A reduced virtual chemistry model for soot prediction in hydrocarbon-air flames

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1 Introduction

Pollutant emission is nowadays a high priority issue for combustion applications. To reduce production of soot particles from combustion of hydrocarbon fuels it is necessary to understand its behavior. However, due to the complexity of chemical and physical phenomena governing the formation and evolution of soot particles, performing numerical simulations in realistic configurations may result in very high computational cost, and even higher in case of turbulent reactive flow, the most common scenario in practical configurations. Yet, Large Eddy Simulation (LES) tools are available to reduce the latter constraint, but closure modeling issues have to be accounted for.

The most recurrent exercise to achieve challenging numerical simulations is to reduce the combustion chemistry. A novel reduced chemistry approach, named virtual chemistry, has recently been developed to predict pollutants formation [1, 2]. The methodology consists in designing a reduced reaction mechanism from scratch, instead of simplifying a detailed mechanism. The reduced mechanism includes virtual species and virtual reactions whose thermodynamics and chemical properties are optimized using a genetic algorithm to capture user-specified target flames quantities. Chemical rate constants are also optimized to fit a given set of constraints such as the temperature profile, the heat release and the pollutants formation.

The present work aims at extending this technique to predict soot formation. This is done in two successive steps: (I) by first focusing on the analysis of soot precursors, $i.e.$ Polycyclic Aromatic Hydrocarbons (PAHs); and (II) by focusing on the soot itself. Here, soot virtual mechanisms are obtained by targeting a database including 1-D freely-propagating premixed flames.

In a first part, soot formation modeling in combustion is introduced, followed by the methodology of virtual chemistry construction. Then, a virtual main mechanism for ethylene-air combustion is developed, based on virtual chemistry approach. Furthermore, soot formation sub-models (I) and (II) are constructed. The proposed virtual mechanisms are evaluated on 1-D freely-propagating laminar premixed flames.

2   Numerical modeling of PAH and soot formation

Soot production processes can be decomposed in very complex phenomena. Thus, a deep study in detailed modeling may be performed to well capture the soot formation and consumption.

The first stage of soot formation is the production of soot precursors. Some well-known models for PAH formation [3,4] explain soot formation from the very first aromatic elementary rings up to large PAHs. PAHs grow until they reach a characteristic size and are considered to be in an intermediate phase between gas and solid [5]. Collision of two of them could be assumed as soot inception [6]. There exist many models for soot particles production such as semi-empirical models [7, 8], kinetics models [9, 10], and sectional methods [13, 14], etc.

The present work will consider the detailed kinetics model proposed in [10] for soot formalism and extensively validated on several experimental data in many different systems [10–12]. Here, following their size distribution, soot particles can be gathered into classes of lumped pseudo-species called "BINs". Then, BINs are considered as gaseous chemical species and their evolutions are solved together with other chemical species of the detailed kinetics mechanism. This mechanism counts with 297 species and 16797 reactions (including 20 classes of BINs [10]). In practical 3-D turbulent configurations, simulating a sooting flame with such kinetics mechanism is unfeasible. This is why a reduced chemistry model is a good alternative. The following sections present the developed reduced virtual chemistry.

3   Methodology for virtual chemistry modeling

The philosophy of virtual chemistry is to predict certain properties requested by the user, based on user-defined flame configuration sets. The main flame characteristics to be retrieved could be for instance the flame temperature, the flame burning velocity and the formation of pollutants. Moreover, the target flames archetypes should be representative of those encountered in practical configurations.

Figure 1 shows the architecture of virtual chemistry optimization [2]. It is shown that virtual optimized mechanisms are built following two independent blocks. The first one is called main mechanism: it reproduces the global thermodynamics and transport properties and also intervenes in the flame interaction with the reactive flow through the species transport equations. The second module is a satellite sub-mechanism and is exclusively dedicated to predict production of selected pollutants; but contrarily to the main mechanism, there is no feedback to the main reactive flow equations [2].
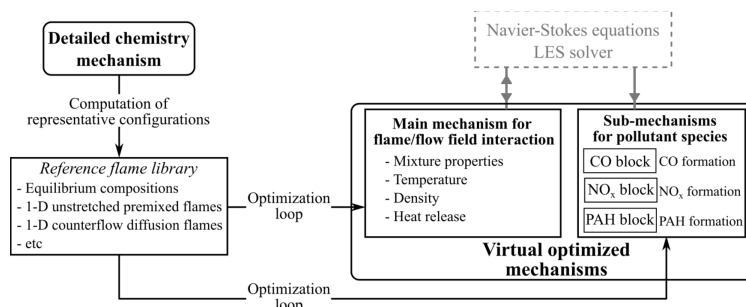

