Combustion of Pyrolysis Gases Involved in Wildland Fire: Experimental Study

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Abstract

In wildland fire the gaseous fuel released from the pyrolysis of vegetation fuels is a complex and highly variable mixture which include CO, CO_2, CH_4, H_2 and light hydrocarbons. A detailed study of the gas-phase oxidation of such a mixture is reported. The experiments were performed in a perfectly stirred reactor (PSR) at 1 atm, over the temperature range 773 – 1273 K and for equivalence ratio of 1 and 1.2. Mole fractions versus temperature were obtained for molecular species (reactants, intermediates and products). These measurements were used to record the behavior of several species during the combustion of a typical pyrolysis gas mixture released from a Mediterranean species involved in wildland fires. Experimental results were compared to the simulations obtained with the CHEMKIN PSR code. Two detailed mechanisms developed for the oxidation of methane were tested The simulated and experimental results are in good agreement for the mixture investigated.

Key words: Wildland fire, perfectly stirred reactor, gas oxidation, detailed mechanism.

Introduction

Flaming combustion of ligno-cellulosic fuels occurs when the gaseous mixture released from the thermal degradation ignites in the surrounding air. The heat of combustion causes the ignition of adjacent unburned fuel. Therefore, the combustion kinetics in the gas phase is decisive for wildland fire modeling and fuel hazard studies (Zhou and Mahalingam, 2001). At temperatures exceeding 573 K, cellulose, lignin and hemicellulose decompose and the products include light, straight-chain hydrocarbons like CH_4, other light fuels and oxides such as CO and CO_2. For existing mathematical modeling of wildland fire, the combustion of the gaseous fuel is not treated in detail (Sero-Guillaume and Margerit, 2002, Porterie et al., 2000). Instead, global rate and thermodynamic parameters are included in the model for a representative fuel and oxidizer air. In a wildland fire, the actual reaction pathways of gaseous fuel combustion determine whether flaming or glowing would occur. Formation of soot particles, CO and NO_x and other products of incomplete combustion depend strongly on the combustion process. These observations motivate our current examination of combustion mechanism of pyrolysis gases. The Perfectly Stirred Reactor (PSR) was used as an experimental test environment. The perfectly stirred reactor consists of a small thermally isolated chamber that has inlet and outlet ducts. A steady flow of fuel and oxidizer are introduced in such a way that high-intensity turbulent mixing causes the contents of the reactor to be nearly spatially uniform. This means that the rate of conversion from the reactants to products is con-

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trolled by chemical reaction rates and not by mixing processes. The flow through the reactor is characterized by a nominal residence time. Because only the exit results are obtained, the detailed flame structure cannot be displayed from PSR.

Experimental

The experimental device was composed of three subsystems: the reactor, the sampling system and the chromatographic system.

The reactor consisted of a small sphere of 60 mm diameter (109 cm^3) made of quartz, equipped with four nozzles (0.3 mm i.d.) for the admission of gases and to achieve the stirring. High purity reactants were used: 99.995% pure. All the gases were preheated before injection to minimize temperature gradients into the PSR. A regulated heating furnace maintained the reactor at the desired working temperature. The device allowed oxidation studies until 1500 K. The gases flow rates were measured and regulated by thermal mass-flow controllers with an uncertainty of ± 0.5 % on the full scale. The reactants were diluted by a flow of argon. The oxidizer (20% O_2 and 80% N_2) and the fuel flowed separately until they reached the mixing point at the entrance of the injectors. The residence time in the injectors τ_{inj} was small compared to the residence time in the reactor τ $\left(\tau_{inj}/\tau \cong 10^{-2}\right)$ avoiding reactions outside the reactor. The stick of gases introduction consisted of a capillary quartz tube (1mm i.d.) and the residence time in this zone was around 5.10^{-2} s. As mentioned in a previous word dedicated to the experimental achievement (Jallais, 2000), a good thermal homogeneity was measured along the vertical axis of the reactor by thermocouple measurements. Typical temperature gradients of <5 K were measured. Because of the high degree of dilution, the temperature rise due to the reaction was generally <10 K. Present experiments were performed at steady state conditions for a constant mean residence time, τ, of 1.3 s and the reactants flowed continually into the reactor. The temperature of the gases entering the PSR was varied stepwise in the following range: 773 K – 1273 K.

