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Accounting for complex chemistry in the simulations of future turbulent combustion systems

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Simulations of complex combustion phenomena such as flame ignition, stabilization, extinction and pollutant formation are very sensitive to detailed chemistry effects. The interactions between detailed chemistry and turbulence are even emphasized in emerging combustion chambers, which aim to limit the pollutant emission by maintaining a low flame temperature. Indeed, chemical reactions are less intense and more affected by mixing processes enhanced by turbulence. Flame quenching and combustion instabilities are also often encountered in such regimes.

The design of stable and low pollutant emissions combustion chambers requires a fine optimization of the combustor geometry. This step needs numerical tools, which are not sufficiently mature today for low-temperature flames, especially for pollutant prediction such as CO, NO_x or soot. Indeed, despite the rapid increase in computational power, performing turbulent simulations of industrial configurations including detailed chemical mechanisms will still remain out of reach for a long time.

This article proposes a review of commonly-used approaches to reduce chemistry with the objective of performing Large Eddy Simulations (LES) of industrial applications. Three main chemistry modeling routes are followed today to perform LES of turbulent flames: analytically reduced chemistry, tabulated chemistry and optimized chemistry. The suitability of these approaches to predict pollutant formations in multi-mode or diluted combustion regimes present in emerging combustion chambers is discussed.

I. Introduction

An efficient solution to reduce NO_x formation in combustors is to maintain a relatively low flame temperature. This can be mainly achieved through two different ways. The first solution is to operate in a lean premixed regime. Premixed flames are however difficult to handle in industrial systems. Indeed, for safety reasons, fuel and oxidizer are usually injected separately in the combustion chamber. Reactants are then mixed inside the chamber under the action of turbulent motions and molecular diffusion. In practice, mixing is never perfect revealing local heterogeneities of equivalence ratio and "stratified" propagating flames. A complex combustion regime, which strongly differs from ideal and widely studied premixed and non-premixed flames, is therefore observed, for example in gas turbines combustors [1]. A second way to reduce burnt gases temperature, is to mix reactants, prior to combustion, with chemically inert diluents such as cooled combustion products. Because of thermal ballast, the flame temperature decreases, limiting the NO_x production. Also, because of the less intense chemical activity, flame turbulence interactions differ from conventional systems and new combustion regimes are observed [2].

Numerical simulations of low-temperature combustors are very challenging. Combustion chemistry is indeed strongly sensitive to the operating conditions: a too low flame temperature may alter the combustion efficiency and may cause an increase in CO and CH_x emissions, whereas high flame temperatures promote the emission of NO_x. As chemical reactivity is reduced in low-temperature situations, mixing processes due to turbulence may lead to flame quenching and combustion instabilities. Whereas infinitely fast chemistry is a reasonable assumption for simulating conventional "high-temperature" flames [3], the computation of emerging low-temperature combustion chambers requires to consider complex chemistry effects.

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Detailed chemistry models consist on an accurate and comprehensive description of kinetic effects over a wide range of operating conditions (initial pressure, temperature and composition) and combustion regimes (auto-ignition, premixed, non-premixed, ...). For simple fuels such as hydrogen, only ten species interacting through about twenty reactions are required to describe complex kinetic effects [4]. For hydrocarbon fuels, as the molecular size of the fuel increases, the number of species and reactions dramatically increases. Mechanisms for light hydrocarbons involve hundreds of species [5, 6], whereas kinetic models for heavier fuels such as kerosene include about 300 species and few thousand reactions [7, 8]. Biofuels involve also complex chemical pathways as bio-diesel mechanisms include about 250 species and a thousand of elementary reactions [9]. When low temperature effects are included, the number of species can reach more than one thousand [10].