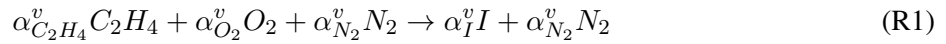Figure 1: Virtual optimized mechanism architecture

A reference flame database is first built by including equilibrium compositions and 1-D premixed and non-premixed flamelets solutions using detailed chemistry and multicomponent transport properties. Next, a

cost function is defined taking into account flame and flow global properties for the effect. Then, the virtual species thermodynamic properties and the virtual reactions kinetic rate parameters are optimized employing a genetic algorithm in order to minimize the cost function. The gas mixture viscosity is calculated using a power-law approximation. The mixture thermal conductivity is related to the Prandtl number, gas viscosity and heat capacity. Finally, the virtual species molecular diffusion term is expressed using a unity Lewis number (see Ref. [2] for more details). It should be noticed that, these assumptions do not limit the prediction of the laminar flame consumption speed, as far as targeted flame solutions include detailed multi-species diffusion effects. The optimization of transport coefficients of virtual species to capture preferential diffusion effects is out of scope in this work.

4   Results

Main virtual mechanism

The strategy presented in the previous section is applied to characterize ethylene-air flames. A 2-step mechanism with 8 species was chosen as the main reduced virtual mechanism, since good overall results were obtained in [1]:

$$\alpha^v_{C_2H_4}C_2H_4 + \alpha^v_{O_2}O_2 + \alpha^v_{N_2}N_2 \rightarrow \alpha^v_I I + \alpha^v_{N_2}N_2 \tag{R1}$$

$$I \rightarrow \sum_{k=1}^{N^v_P=4} \alpha^v_{P_k} P_k \tag{R2}$$

where I represents a virtual intermediate species and P_k virtual products. The detailed mechanism given by [10] is used to build a reference flamelet library including 26 1-D freely-propagating premixed flames and corresponding equilibrium calculations, with equivalence ratios at the inlet from lean to rich flammability limit ($\phi = [0.5; 3.0]$). All simulations were done using the REGATH package [15], developed in EM2C laboratory. Figure 2 shows the predictions for the laminar burning speed S_L of the optimized virtual mechanism, where the agreement is very good for the whole range of flammability. The zone of interest in this paper is towards the rich region, since soot production is promoted by the presence of high carbon content species.
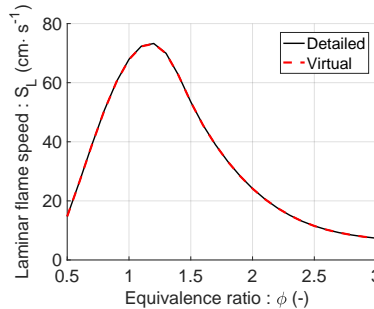

Figure 2: Laminar premixed ethylene-air flame speed as a function of equivalence ratio

Figure 3 shows the temperature spatial profiles for a given set of premixed ethylene-air flames from stoichiometry to very rich flames, more specifically, for $\phi = \{1.0, 1.5, 2.0, 2.5\}$. The virtual mechanism has a good capability to well capture the temperature, even though for very rich flames ($\phi > 2.4$) the temperature
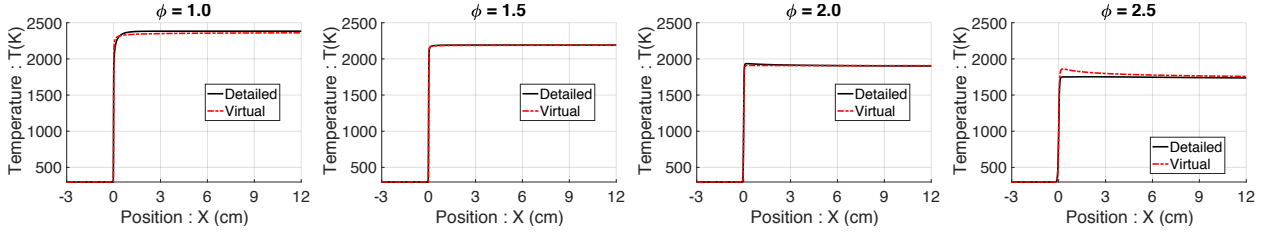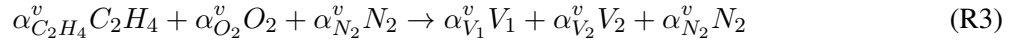
Figure 3: Temperature profiles for premixed ethylene-air flames

is moderately over-predicted. The global virtual mechanism can be considered satisfactory as a first model. However, a pyrolysis reaction model could be included in a future work as a palliative of heat production.

