Experimental and Detailed Kinetic Modeling of the Oxidation of Natural Gas, Natural Gas/Syngas Mixtures and Effect of Burnt Gas Recirculation

Tanh Le Cong, Philippe Dagaut

C.N.R.S.
1C, Avenue de la Recherche Scientifique
45071 Orléans Cedex 2, France

1 Introduction

Flameless combustion is an emerging combustion concept particularly useful for reducing pollutant emissions [1], mostly NOx, and improving combustion efficiency. In such combustors, reactants are preheated and diluted by exhaust gases, mainly CO, CO_2 and H_2O, and traces of NOx. Its application to gas turbine is currently studied and the use of syngas (CO/H_2) in gas turbines is getting more and more attention. Therefore, it is very important to study the effect of such compounds on the kinetics of oxidation of conventional fuels such as natural gas. The effect of NOx recirculation was addressed previously [2,3] whereas that of the other components of recycled gases were not. In this paper, we present new experimental results obtained for the oxidation of natural gas blends in a JSR at 1-10 atm, over a wide range temperatures (900-1400) and of equivalence ratios (0.1 to 1.5), K. The oxidation of methane-based fuels under JSR, shock-tube and premixed flame conditions is also modeled. Kinetic analyses are used to rationalize the results.

2 Experimental set-up

The experimental set-up used in this work is that employed earlier [2,3]. The JSR consisted of a small sphere of 4 cm diameter ($30cm^3$) made of fused-silica (to minimize wall catalytic reactions), equipped with 4 nozzles of 1 mm I.D. for the admission of the gases which are achieving the stirring. A nitrogen flow of 100 L/h was used to dilute the fuel. As before [2,3], all the gases were preheated before injection to minimize temperature gradients inside the reactor. The flow rates were measured and regulated by thermal mass-flow controllers. The fuel and oxygen flowed separately until they reach the mixing point at the entrance of the injectors. Previous residence time distribution studies showed that this reactor operates under macro-mixing conditions. The JSR operated under steady-state conditions and, due to the high-dilution of the reactants, no flame occurred. Thus, a perfectly-stirred-reactor model could be used. As before [2,3], a good thermal homogeneity was observed along the vertical axis of the reactor by thermocouple measurements. A Pt/ Pt-Rh 10% thermocouple, located inside a thin-wall (<0.5 mm) fused-silica tube to prevent catalytic reactions on the metallic wires of 0.1 mm in diameter was used. Typical temperature gradients of <2.5 K/cm were measured. Since a high degree of dilution was used, the temperature rise due to the reaction was generally < 30 K. Low pressure samples of the reacting mixtures were taken by sonic probe sampling and collected in 1 liter Pyrex bulbs at c.a. 50 mbar for immediate gas chromatography (GC) analyses as in [3]. 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 of 0.53 mm i.d. (Poraplot U and Molecular sieve 5A) were used with a thermal conductivity detector (TCD) and a flame ionization detector (FID) for the measurements of gases, except hydrogen measured on another GC system. Helium was used as a carrier gas. For hydrogen measurements, a GC

Correspondence to : dagaut@cnrs-orleans.fr

operating with nitrogen as carrier gas, a Carboplot (0.53 mm i.d.) and a TCD was used. On-line Fourier transform infrared (FTIR) analyses of the reacting gases were also performed by connecting the sampling probe to a temperature controlled (140 °C) gas cell (2 or 10 m path length) via a Teflon heated line (130 °C). The present analytical system allowed the measurements of methane, ethane, ethylene, acetylene, H_2, O_2, H_2O, CO, CH_2O, and CO_2. Very good agreement between the GC and FTIR analyses was found for the compounds measured by both techniques (methane, ethylene, acetylene, CO, CO_2). The reported profiles for hydrocarbons were obtained by GC-FID and those for CO and CO_2 where measured by FTIR. The reported mole fractions were above the detection limits. Quantitative measurements were limited to 1 ppm for hydrocarbons, and 20 ppm for oxygen, hydrogen, water, CO, formaldehyde, and CO_2. Carbon balance was checked for every sample and found good within 100+/-8%.