Oxidation of practical fuels proceeds through numerous intermediate and radical species. These species, rapidly consumed after their production, feature very small characteristic chemical times and reactive thicknesses in comparison with final products. This large scattering of time-scales is illustrated in Fig. 1 which shows estimates of the species chemical time-scale (τ_k) for a one-dimensional freely propagating laminar methane/air flame. The chemical time-scale of species k is evaluated with the simple definition proposed by Hong et al. [11]; $\tau_k = \max(\rho Y_k) / W_k \max(\dot{\omega}_k)$, where Y_k , W_k and $\dot{\omega}_k$ are the mass fraction, the molar mass and the molar reaction rate of species k , respectively. Intermediate species such as H, CH₃ or C₂H₂ present very fast chemical times of the order of 10⁻⁵ s while the chemical time associated with CO₂ and H₂O is one order magnitude higher. NO_x species formation is characterized by very slow chemical time of the order of the millisecond.

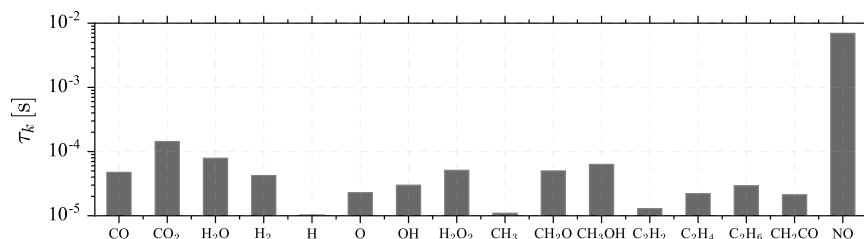


Fig. 1 Species chemical time-scale (τ_k) evaluated from a methane/air 1-D premixed flame at $\phi = 1.0$ and atmospheric conditions.

Despite the rapid increase in computational power, the use of detailed kinetic mechanisms for the simulation of practical configurations remains out of reach. First, each species involved in the detailed kinetic scheme requires the solving of an additional balance equation. Secondly, the numerical resolution of fast radical requires high grid-resolution as well as very small timesteps or implicit integration algorithms. Three major routes, namely analytical, tabulated and optimized chemistry have been proposed to describe kinetic effects in simulations of practical configurations at a reduced computational cost. The objective of this article is to establish a brief state-of-the-art of the kinetic reduction methods and to discuss their suitability for the simulation of emerging combustion technologies. The study is restricted to the Large Eddy Simulation (LES) context, which is well appropriate to capture unsteady interactions between chemistry and turbulence. The question of chemistry coupling with the LES flow solver, i.e. the modeling of flame turbulence interactions, will not be addressed in this article.

Sections II, III and IV are devoted to analytical, tabulated and optimized chemistry, respectively. In each section, the basis of the method is first introduced before discussing their practical application for the simulation of turbulent flame configurations. Section V proposes a comparison of a representative panel of reduction techniques on 1-D and 2-D laminar flames. Conclusions and perspectives are presented in section VI.

II. Direct chemistry reduction

A. From detailed to skeletal chemistry

Skeletal mechanisms constitute the first level of reduction of a detailed scheme and are built through a "chemistry driven reduction method" consisting in decreasing the number of reactions and species involved in a detailed kinetic scheme. According to [12], species can be classified into three classes: i) important species whose precise description is essential to represent combustion processes, ii) necessary species that are required for the prediction of important species and iii)

redundant species that can be removed without affecting the reproduction of combustion phenomena. Considering a set of target flame properties, a range of applicability and a precision accuracy, skeletal reduction techniques aims at identifying and removing the redundant species and/or reactions that are considered as unimportant for the prediction of the targets. Main strategies developed for that purpose are summarized below.

1. Sensitivity analysis methods

Strategies based on the measure of the interactions between species through Jacobian matrix analysis have been proposed to identify redundant species [13, 14]. Species strongly coupled to a chosen set of target species are conserved, while the other are removed from the skeletal mechanism. Difficulties arise in situations where the coupling between necessary and important species is not direct. A more complicated iterative procedure is therefore necessary to identify the necessary species [13, 15].