Virtual sub-mechanism, PAH approach

Now, the soot formation sub-models are presented. As mentioned in the introduction, the first approach (I) consists in predicting the PAHs (that could be eventually coupled to a soot equations solver). However, two methods are found in the literature; (Ia) predicting one selected PAH species representative of all PAHs in the detailed mechanism; or (Ib) an equivalent lumped PAH species made of the composition of several PAH species [16, 17]. In both cases, the structure of the virtual mechanism is proposed as:

$$\alpha^v_{C_2H_4}C_2H_4 + \alpha^v_{O_2}O_2 + \alpha^v_{N_2}N_2 \rightarrow \alpha^v_{V_1}V_1 + \alpha^v_{V_2}V_2 + \alpha^v_{N_2}N_2 \tag{R3}$$

$$C_2H_4 + V_1 \rightarrow C_2H_4 + \mathcal{PAH} \tag{R4}$$

$$\mathcal{PAH} + O_2 + V_1 \rightarrow O_2 + 2V_2 \tag{R5}$$

where V_1 and V_2 are two additional virtual species. For the case (Ia) we consider $\mathcal{PAH} = \{C_{10}H_8\}$; while for the case (Ib) we take $\mathcal{PAH} = \{C_6H_6, C_{10}H_8, C_{14}H_{10}, C_{16}H_{10}\}$, where the mass fraction of the lumped PAH is equal to the sum of the mass fractions of each individual PAH, $Y_{PAH} = \sum_{i=1}^4 Y_{PAH_i}$. The spatial evolutions of the PAH mass fraction using the developed virtual models (Ia) and (Ib) for a given set of equivalent ratios are shown in Figs. 4 and 5. Predictions are in good agreement with detailed chemistry in all cases presented. However, when PAH production starts to be important ($\phi = 2.0$ case (Ib)), a small under-estimation is obtained just after the peak, but it is recovered for higher equivalence ratios.
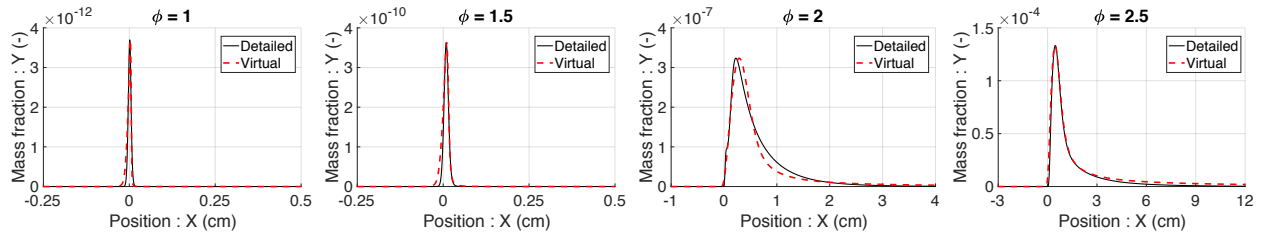
Figure 4: Case (Ia): Naphthalene ($C_{10}H_8$) mass fraction profiles for premixed ethylene-air flames

Virtual sub-mechanism, BIN approach

The second approach (II) is defined by considering the soot inside the gas phase kinetics model. The formalism and different modeling approaches are well discussed in [9, 10]. Hence, the total soot volume fraction f_v is obtained from the contribution of several BIN_i as $f_v = \sum_i f_{v,i}$; with:

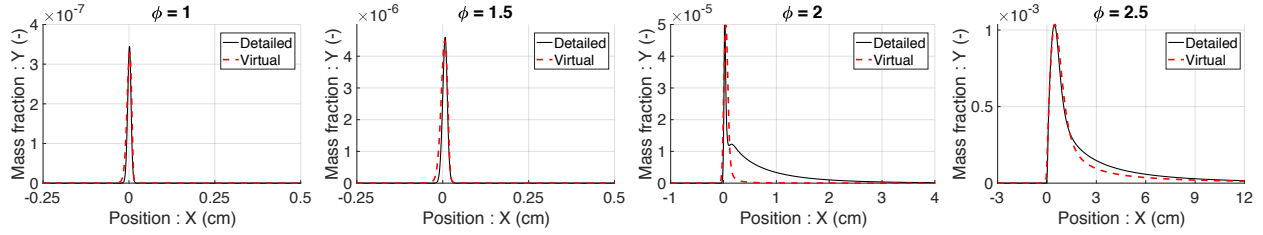$$f_{v,i} = \frac{\rho_{gas}Y_{BIN_i}}{\rho_{BIN_i}} \tag{1}$$