3   Kinetic modeling

The kinetic modeling of premixed flames, was performed using the Premix computer code [4]. The ignition delays, were simulated using the SENKIN code [5]. For the JSR computations, we used the PSR computer code [6] that computes species concentrations from the balance between the net rate of production of each species by chemical reactions and the difference between the input and output flow rates of species. These rates are computed from the kinetic reaction mechanism and the rate constants of the elementary reactions calculated at the experimental temperature, using the modified Arrhenius equation. The reaction mechanism used here has a strong hierarchical structure. The reaction mechanism used here consisted of 98 species and 737 reversible reactions. This mechanism, including references and thermochemical data, is available from the authors. The rate constants for reverse reactions are computed from the corresponding forward rate constants and the appropriate equilibrium constants, $K_c = k_{forward} / k_{reverse}$ calculated using thermochemical data [3].

4   Results and discussion

This study yielded a large set of experimental results for the oxidation of CH_4-based fuel mixtures for various initial mole fractions of methane, hydrogen, carbon monoxide, and carbon dioxide. The experiments were performed at a constant residence time of 120 ms at 1 atm, and 250 ms at 10 atm. The reaction was studied by varying the operating temperature in the JSR. Concentration profiles for the reactants, stable intermediates and final products (O_2, H_2, H_2O, CO, CO_2, CH_2O, CH_4, C_2H_6, C_2H_4, and C_2H_2) were obtained.

Methane and Methane-CO_2 oxidation
The present results allows a comparison of the kinetics of the neat oxidation of methane with that of methane-carbon dioxide mixtures (Figs. 1,2). As can be seen from these figures, the presence of 20% carbon dioxide tends to slightly inhibit the oxidation of the fuel: a shift of the concentration profiles by ca. 10 K is observed in the experiments, in agreement with the computations. A good agreement between the data and the model is observed. The kinetic modeling shows that CO_2 has an inhibiting effect via the reaction $CO_2 + H =>$ $CO + OH$ that competes with the H-abstraction reaction $CH_4 + H => CH_3 + H_2$, decreasing the consumption of methane. The model was further tested via simulating the flame speeds of methane-air (Fig. 3) and that of methane-oxygen in presence of increasing quantities of carbon dioxide (Fig 4) reported recently [7].

Methane-Hydrogen and Methane-H_2-CO_2 oxidation
As demonstrated earlier, the reactivity of methane-hydrogen mixtures is higher than that of methane. The effect of carbon dioxide on the kinetics of oxidation of such mixtures was studied. The present results clearly show the higher reactivity of the CH_4-H_2 mixtures. The effect of carbon dioxide on the kinetics of oxidation of methane-hydrogen mixtures was studied. The present results show an increased inhibition of the fuel oxidation due to CO_2 with increasing equivalence ratio. Temperature shifts of 10, 20, and 70K are observed at respectively φ=0.1, 0.3, and 0.6. The kinetic modeling shows that CO_2 has an inhibiting effect via the reaction $CO_2 + H =>$ $CO + OH$ that competes with the H-abstraction reaction $CH_4 + H => CH_3 + H_2$, reducing the consumption of methane. Since the importance of CH_4+H is increasing with increasing equivalence ratio, the inhibiting effect of CO_2 is more pronounced at φ =0.6 that it is at φ=0.1, as observed in the present experiments and modeling.
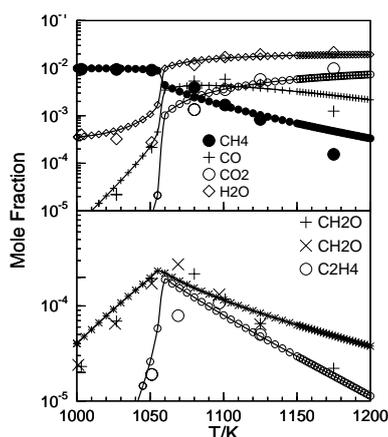
Figure 1: The oxidation of methane in a JSR (1 atm, τ=120 ms, 1% CH_4, φ=0.1, dilution by nitrogen).
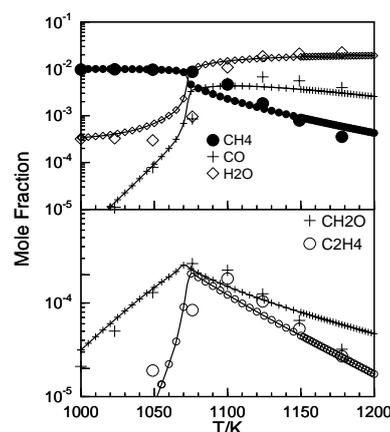
Figure 2: The oxidation of methane with CO_2 in a JSR (1 atm, τ=120 ms, 1% CH_4, 20% CO_2, φ=0.1).
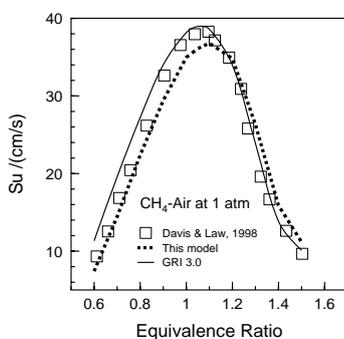
Figure 3: The laminar burning velocities of methane-air mixtures at 1 atm and 298 K. The data of [8] (symbols) are compared to the present modeling (dashed line) and the GRI3.0 predictions (continuous line) [9].
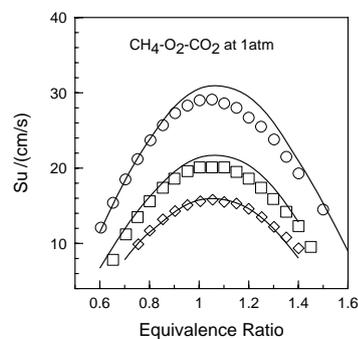
Figure 4: The laminar burning velocities of CH_4-O_2 premixed flames in presence of CO_2 (1 atm, dilution ratio $O_2/(O_2+CO_2)$= R varied). The conditions were: O, R=0.35; □, R=0.3155; ◊, R=0.29 [7].