Sensitivity analysis are also used to identify redundant reactions. This method relies on the study of normalized sensitivity coefficients characterizing the effect of a reaction rate parameter change on the chemical system. A reaction is considered as unimportant if the perturbation of its rate has a small impact on the prediction of species concentrations. Either reaction rate or concentration sensitivity coefficients can be considered [16], however reaction rate sensitivity coefficients are preferred as they can be expressed analytically from reaction rate expression. Sensitivity coefficients contain high quality information on the chemical system. However, when the size of the detailed scheme increases, the derivation of meaningful information from the large number of matrices elements becomes a difficult task. To extract the most information from the sensitivity analysis, Vajda et al. [17] suggested to analyze the eigenvalues of the sensitivity matrix. This method, called Principal Component Analysis (PCA), identifies the more important and strongly coupled reactions as those featuring the largest eigenvalues and the largest eigenvector elements respectively. Example of PCA applications include the reduction of H₂/air [18], CH₄/air [19] and n-decane/air mechanisms [15].

2. Directed Relation Graph approaches

Lu and Law [20] introduced an original method based on Directed Relation Graph (DRG). In this approach, the degree of coupling between species is mapped to a Directed Relation Graph so as to identify the dependency relation between species. In this graph, nodes represent species, and directed edges illustrate the direct influence of one species to another. Through a linear graph search, necessary species are identified as species strongly coupled to target species or its dependent set of species, while species presenting a weak coupling with important ones are detected as redundant. Contrarily to sensitivity analysis based methods, DRG does not require the resolution of additional specific differential equation. Construction of the graph mainly consists in analyzing a reference database composed by a selection of detailed chemistry solutions representative of the targeted combustion problems and operating conditions.

Although the interest of the DRG approach has been demonstrated for the reduction of various detailed mechanisms [20, 21], several limitations exist. First, as equal importance is given to all species, some chemical compounds are kept in the mechanism even if they have a low influence on the target flame properties. To remedy this problem, Pepiot and Pitsch [22] extended the DRG with Error Propagation (DRGEP), where the error is damped as it propagates along the graph. A second problem of the original DRG method concerns the treatment of systems featuring fast dynamics (QSS species or PEA reactions). Alternative definitions of the direct interaction coefficients based on different normalizing coefficients were therefore introduced [23, 24]. Finally, group-based interaction coefficients accounting for the effect of removing species on the target quantities were proposed [24]. The DRG method along with its improved versions is now widely used for its efficiency, low cost and relatively easy implementation [25–28].

3. Optimization-based skeletal reduction

Elimination of redundant species and reactions can also be performed through optimization-based techniques. These strategies aim at identifying the minimal set of species and their associated reactions that best reproduce the target flame quantities. Edwards et al. [29] first used genetic algorithms (GA) to derive reduced model with controlled error on quantities of interest. Fixing the number of species in the reduced mechanism N_s^{red} , Elliott et al. [30] identified through a binary encoded GA the $N_s^{\text{d}} - N_s^{\text{red}}$ redundant species and in a second stage originally suggested to optimize the reaction rate parameters to fit a set of experimental data. More recently, Sikalo et al. [31] suggested to include the computational

time associated to the integration of the chemical system in the minimization problem. With such an approach one may expect to obtain an optimal kinetic scheme involving a minimal number of species featuring a reduced chemical stiffness.

B. From skeletal to analytic chemistry

1. General concept

Analytically-reduced mechanisms are derived through a chemistry-driven reduction approach aiming at i) decreasing the number of transported species and ii) lessening the stiffness of the chemical system. The key ingredient of the reduction method is to decouple the fast species and reactions from the controlling slow ones. Two main strategies are reported in the literature to remove short chemical time-scales. The first one called, Partial-Equilibrium Approximation (PEA), assumes that some very fast reversible reactions, featuring high nearly balanced forward and backward reaction rates, are in partial-equilibrium. In this condition, algebraic relations between reactant and product concentrations are obtained. The second approach referred to as Quasi-Steady State Approximation (QSSA) assumes that some fast species, featuring very low concentration and net production rate, are in an equilibrium state. This supposition allows to shift these fast species, also called Quasi-Steady State (QSS) species, to an algebraic equations sub-system. According to [32] and [33], a species k may be considered as QSS, if its production rate is rapidly balanced by its destruction rate, leading to low species concentration and negligible net production rate. QSSA is in practice preferred to PEA as it allows a higher degree of reduction [34].