Figure 5: Case (Ib): Equivalent lumped PAH species mass fraction profiles for premixed ethylene-air flames

where ρ_{gas} and ρ_{BIN_i} are gas mixture and the BIN_i densities, respectively; and Y_{BIN_i} the mass fraction of BIN_i in the gas phase. Here, the total soot volume fraction f_v is given by the contribution of 16 BIN_i ($i = 5, \ldots, 20$) [10]:

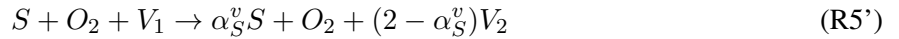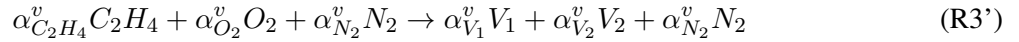$$f_v = \sum_{i=5}^{20} \frac{\rho_{gas} Y_{BIN_i}}{\rho_{BIN_i}} \tag{2}$$

Now we define be the equivalent lumped soot mass fraction Y_S as:

$$Y_S = \sum_{i=5}^{20} \frac{\rho_{BIN_{20}} Y_{BIN_i}}{\rho_{BIN_i}} \tag{3}$$

The soot volume fraction is then written as:

$$f_v = \frac{\rho_{gas}}{\rho_{BIN_{20}}} Y_S \tag{4}$$

This means that for the virtual mechanism, Y_S can be transported while the optimization target is the soot volume fraction f_v. Therefore, it could be possible to "extend" the PAH virtual mechanism as follows:

$$\alpha_{C_2H_4}^v C_2H_4 + \alpha_{O_2}^v O_2 + \alpha_{N_2}^v N_2 \to \alpha_{V_1}^v V_1 + \alpha_{V_2}^v V_2 + \alpha_{N_2}^v N_2 \tag{R3'}$$

$$C_2H_4 + V_1 \to C_2H_4 + S \tag{R4'}$$

$$S + O_2 + V_1 \to \alpha_S^v S + O_2 + (2 - \alpha_S^v) V_2 \tag{R5'}$$

where S stands for the equivalent lumped soot species (in gas phase). Figure 6 presents the soot volume fraction profiles obtained by the virtual sub-model against the detailed mechanism. As in the previous studies, the virtual model well reproduces the soot volume fraction. It should be noted that for $\phi < 1.8$ soot formation is negligible, so the optimization is not necessary under this equivalence ratio.
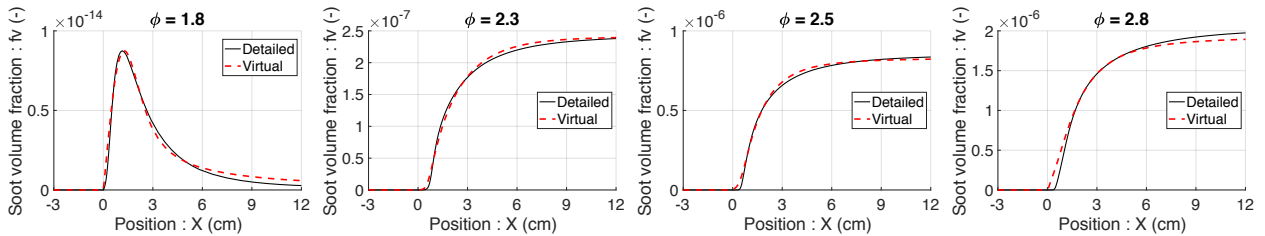

Figure 6: Soot volume fraction profiles for premixed ethylene-air flames

5 Conclusion

A new reduced chemistry model based on virtual chemistry optimization was built to predict the temperature profiles (heat release) and soot formation in premixed ethylene-air flames. Soot prediction was implemented in two different ways, one through the path of PAHs, and the other using a more straightforward technique that attacks directly the soot volume fraction. The resulting mechanisms were compared against detailed mechanism solutions, using 1-D freely-propagating premixed flames. Even though PAH and soot formation are very complex phenomena, it was possible to reduce from 297 species and 16797 reactions to a 11 species and 5 virtual reactions and obtain a good agreement in prediction. Nevertheless, further extension of the database will be done, considering 1-D counterflow diffusion flames. Also, flame problems of interest such as auto-ignition, cold flames or non-adiabatic conditions would reinforce the mechanism if they are included in the reference flame library. This would be very useful, especially when applying to turbulent flames using LES in realistic applications, and also to enhance the accuracy of the method.

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