Methane-Hydrogen-CO oxidation

The oxidation of methane-syngas mixtures was also studied in a JSR (Figs. 5, 6). The examination of the present results allows a comparison of the kinetics of oxidation of methane-hydrogen with that of methane-carbon monoxide mixtures. When CO is added to a CH_4+H_2/O_2/N_2 mixture, the formation of OH is mainly due the reactions of the H_2/O_2 system, H + O_2 => OH + O and HO_2 + H => 2OH. The competition between CH_4 + OH => CH_3 + H_2O and CO + OH => CO_2 + H does not affect the production of OH, as observed in absence of H_2. The reaction CO + OH => CO_2 + H promotes the oxidation of the fuel through the production of H atoms.

5   Conclusion

New experimental results were obtained for the oxidation of methane-based fuels (CH_4, CH_4/CO_2, CH_4/H_2, $CH_4/CO/H_2/$, $CH_4/H_2/CO_2$) in a JSR at 1-10 atm, 900-1400 K, from fuel-lean to fuel-rich conditions. A kinetic modeling of these experiments, literature burning velocities, and ignition delays was performed with success. Reaction paths analyses were used to delineate the important reactions influencing the kinetic of oxidation of the fuels in presence of variable amounts of burnt gases. The kinetic modeling indicates that the effect of carbon dioxide addition mainly results from the perturbation of the equilibrium of the reaction CO + OH = CO_2 + H.
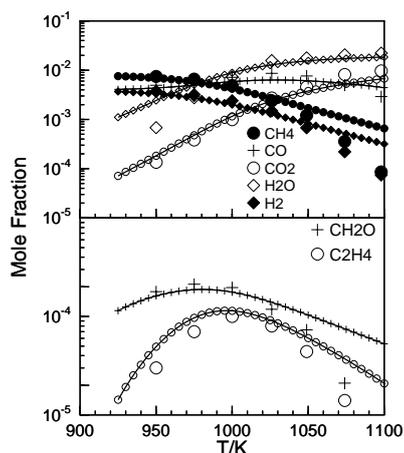
Figure 5: The oxidation of methane-H_2-CO in a JSR (1 atm, τ=120 ms, 0.8% CH_4, 0.4% H_2, 0.4% CO, φ=0.1, dilution by nitrogen).
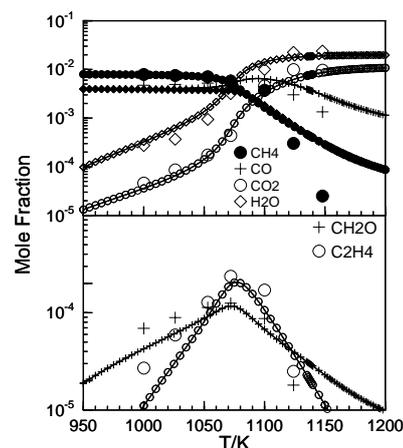
Figure 6: The oxidation of methane-H_2-CO in a JSR (1 atm, τ=120 ms, 0.8% CH_4, 0.4% H_2, 0.4% CO, φ=0.6, dilution by nitrogen).

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