2. Selection of QSS species

The automatic identification of QSS species relies on the study of species production rates, time-scale analysis and optimization algorithms.

Considering QSS species characteristics, some criteria based on the comparison of production and destruction rates have been proposed [15, 35, 36]. Very simple to use, these methods feature several drawbacks [37]. Indeed, though consistent with the definition of a QSS species, the criteria based on species production rates do not guarantee that the stiffness of the mechanism is reduced. Moreover, these simple criteria do not account for the sensibility of the targeted quantities to the error induced by assuming a species in QSS.

Time-scale analysis is in practice preferred for QSS species identification. The Computational Singular Perturbation (CSP), first introduced by Lam [38], exploits the eigenvalue analysis of the Jacobian matrix to decouple slow and fast subspaces. Species featuring small chemical time-scales are considered as QSS, while species with large time-scales are considered as slow and are transported in the system. As the Jacobian matrix is time dependent, the evaluation and diagonalization of the Jacobian matrix is complex and CPU demanding. To overcome these drawbacks some refinement procedures have been developed [39, 40], but the CSP strategy remains costly. An alternative method called Level Of Importance (LOI) combining lifetime and species sensitivity has been proposed by Løvås et al. [41]. This method simpler and less expensive than CSP approach has been successfully used for the derivation of numerous detailed kinetic schemes [42, 43].

Due to the difficulties related to QSS species identification, Montgomery et al. [37] alternatively used GA to optimally detect the species that can be viewed as QSS. As previously described for skeletal reduction, this brute force approach seeks the set of QSS species that minimizes the error between the reduced and the detailed mechanism regarding the capture of selected flame properties on a defined range of operating conditions. This method may be efficient but is also computationally expensive as it requires to solve the system of differential equations for each reduced scheme considered.

C. Application to hydrocarbon fuels

Table 1 shows four consecutive applications of skeletal and analytical reduction methods to detailed mechanisms. Different fuels and techniques have been used, leading to variable reduction efficiencies. For each case, the final number of species involved in the skeletal mechanism is too high for the simulation of practical configurations. In addition, radical species featuring low characteristic time and small reactive thickness are kept in the reduced mechanism and require small integration time and high spatial resolution. Number of species and stiffness of the reactions rates are

significantly reduced by analytical reduction methods.

To automate the generation of precise and highly reduced analytic schemes, various multi-stage reduction tools were proposed in the literature. Among them we can mention the YARC tool, developed by Pepiot [26], and based on DRGEP and LOI method. Another recent contribution combines; i) identification of chemical trajectories accessed in the target configuration, ii) the application of classical skeletal and analytical reduction methods as well as iii) the optimization of reaction rate parameters to derive Optimized Reduced Chemistry (ORCh) [28].

Authors	Fuel	Detailed mechanism	Reduction method	Skeletal mechanism	QSS species identification	Analytical mechanism
Lu and Law [40]	Methane	53 species 325 reactions	DRG DRGASA	36 species 222 reactions	CSP	21 species* 222 reactions
Luche et al. [44]	Kerosene	225 species 3493 reactions	Atomic flux analysis and PCA	134 species 1220 reactions	Lepage [15] criterion	94 species* 1220 reactions
Pepiot [26]	Iso-octane	850 species 7212 reactions	DRGEP	195 species 802 reactions	LOI	100 species* 802 reactions
Jaravel [45]	Dodecane	137 species 1222 reactions	DRGEP	47 species 452 reactions	LOI	27 species* 452 reactions

Table 1 Example of skeletal and analytical mechanisms for selected hydrocarbon/air mixtures. Different reduction methods have been combined. Species* refer to the resulting transported species whereas species in quasi-state are excluded.