Low pressure samples of the reacting mixture were taken by sonic sampling and collected in a stainless steel chamber equipped with a piston for immediate gas chromatography (GC) analyses. The samples were pressurized at 1 bar before injection into the GC column. Packed columns of 2 mm i.d. (Porapack Q, activated alumina) and a molecular sieve

5A were used with a thermal conductivity detector (TCD) in series with a flame ionization detector (FID) for the measurement of gases, except hydrogen measured on another system. Helium was used as a carrier gas. For hydrogen measurements, a GC operating with argon as carrier gas, a molecular sieve 13X column (4 mm i.d.) and a TCD was used. The present analytical system allowed the measurements of methane, ethane, ethylene, acetylene, H_2, O_2, CO and CO_2. Figure 1 represents the oxidation reactor.

For practical reasons the reactor inlets were the following: $CH_4/CO/N_2$ and $O_2/CO_2/Ar$.

The equivalence ratio was given by:

$$\phi = \left(\% \ fuel/\% \ O_2\right)\Big/\left(\% \ fuel/\% \ O_2\right)_{\phi=1} \quad (1)$$

In order to obtain different equivalence ratio, the percentage of O_2 was calculated according to Eq. (1) for CH_4 and for CO with : $\% \ (CH_4)_{\phi=1}\Big/\% \ (O_2)_{\phi=1} = 1/2$ and $\% \ (CO)_{\phi=1}\Big/\% \ (O_2)_{\phi=1} = 2$.

Several dilution factors were used for the reactants in argon to ensure a low temperature elevation in the reactor. We found the optimal dilution factor of 9.2 from the composition obtained in the tubular furnace experiments. Table 1 presents the molar fraction percentages of the different reactants to be injected in the PSR according to the desired equivalence ratio.

Table 1. Molar fractions (%) inlets for the PSR.

ϕ	CH_4	CO	CO_2	O_2
1.0	2	3.33	5.57	5.66
1.2				4.72

The percentages of N_2 were calculated for each equivalence ratio according to air composition: $\%(N_2)/\%(O_2) = 4.76$.

In our study the working pressure is equal to the atmospheric pressure and the flow of each gas species i was then calculated according to:

$$D_i = X_i D_t = X_i \left(V/\tau\right)\left(T_0/T\right) \quad (2)$$

Kinetic modeling

We used the PSR computer code from CHEMKIN (Kee et al., 1989) for the PSR modeling. Mechanisms used were detailed chemical kinetic reaction mechanisms developed for the modeling of CH_4 oxidation: Gri Mech 3.0 (Smith et al., 2000) and Jallais
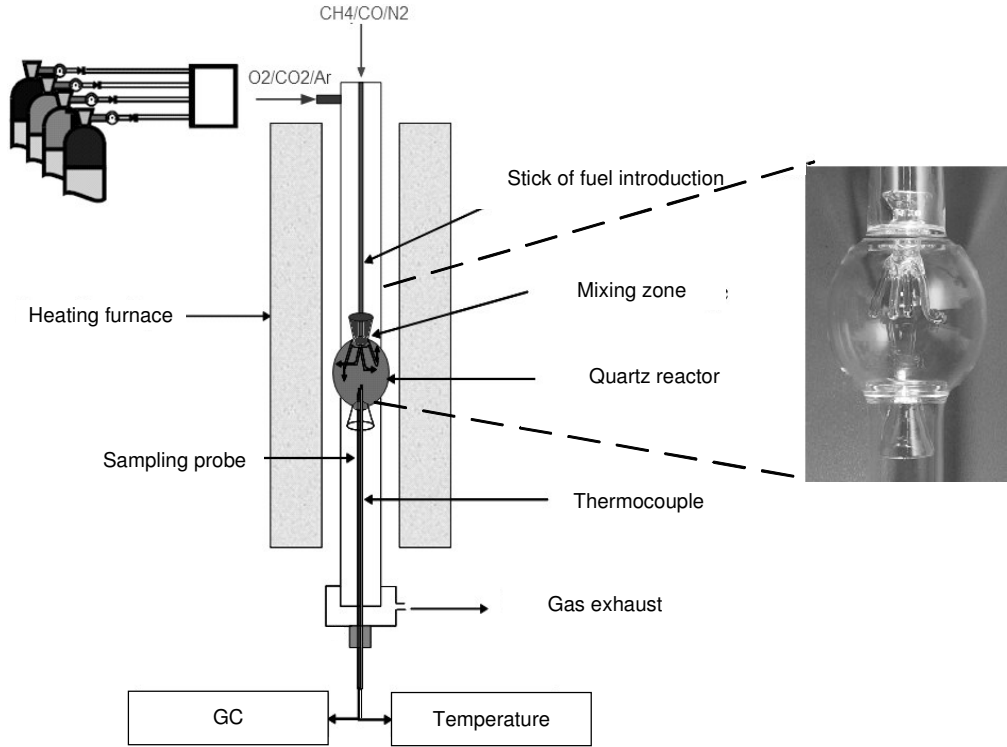
Figure 1. The Perfectly Stirred Reactor.

