over-predicts the concentration of the intermediates across the range of temperature except for the C_2H_2 concentration that is consistently under-predicted. The predictions in all the conditions tested suggest that the model exhibits a weaker CO_2 dependence on rate than observed experimentally. This might indicate that the rate coefficients for the reactions are not well-determined

and further research is desirable due to the lack of literature studies of these reactions.

4. Conclusions

The present work has presented a kinetic study of the oxidation of propane at near-atmospheric pressure in a jet stirred reactor over the temperature range 720-1080 K, from lean ($\phi = 0.5$) to rich ($\phi = 1.5$) conditions. The influence of CO₂ addition has been analyzed ranging the CO₂ molar fraction from 0 to 0.9. Gas chromatography was used as method of analysis.

The presence of CO₂ has shown its influence particularly on the intermediate to high temperature oxidation regimes. The relative importance of the effect of CO₂ on the species concentrations increases as more CO₂ is added to replace N₂. The measurements were also compared to simulations based on a kinetic mechanism to verify its validity at MILD combustion operative conditions. Overall, the mechanism performs in qualitatively capturing the major features of relative reactivities of various fuel mixtures. Moreover, in many cases there is no quantitative agreement between the model prediction and experimental data. Improving the accuracy of the models would enhance their use in detailed design of combustors for new technologies.

Acknowledgments

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