Provided that QSS species are properly identified, the application of QSS approximation does not affect much the predictive capabilities of the initial skeletal kinetic mechanism. However, as the efficiency of the reduction is mainly dependent on the targets (variables of interest and canonical combustion problems) and required precision, it is difficult to control it without compromising the predictive capabilities of the analytical scheme. If heavy hydrocarbon molecules such as soot precursors are targeted, more chemical paths and species will be required, increasing the CPU costs. Additionally, derivation of analytic kinetic schemes describing the combustion of complex and heavy fuels such as alternative fuels may result in high dimensionality mechanisms.

D. Suitability for turbulent simulation of industrial combustors

Approaches derived to couple reduced chemistry formalism with a turbulent flow solver in an LES context are either based on geometrical, statistical or mixing theories [46]. Statistical approaches, that include transported Filtered Density Functions (FDF) [47], Conditional Moment Closure (CMC) [48] or Multiple Mapping Conditioning (MMC) [49] are well adapted to model SGS mixing-chemistry interactions that govern turbulent non-premixed flames. These methods have been successfully used to simulate turbulent configurations such as auto-igniting jet flames [50, 51] or spray flames [52, 53]. The statistical resolution requires however a significant computational cost, which prevents an integration in a daily design process of industrial applications. Geometrical approaches [54], designed to capture the flame front propagation, are well adapted to premixed or stratified combustion regime. Among them, the Thickened Flame model for LES [55] enables a basic but robust coupling of a reduced chemical scheme with a LES flow solver without altering the CPU cost. This strategy is currently followed by the CERFACS group to include analytical mechanisms in the simulation of realistic two phase aeronautical combustors [27, 43, 56] and sooting flames [57].

III. Tabulated chemistry

A. General concept

Tabulated chemistry aims at expressing the thermochemical variables in a reduced chemical state space prior to a

CFD computation. The set of species mass fractions involved in detailed mechanisms is replaced by a reduced set of coordinates $(\psi_1, \psi_2, \dots, \psi_n)$, where n is the number of dimensions of the thermochemical database. Tabulated chemistry is efficient in comparison with detailed chemistry if $n \ll N_s$, where N_s is the number of species in the original detailed mechanism. This method relies on the observation that the chemical trajectories accessed during the combustion process are confined to a sub-space of low dimension n called manifold. Such manifold does not have an analytical expression but is defined in a discrete form through a chemical look-up table evaluated with detailed chemistry, explaining the terminology *tabulated chemistry*.

A pioneering mathematical technique for chemistry tabulation is the ILDM (Intrinsic Low-Dimensional manifold) method, introduced by Maas and Pope [58, 59]. This is based on a direct identification of the dynamic behavior of the nonlinear response of the chemical system. An attractor subspace is determined by examining the eigenvalues and eigenvectors of the system of equations and by neglecting and cutting-off fast time-scales smaller than a given time limit. Depending on the cut-off time-scale, one, two or more coordinates of this state space (equivalent to chemistry parameters) are sufficient to accurately reproduce the kinetic properties of the full reactive system. This attractor subspace constitutes the *manifold* and the number of its coordinates corresponds to the minimum number of scalars that need to be transported to describe the full reactive system.

An alternative is to include physical hypothesis during the chemical database design. This assumption is the foundation of flamelet models which assume that a turbulent flame front can be decomposed in a collection of 1-D flame elements [54]. This strategy, developed for example by Peters [60] and Bradley *et al.* [61] for turbulent non-premixed and premixed flames respectively, is effective and well adapted for complex geometry reactors. Key issues of tabulated chemistry techniques are the identification of the flamelet archetype retained for tabulation purpose and the choice of look-up table coordinates. These issues are summarized below. For more details regarding the generation of chemical tables, the reader may refer to recent reviews from Fiorina *et al.* [62] and Oijen *et al.* [63].

B. Selection of the tabulated flamelet archetype

The combustion element archetype retained to build-up the chemical look-up table must be representative of targeted turbulent flame configurations. The strategy followed depends therefore on the turbulent flame regime investigated. A few examples are given below.

