Kinetic effect of hydrogen addition on natural gas premixed flames

S. de Ferrières [b], A. El Bakali [a,*], L. Gasnot [a,b], M. Montero [b], J.F. Pauwels [a]

[a] PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR 8522 CNRS/Lille1, Université Lille1 Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France
[b] GDF SUEZ, CRIGEN, BP 33, 93211 Saint Denis La Plaine Cedex, France

ABSTRACT

The chemical structure of laminar premixed natural gas flame with and without 60% of hydrogen on the fuel has been studied experimentally and numerically at atmospheric pressure. This work completes our recent results reported for low-pressure premixed flames. Both flames have been stabilized under similar conditions (similar cold velocity and C/O). Stable mole fraction profiles have been obtained by gas chromatography, FTIR and GC–MS. Temperature profiles have been measured by thermocouple and corrected from radiation losses. Comparatively to low pressure, more traces species have been observed at atmospheric pressure. These new results have been modeled and a revised version of GDF-Kin®3.0-NCN is reported. This version is able to predict the present data (mole fraction profiles and recent burning velocities of natural gas and natural gas/hydrogen flames) without alteration of previous predictions. Reactions path analysis confirms that hydrogen enhances H-abstraction reactions by H atoms under lean conditions. It also enhances the oxidation of C_1 sequence and disfavors the C_2 sequence. Consequently, a reduction of C_2 intermediate specie mole fraction could be observed.

© 2012 Published by Elsevier Ltd.

1. Introduction

Major challenges as local pollution, greenhouse gas emissions and future depletion of fossil fuel reserves have to be worked out. Hydrogen is a convincing source of power to bring about long-term improvement in our energy situation. It offers a number of advantages as a source of energy. It can be produced from a large number of primary energy sources, including fossil fuels with CO_2 sequestration at source and renewable energies or used in mobile and static applications, in particular through fuel cell technology. Natural gas, compared to other fuels, is responsible for relatively low pollutants emissions. Natural gas/hydrogen as a fuel can be a transitional solution towards hydrogen energy, using the technologies, infrastructures and skills involved in natural gas vehicle fuel.

Natural gas combustion has been studied extensively for more than 10 years in our laboratory in partnership with GDF SUEZ. Our previous studies, performed at low pressure, concerned the effect of additives C_1 to C_4 to methane. The higher alkanes significantly enhanced methane reactivity, leading to smaller ignition delay times and faster burning velocities [1–3]. This chemical effect is due to an increase of methyl and ethyl radicals produced by the decomposition of the fuel and an increased production of atomic hydrogen which enhances the production of more reacting radicals, boosting the oxidation. However, the role of alkanes higher than C_3 is minor and the oxidation of methane/ethane/propane

mixture was found the best model for natural gas combustion [1,2].

Recently the effect of another additive to natural gas, hydrogen, was studied in laminar premixed low pressure flames (0.079 atm) [4] at stoichiometric and lean conditions. The carbon to oxygen ratio was kept constant to evaluate the kinetic effect of hydrogen addition on natural gas combustion. The addition of H_2 to natural gas mainly benefits the C_1 oxidation sequence due to the enhancement of the recombination of H and C_2H_5 reaction yielding methyl radicals and then disfavored the C_2 sequence. H-abstraction reactions by H-atoms mainly dominate the natural gas/hydrogen system. Moreover, hydrogen as an additive to methane has similar global effect as higher alkanes by increasing burning velocity and decreasing ignition delays [5–7].

The goal of this work is to investigate the kinetic effect of hydrogen in a natural gas/hydrogen mixture at a higher pressure. The new experimental configuration at atmospheric pressure allows us to examine the effects of fuel blending on the chemical structure of lean and stoichiometric flames and emissions characteristics by stabilizing natural gas and natural gas/hydrogen premixed flames at the same carbon to oxygen content in the initial mixtures. A new version of our mechanism of natural gas combustion (GDF-Kin®3.0-NCN) is presented and validated at atmospheric pressure. A large number of intermediate specie which were not detected in [4] have been analyzed and their formation and consumption have been reviewed. Modeling has been used to identify the dominant pathways associated with the various pollutant species for natural gas/hydrogen blends.

2. Experimental setup

Detailed and accurate experimental data on mole fraction profiles of stable species of laminar premixed natural gas (NG)/H_2/O_2/N_2 flames are presented. The initial conditions of the two flames reported in this article are shown in Table 1. The flow rates of the natural gas blend (2.00 ± 0.04% C_3H_8 and 9.00 ± 0.18% C_2H_6 in methane), hydrogen (99.999% pure), nitrogen and oxygen (99.996% pure) were measured and regulated by thermal mass-flow controllers (Brooks 5850S). The diagram of the experimental setup is given in Fig. 1. The flames have been stabilised on a water-cooled, plug, flat flame burner (6 cm in diameter) at atmospheric pressure. A refractory steel plate of 20 cm diameter is placed 1 cm above the burner surface to move the flame upstream (Fig. 1). The burner is surrounded by a Pyrex glass to avoid aerodynamic perturbation.

