

The oxidation of hydrogen-enriched natural gas blends: Experimental and detailed chemical kinetic modeling study kinetic

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Introduction

The lean-premixed combustion in gas turbines could be used for reducing carbon dioxide and nitrogen oxides emissions. A net reduction of CO₂ emissions could be achieved using CO₂-neutral bio-fuels, hydrogen-enriched fuels, using hydrogen from non-CO₂ producing sources, by-products of steel and coal industry (hydrogen and/or carbon monoxide). Previous studies showed that adding hydrogen to conventional fuels improves flame stability, yields leaner blowout limits, and reduces CO and NO_x emissions [1-5]. The use of hydrogen-enriched fuels allows operation under fuel-lean conditions where the emission of NO_x is strongly reduced. These fuel mixtures could serve as a transition towards the longer term switch to carbon-free energy production. Therefore, lots of studies have been performed to better characterize the combustion of hydrogen-enriched fuels. However, high-pressure kinetic studies of the oxidation of hydrogen-enriched natural gas are still missing, although until recently, it was expected that recent kinetic schemes represent the ignition and combustion of hydrogen-enriched simple fuels. Actually, a recent computational study [6] showed that several kinetic models [7-10] failed predicting the ignition delays of hydrogen-methane mixtures [6] whereas a former version of the presently proposed kinetic scheme could be used to simulate the available [11,12] H₂-CH₄ ignition data. New experiments were performed for the oxidation of a natural gas blend (NGB), containing methane and ethane, or methane-ethane and propane, and hydrogen-NGB mixtures, over a wide range of initial concentrations, temperatures and equivalence ratios. These data were obtained over the pressure range 1-10 atm. A detailed chemical kinetic reaction mechanism [13] was used to simulate these experiments and rationalize the results.

Experimental

We used a spherical fused silica jet-stirred reactor (JSR) surrounded by a regulated electrical resistance system of c.a. 1.5 kW, wrapped with insulating material and located inside a stainless-steel pressure resistant jacket (1-10 atm). The natural gas blends (c.a. 90% of CH₄, 10% of C₂H₆ and 89% of CH₄, 9% of C₂H₆, 2% of C₃H₈ in nitrogen), hydrogen (99.995 pure), oxygen (99.995% pure) and nitrogen (<50 ppm of O₂; <1000 ppm of Ar; <5 ppm of H₂) flow rates were measured and regulated by thermal mass-flow controllers. The reactants were diluted by a flow of nitrogen. The fuel and the mixture O₂-N₂ were pre-heated. They flowed separately up to the mixing point at the entrance of the injectors. Previous residence time distribution studies showed that this reactor operates under macro-mixing conditions. Consequently, a perfectly-stirred-reactor model could thus be used [14]. As before [14-16], a good thermal homogeneity was measured along the vertical axis of the reactor by thermocouple measurements (Pt/ Pt-Rh 10%, 0.1 mm diameter located inside a thin-wall fused-silica tube, <0.5 mm, to prevent catalytic reactions on the metallic wires). Typical temperature gradients of <10 K were measured. Due to the high degree of dilution, the temperature rise due to the reaction was generally < 30 K. Low pressure samples of the reacting mixtures were taken by sonic sampling and collected in 1 liter Pyrex bulbs at c.a. 50 mbar for immediate gas

chromatography (GC) analyses as in [15,16]. In order to improve the GC detection, these samples were pressurized at 0.8 bar before injection into the GC column, using a glass home-made piston. Capillary columns The present analytical system allowed the measurements of methane, ethane, propane, ethylene, acetylene, H₂, O₂, H₂O, CO, CH₂O and CO₂. As previously [15,16], very good agreement between the GC and FTIR analyses was found for the compounds measured by both techniques (methane, ethylene, acetylene, CO, CO₂). Carbon balance was checked for every sample and found good within 100± 8%.

Modelling

PSR [17] was used for the JSR modeling. The kinetic reaction mechanism used here is the detailed chemical kinetic reaction mechanism previously used for the kinetic modeling of the hydrogen-enriched natural gas oxidation under atmospheric pressure conditions [13], similar to that used for modeling the oxidation of LPG [18] and of various fuels from methane to kerosene [19]. It includes both low and high temperature combustion chemistry. A sub-set of the scheme is given in Table 1. The full kinetic reaction mechanism, including thermochemical data, is available from the authors (dagaut@cnr-orleans.fr). The pressure-dependencies of unimolecular reactions and of some pressure-dependent bimolecular reactions were taken into account when information was available (i.e., $k(P, T)$). The rate constants for the reverse reactions were computed from the forward rate constants and the appropriate equilibrium constants calculated using thermochemical data [14,16].