For premixed and weakly stratified configurations, Gicquel *et al.* [64] and Van Oijen *et al.* [65] suggested to build the manifold from 1-D laminar premixed flames, computed under detailed chemistry assumptions. Chemical trajectories are generally mapped as a function of two coordinates: the progress variable Y_c describing the progress of the reaction and the mixture fraction Z characterizing the fresh gas equivalence ratio. Accounting for heat losses phenomena requires a third coordinate, the enthalpy h , which can be covered by adding burner stabilized flames in the chemical look-up table [66]. As discussed by Fiorina *et al.* [67], predictive capabilities are impressive as soon as the turbulent flame regime remains close the canonical premixed flamelet regime.

The chemical structure of turbulent non-premixed flames is well approximated by chemical look-up tables made of steady counterflow diffusion flames. In the original Peters flamelet model [60], initially developed for RANS simulations, the chemical look-up table is parametrized by the mixture fraction Z and by the scalar dissipation rate of the mixture fraction χ_z . In order to tackle unsteady phenomena, Pierce and Moin [68] suggested to tabulate both stable and unstable branches of the S-curve [69] and to replace the scalar dissipation rate coordinate by a progress variable. This approach is called Flame-Progress Variable (FPV) model.

If auto-ignition is an important physical phenomenon occurring in the target turbulent flame, then auto-igniting flame elements must be included in the manifold. Chemical table designed for internal combustion engines are in practice build-up from homogeneous reactors [70, 71].

The use of single flamelet archetype is efficient to capture the chemical structure of well-identified flames (such as purely premixed or diffusion flames) but introduces bias in the prediction of the chemical structure of more complex situation such as stratified flames [67]. Both premixed and non-premixed flamelet ingredients must be combined in the same look-up table. A solution is to solve the projection of the full set of mass conservation species balance equations into a restricted subset of the composition space [72, 73] or to use 1-D partially-premixed flamelets to generate a chemical look-up table [74].

C. Suitability for turbulent simulation of industrial combustors

Among the geometrical approaches initially written under global step chemistry assumptions, thickened [55] and filtered flamelet models [75, 76] have been formulated in a tabulated chemistry framework, leading to FGM/FPI TFLES [77, 78] or Filtered Tabulated Chemistry for LES (F-TACLES) [79], respectively. The recent comparative and collaborative study conducted between 5 research groups [80] confirms the good ability of premixed-based flamelet methods to capture the flame front propagation speed and the stabilization mechanism of weakly-stratified flames. Despite lower predictive capabilities than transported FDF methods, presumed FDF approaches are in practice a good compromise to account for sub-grid scale mixing phenomena in non-premixed turbulent flame LES [81]. As chemical trajectories in the composition space are *a priori* known, tabulated chemistry is remarkably well adapted to presumed FDF.

By offering a high level of chemistry modeling for a low CPU cost, tabulated chemistry is used for a long time to perform LES of practical turbulent combustion systems. For instance, F-TACLES has been used to compute an helicopter combustion chamber [82] or the ignition sequences of an annular combustor under gaseous [83] and two-phase flow conditions [84]. FPV approach combined with presumed FDF has been successfully applied to predict NO_x formation in a Pratt & Whitney aircraft engine combustor [85].

Despite this high popularity, tabulated chemistry suffers however from several intrinsic drawbacks, such as the coordinates identification difficulties [86, 87] or storage issues especially on massively parallel machines [88, 89]. But the major counterpart of the high efficiency of tabulated chemistry is a limited range of validity. Indeed, tabulated chemistry methods are designed to reproduce turbulent flame configurations whose structure is close to the flame elements used to build-up the chemical table. When complex configurations are targeted, different flame archetypes must be merged in the same look-up table. It complicates the flamelet library generation and also systematically increases the number of coordinates required to track all degrees of freedom covered by the multiple physical phenomena targeted.