(Jallais, 2001). The PSR code allows the calculation of steady-state temperature and species composition in a perfectly stirred reactor. The reactor is characterized by a reactor volume, residence time or mass flow rate, heat loss or temperature, and incoming temperature and mixture composition. The PSR is governed by the species conservation equation and the conservation of energy:

$$\dot{m}\,(Y_k - Y_k^*) - \dot{\omega}_k W_k V = 0 \qquad (3)$$

$$\dot{m} \sum_{k=1}^{K} (Y_k h_k - Y_k^* h_k^*) + Q = 0 \qquad (4)$$

The normal residence time (τ) is related to the reactor volume and the mass flow rate $(\dot{m})$ by:

$$\tau = \rho V / \dot{m} \qquad (5)$$

The net chemical production rate $\dot{\omega}_k$ of each species results from a competition between all the chemical reactions involving this species. Each reaction proceeds according to the law of mass and the forward rate coefficients are in the modified Arrhenius form. The rate constants for the reverse reactions were computed from the forward rate constants and

the appropriate equilibrium constants calculated using thermochemical parameters (Smith et al., 2000). As mentioned in the experimental part of the present paper, the temperature rise due to the reaction was generally lower than 10 K. Hence, a constant temperature was assumed simplifying the calculation procedure since only Eq. 3 needed to be solved.

Results

The present work focused on the oxidation of a gas mixture constituted of methane, carbon monoxide and carbon dioxide. This choice agrees with the results obtained in a previous study concerning the determination of the composition of the pyrolysis gas mixture for different Mediterranean species (Santoni et al., 2006). Pyrolysis gas mixture was obtained by tubular furnace experiments.

We chose to study the gas-phase combustion of a mixture representative of *Pinus pinaster* fuel (CO: 30.5%, CO_2: 51.1 % and CH_4: 18.4%). As previously mentioned in the experimental section, the gas mixture has to be diluted. The mixture composition is reported in Table 1 for the different equivalence ratios. The resulting experimental concentration profiles for O_2, CO, CO_2, CH_4, C_2H_4, C_2H_6 are

provided in Figures 2 to 7. Simulation results are superimposed on Figures 2 to 5. We did not calculate molar fractions of C_2 species since these are intermediates and we only focused in this work on reactants. Also, H_2O do not appear in experimental and simulations results since we could not measure this species with our chromatographic device.
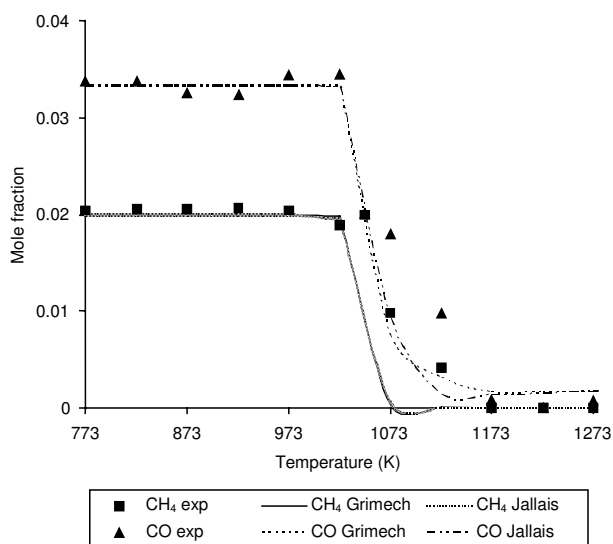