Results and Discussion

This study yielded a large set of experimental results for the oxidation of the NGB and hydrogen-NGB mixtures over the temperature range 900-1200 K, for equivalence ratios ranging from 0.3 to 1, and for various mole fractions of NGB and hydrogen (0%, 0.4% and 1.75% in mole). The experiments were performed at a constant residence time and the reaction was studied by varying the operating temperature in the JSR. Concentration profiles for the reactants, stable intermediate compounds and final products (O₂, H₂, H₂O, CO, CO₂, CH₂O, CH₄, C₂H₆, C₃H₈, C₂H₄, and C₂H₂) were measured. The proposed kinetic reaction mechanism was used to simulate the present experiments.

Oxidation at 1 atm

Examples of the experimental results obtained for the oxidation of the NGB are presented in Fig. 1 together with the modeling results. They show that the proposed kinetic scheme gives very good predictions of the data. Similar experiments were performed replacing 40% in mole of the NGB by hydrogen. Examples of the experimental results are presented together with the modeling in Fig. 2. The replacement of a fraction of methane by hydrogen results in an increased reactivity of the fuel mixture. The temperature at which the oxidation of the fuel produces intermediates (CO, ethylene) at the same level of concentration with the NGB and the H₂-NGB mixtures is reduced by 50-100 K. Also, the temperature at which a 50% methane consumption is measured is reduced by 30-75 K when hydrogen is present. Similar experiments were performed replacing 40% in mole of the NGB by H₂, using the same initial concentration of oxygen as in the neat NGB oxidation experiments. The data showed that the replacement of the same fraction of the NGB by a larger fraction of hydrogen yields a still increased reactivity of the fuel. The temperature at which 50% of methane is consumed is reduced by 100-150 K when hydrogen is present. Again, the kinetic model used here describes fairly well the experimental observations.

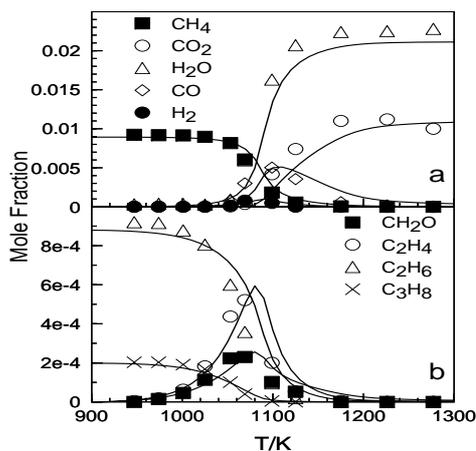


Fig.1 The oxidation of a natural gas blend in a JSR. The initial conditions were $\Phi=0.3$, 120 ms, 8928 ppm of CH_4 , 879 ppm of C_2H_6 , 198 ppm of C_3H_8 , 73000 ppm of O_2 . The experimental results (symbols) are compared to the modeling results (lines).

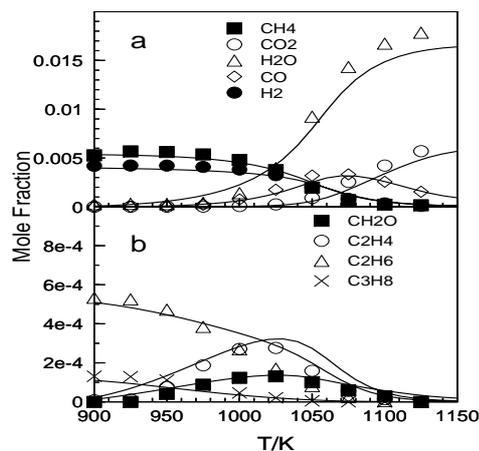


Fig. 2 The oxidation of a hydrogen-natural gas blend in a JSR. The initial conditions were $\Phi=0.3$, 120 ms, 4000 ppm of H_2 , 5357 ppm of CH_4 , 525 ppm of C_2H_6 , 119 ppm of C_3H_8 , 50500 ppm of O_2 . The experimental results (symbols) are compared to the modeling results (lines).