Species analyses were achieved by quartz probe sampling along the symmetry axis of the flame. Mole fraction profiles of species have been described by moving vertically the probe. Samples of 0.8 atm of the reacting mixtures were directly analyzed by gas chromatography (GC) analyses (Varian CP-3800) or Fourier Transform InfraRed spectroscopy (FTIR). Reactants as methane, ethane and propane as well as a large number of C_2 to C_4 intermediate species (ethylene, acetylene, propene, propyne, n-butane, isobutane, trans-2-butene, cis-2-butene, 1-butene, isobutene, 1,3-butadiene and 1-butyne) were analyzed with a HP-Plot Al_2O_3 capillary column (Ø 0.32 mm) and a flame ionization detector (FID). Hydrogen, oxygen, nitrogen and carbon monoxide are separated in a molecular sieve 5A column (Ø 0.53 mm) and detected with a thermal conductivity detector (TCD). Helium was used as a carrier gas, except for hydrogen measurement which used nitrogen as carrier gas to improve the sensibility. The species are directly calibrated before each measure range with cold known concentration standards. Analyses of H_2O, CO and CO_2 were performed by Fourier Transform InfraRed spectroscopy (FTIR) with a spectrometer NEXUS THERMO-OPTEK as described in a previous paper [4].

Temperature profiles are obtained using a coated Pt/Rh 6%-Pt/Rh 30% thermocouple. Conduction heat losses are avoided by setting the thermocouple in a plane perpendicular to the laminar flow. Radiative heat losses are corrected using the electric compensation method. Errors in the peak temperatures were estimated to be ±100 K.

Oxygen and carbon balance was checked for every sample and found to be less than 10%. Hydrogen balance is found to be inferior to 15%. The deviation observed for atomic hydrogen can be attributed to the water lost through the analysis system. Uncertainties are around 10% for major species (CO, CO_2, H_2, CH_4, C_2H_6), around 10–15% for minor species and H_2O.

3. Modeling

We used PREMIX code for the flames modeling [8]. Our detailed kinetic reaction mechanism GDF-Kin®3.0-NCN [9], optimized for natural gas oxidation, is used to simulate the present experimental results. Note that GDF-Kin®3.0-NCN has been validated on a wide range of conditions [2,4,9]. It is able to reproduce correctly global data (burning velocities, ignition delays) and species mole fraction
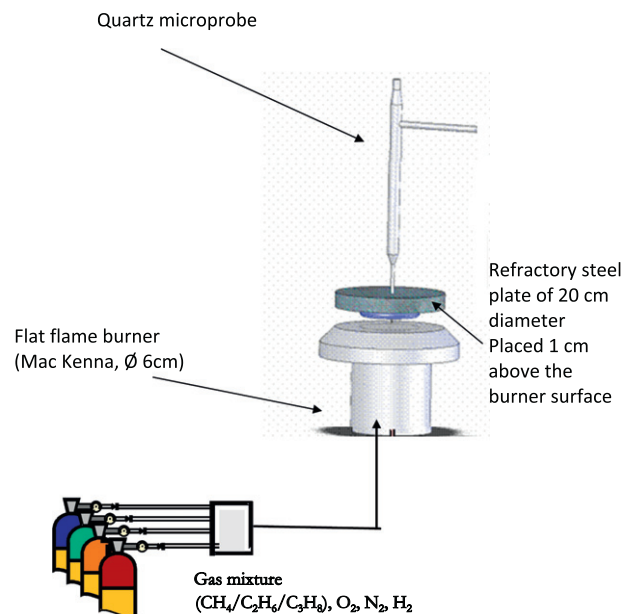

Fig. 1. Diagram of the experimental setup.

profiles obtained in different configurations like premixed laminar flames, jet stirred reactor and shock tube. Regarding flames, the mechanism was validated solely at low pressure and equivalence ratios near stoichiometry ($0.5 \leqslant \phi \leqslant 1.3$). In this work, the mechanism is updated to simulate the effect of hydrogen addition on the chemical structure of laminar premixed natural gas flames operating at atmospheric pressure. The updated version includes 1287 reversible reactions and 192 species and is available at the address: gdfkin@gdfsuez.com.

Thirty-one reactions have been updated, adjusted or added in the GDF-Kin®3.0-NCN mechanism to optimize minor species as propyne, isobutane, 1-butene and isobutylene formation and to take into account the effect of pressure (Table 2). Note that the previous version [9] has never been validated for these intermediate species and do not take into account 1-butyne and 1,2-butadiene. Table 3 compares the predictions of the present mechanism and the previous version in the case of the intermediate species where we observed significant differences. One can note that the current mechanism makes a clear improvement, in particular in the case species in C_4 (isobutane, butenes, dienes) and C_3 (propyne). The majority of these species were very largely underestimated in our preceding version. Literature oxidation sub-mechanisms for benzene [10,11] and toluene [12] have been introduced. Earlier experimental values are still well reproduced by the modified mechanism [1,2,4,9] (see Table 4).

Flame simulations were both run with the experimental profile and by solving the energy equation. The numerical profile of temperature was found to be very close to the experimental one. It shows that due to the care taken for stabilizing the flame far from the burner surface, the flames are almost in adiabatic conditions. In this case it is possible to use the experimental temperature profiles as a first approximation input data and perform flame simulations with the "free" option as in references [13-15].

Table 1
Initial conditions of the flames studied at atmospheric pressure.

	X_{CH4}	X_{C2H6}	X_{C3H8}	X_{H2}	X_{O2}	X_{N2}	D_T(L./h)	ϕ_{C+H}	ϕ_C	C/O	Ta_{dia} (K)
NG	5.8×10^{-2}	5.9×10^{-3}	1.3×10^{-3}	–	0.19	0.74	1314	–	0.74	0.191	1960
NG/60%H_2	3.6×10^{-2}	3.6×10^{-3}	8×10^{-4}	6×10^{-2}	0.12	0.78	1262	1.00	0.74	0.191	1768