Figure 2. Experimental and simulated results for CH4 and CO mole fractions ($\phi = 1$).

For equivalence ratios of 1 and 1.2, the experimental results indicated a stiff consumption for CH_4 in the temperature range 973-1073 K. The consumption was complete in this temperature range. For the gas mixture studied in this work, consumption reactions were active in this temperature range which corresponds to actual conditions in wildland fires. On the other hand, CO consumption was less stiff in the occurring temperature range. Contrary to CH_4, the consumption of CO depend on the equivalence ratio since we obtained around 100% for $\phi = 1$ and only 50 % for $\phi = 1.2$. The mechanisms used in this study were developed for the modeling of natural gas oxidation. This is the reason why the simulation results exhibited a better agreement for the prediction of CH_4 concentration than for CO.

However, although the simulated data did not match perfectly experimental data, the global behaviour of CO was well represented. The difference between Figure 2 and Figure 3 showed that both mechanisms represent the weak conversion of CO at $\phi = 1.2$ and the complete conversion of CO at $\phi = 1$.
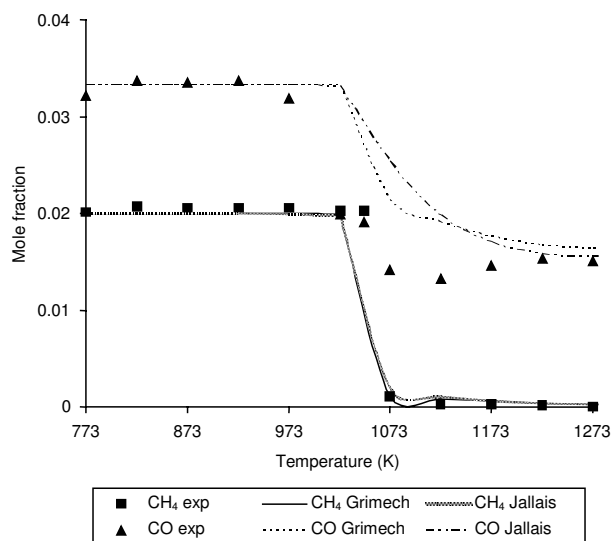

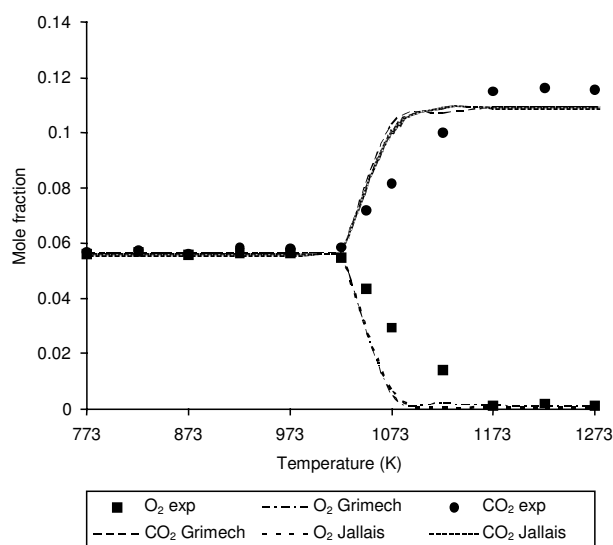**Figure 3.** Experimental and simulated results for CH_4 and CO mole fractions ($\phi = 1.2$).

Figure 4. Experimental and simulated results for O_2 and CO_2 mole fractions ($\phi = 1$).