Oxidation at 10 atm

Examples of the experimental and modeling results for the oxidation of the neat NGB from fuel-lean to stoichiometric conditions are presented in Fig. 3. Similar experiments were performed replacing 40% in mole of the NGB by hydrogen (Fig. 4). The replacement of a fraction of methane by hydrogen results in an increased reactivity of the mixture. The temperature at which the intermediates (CO, formaldehyde, ethylene) reach their maximum mole fraction is reduced by c.a. 50 K when going from the NGB to this H_2 -NGB mixtures. Similar experiments were performed replacing 40% in mole of the NGB by H_2 , using the same initial concentration of oxygen as in the neat NGB oxidation experiments. The results show that the replacement of the same fraction of the NGB by a larger fraction of hydrogen yields a still increased reactivity of the fuel. Thus, increasing the fraction of hydrogen in the fuel results in an increased production of OH radicals through the following scheme: The addition of hydrogen results in an increased production of H-atoms via $\text{H}_2 + \text{OH} \Rightarrow \text{H}_2\text{O} + \text{H}$ (9). As a result, the production of hydroperoxyl radicals via $\text{H} + \text{O}_2 + \text{M} \Rightarrow \text{HO}_2 + \text{M}$ (7) is increased as well as the production of hydrogen peroxide via $2 \text{HO}_2 \Rightarrow \text{H}_2\text{O}_2$ (16). The decomposition of hydrogen peroxide yields two OH radicals that react with the fuel mixture. Furthermore, the importance of $\text{CH}_3 + \text{H}_2 \Rightarrow \text{CH}_4 + \text{H}$ (-41) is increased in the presence of hydrogen in the fuel, as well as that of $\text{H} + \text{HO}_2 \Rightarrow \text{OH} + \text{OH}$ (14). It should be noted that in the neat NGB oxidation, reaction (41) consumes methane and H whereas in the hydrogen-enriched NGB cases, this reaction operated in the reverse direction, producing methane and H.

Conclusion

New experimental results were obtained for the oxidation of H_2 in diluted conditions in a JSR at 1-10 atm. The effect of the addition of NO and NO_2 was studied. A detailed kinetic model is proposed to interpret the results. This model was also validated against the available data for the ignition of hydrogen-air mixtures and H_2 -air- NO_x mixtures, and for the flame speeds of hydrogen air mixtures. The proposed model allows a good representation of the set of data considered here. The present results confirm the rate constant of [15] for the reaction of NO_2 with H_2 .

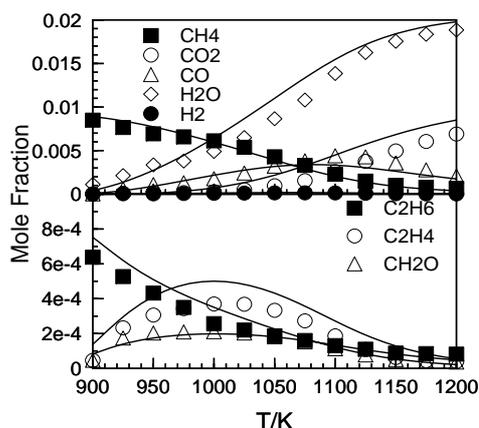


Fig. 3 Figure 4. The oxidation of a natural gas blend in a JSR at 10 atm. The initial conditions were $\Phi=0.3$, 250 ms, 9132 ppm of CH_4 , 868 ppm of C_2H_6 , 71005 ppm of O_2 . The experimental results (symbols) are compared to the modeling results (lines).

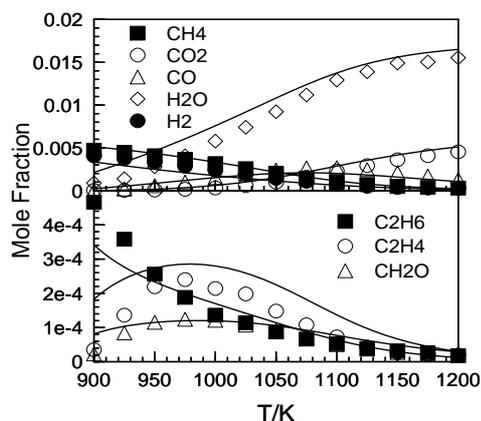


Fig. 4 The oxidation of a hydrogen-natural gas blend in a JSR at 10 atm. The initial conditions were $\Phi=0.3$, 250 ms, 4000 ppm of H_2 , 5479 ppm of CH_4 , 521 ppm of C_2H_6 , 49269 ppm of O_2 . The experimental results are compared to the modeling results (lines)

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