The evolution of O_2 and CH_4 followed roughly the same tendency with an infinitesimal consumption for T < 973 K and an abrupt consumption in the range 973-1073 K. The production of CO_2 was symmetrical to the consumption of O_2. Simulation results matched well the experimental molar fractions of O_2 and CO_2 as shown on Figure 4 and Figure 5.
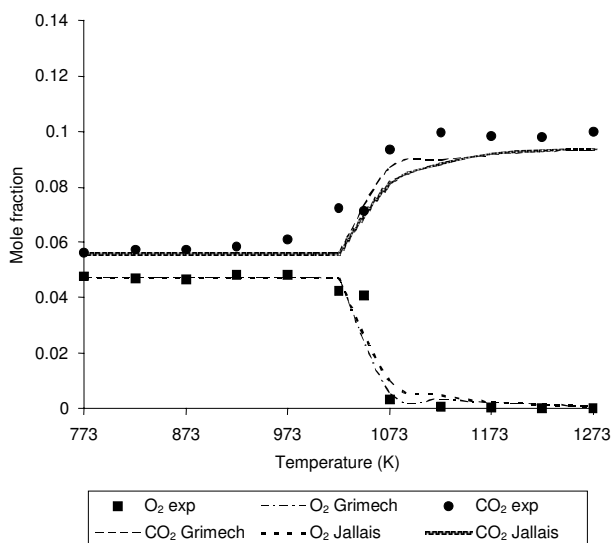
Figure 5. Experimental and simulated results for O_2 and CO_2 mole fractions ($\phi = 1.2$).

A slightly under-estimation of the molar fraction of CO_2 was observed at high temperatures, this is probably caused by the gas mixture used which contains a large amount of CO_2 whereas the mechanisms were developed for natural gas with a very low CO_2 content. It is important to notice that simulations are very similar with both mechanisms. In this preliminary work we compared a well known mechanism to a mechanism developed at the same time of the experimental device for the conditions of this reactor. In the future and for the developments of this work we will use the Gri-Mech 3.0 mechanism.

Figures 6 and 7 represent the experimental molar fractions of C_2 species. We chose to follow these species as they play an important role in soot formation. In wildland fire soot particles are important since they actively participate to the flame radiation. These species were found to be intermediates ones since they were identified only in the reaction zone for the range 973-1273 K. These experimental results showed that C_2 species could not be neglected in a kinetic mechanism able to predict the combustion of vegetation fuels. Ethane is formed essentially according to a radical-radical reaction: $CH_3 + CH_3 + M = C_2H_6 + M$ where M is a third body species. Ethylene is formed according to a radical reaction: $CH_3 + HCO = C_2H_4 + O$ and according to hydrogen abstraction from C_2H_6 to C_2H_5 until C_2H_4 in the following sequence:
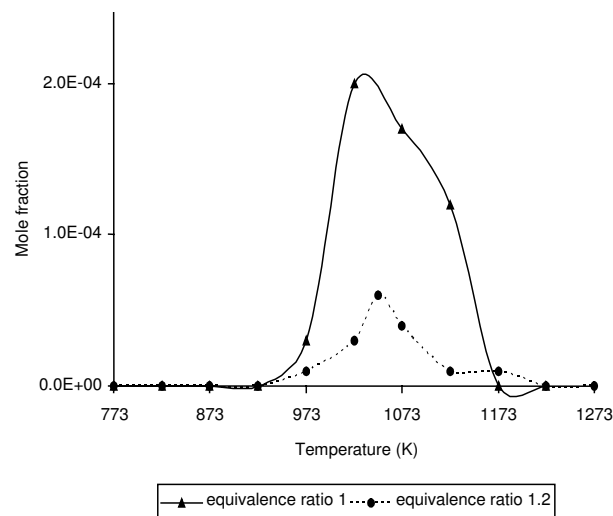

Figure 6. Experimental results for C_2H_6 mole fractions.
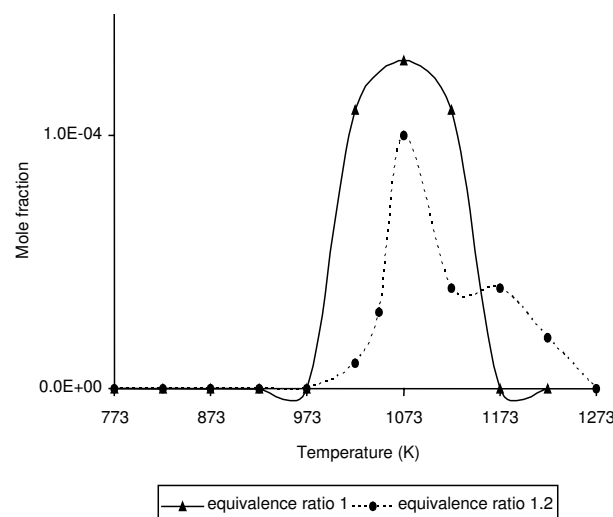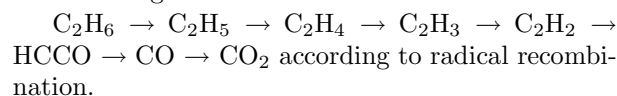

Figure 7. Experimental results for C_2H_4 mole fractions.

1. $C_2H_6 + CH_3 = C_2H_5 + CH_4$

   $C_2H_6 + O = C_2H_5 + OH$

   $C_2H_6 + H = C_2H_5 + H_2$

   $C_2H_6 + OH = C_2H_5 + H_2O$

2. $C_2H_5 + M = C_2H_4 + H + M$

   $C_2H_5 + O_2 = C_2H_4 + HO_2$

This scheme is a part of a mechanism involving the following mechanism :

$C_2H_6 \rightarrow C_2H_5 \rightarrow C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2 \rightarrow HCCO \rightarrow CO \rightarrow CO_2$ according to radical recombination.

Conclusion

New experimental results were obtained for the kinetic of oxidation of $CO/CO_2/CH_4$ mixture in a Perfectly Stirred Reactor for wildland fire modeling purpose. The experimental system was classical and was already used for CH_4 oxidation so, this was a reliable device. The reactor operated at 1 atm and over the temperature range 773-1273 K. Probe sampling followed by off-line GC-TCD/FID analysis were used to measure the concentration profiles of the reactants, stable intermediates and the final products. It was a hard task to reproduce exactly the experimental data since we studied a gas mixture of $CO/CO_2/CH_4$ with CO as a reactant and a product. Moreover, in a spite of the precision of detailed mechanisms, the literature is very poor in studies concerning the oxidation of such mixtures (Lee et al., 2007). Full mechanisms were developed in order to study the oxidation of natural gas blend and methane (Dagaut and Nicolle, 2005) or LPG fuel blend (Dagaut and Hadj, 2003) with a very low content of CO_2 and CO. The present experiments were modeled using detailed chemical kinetic reaction mechanisms. We obtained an overall good agreement between the present data and the simulations with the PSR code from CHEMKIN II package. The molar fractions of the reactants and the products were satisfactorily represented by the simulations. Additionally, we recorded two intermediate C_2 species (C_2H_4 and C_2H_6) which can a play an important role in soot formation since they were produced during the consumption reactions of CO and CH_4. As a development, we intend to reduce a detailed mechanism (Gri-Mech or Jallais) taking into account the chemistry of C_2 species.

Nomenclature

τ residence time (s)
V reactor volume (cm^3)
D_t total inlet flow (cm^3 s^{-1})
D inlet flow (cm^3 s^{-1})
T reactor temperature (K)
T_0 ambient temperature (K)
X molar fraction
Y mass fraction
W molecular weight (Kg mol^{-1})
$\dot{\omega}$ molar rate of production (mol cm^{-3} s^{-1})
h specific enthalpy (KJ mol^{-1})
Q heat loss (KJ)
Y^* inlet mass fraction
h^* inlet enthalpy.(KJ mol^{-1})
ρ mass density (Kg cm^{-3})
$\dot{m}$ mass flow rate (Kg s^{-1})

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