A first example is the simulation of multi-regime turbulent flame, where both premixed and non-premixed flame structures are observed. As discussed before, the generation of hybrid chemical database is possible [72–74] but highly complex. In addition, it raises strong theoretical difficulties to close the balance equations for the coordinates in a turbulent formalism [62].

Another issue is the simultaneous treatment of complex phenomena such as: heat losses, multiple fuel inlets or dilution by hot gases. In the case of low-temperature diluted combustion, Lamouroux et al. [90] claim that at least five coordinates are required to simulate the impact of fresh gas dilution by recirculating products. Good agreements have been observed between the numerical prediction and measurements in a non-adiabatic diluted combustor, but the generation of this chemical look-up table is very sophisticated, requiring the computation of 100,000 flamelets. Another limitation comes from the assumption that the inner structure of the turbulent flame front is close to a laminar flame. This hypothesis, valid for some conventional combustors, becomes very questionable for low temperature flames. Indeed, when the chemical activities slow down, turbulent eddies penetrate the flame front and affect the chemical trajectories. Extending tabulated chemistry to capture such combustion regimes is a difficult task and will necessarily lead to the addition of dedicated coordinates.

IV. Optimized chemistry

A. Global and semi-global chemistry

Empirical reduction aims at generating small mechanisms (from 1 to 4 steps in general), whose kinetic rate parameters are optimized to capture global flame properties such as for example the burning velocity, the burnt gas temperature or auto-ignition delay times [91–94]. Pioneering work is due to Westbrook and Dryer [91] who proposed one and two global reaction steps with Arrhenius kinetics by tuning the pre-exponential factor, the activation energy and the reaction order. More recently, Fernandez-Tarrazo et al. [94] investigated the applicability of one-step irreversible Arrhenius kinetics with unity reaction orders for the description of partially premixed methane-air combustion. For more complex hydrocarbons such as kerosene, a simple technique has been proposed to derive two-step schemes in an automatic fashion [95]. In this work, the pre-exponential constants of the two reactions are tabulated as a function of the local equivalence ratio to fit the laminar burning velocity over a wide range of fresh gases equivalence ratio. Moreover, the

fuel and oxidizer exponents are adjusted to reproduce dependence of premixed laminar burning velocity with mean pressure.

An original approach based on genetic optimization was introduced by Polifke et al. [96]. Instead of selecting the chemical rate parameters by hand or by kinetic intuition, an evolutionary optimization algorithm is used to automatically identify the best set of unknown kinetic coefficients.

Moreover, contrarily to classical global reduction methods that target global flame properties, the optimization procedure aims at capturing species production or heat release rate. This strategy provides a satisfactory description of flame temperature and major species, but intermediate species (CO and H₂) profiles do not match the reference solution. In addition, the optimization is performed for a unique equivalence ratio limiting the overall representativity of the procedure. Following the work of [96], methods have been developed to automatically optimize the chemical rate parameters of semi-global schemes [93, 97, 98]. An example of application is provided in [98] to predict selective non-catalytic reduction DeNO_x process. Global mechanisms efficiently capture global flame properties such as flame propagation. However, such simplified mechanisms cannot describe the chemical structure of the flame itself, and pollutant formation.

B. Virtual chemistry

An original chemistry description approach aiming at capturing selected flame properties of interest on a range of representative flame configurations was recently proposed [99]. The originality of the method consists in: i) building-up a reduced chemical mechanism from scratch instead of reducing a detailed scheme, and ii) using virtual species and reactions. Chemical rate constants are calibrated by a genetic algorithm to fit a given set of constraints such as the temperature profiles, the heat release but also the pollutant formation or even the influence of active species generated by a plasma. Although, the idea of optimizing chemical mechanism by genetic algorithm is not new [96], Cailler et al. [99] demonstrated that the efficiency of the procedure is strongly limited by the use of real elementary reactions and real species with fixed thermo-chemical properties. The novel idea is to use instead virtual species, whose thermo-chemical properties (heat capacity, standard enthalpy of formation or molecular weights) are also optimized. Moreover, the reactions between virtual species composing the virtual mechanism do not represent real chemical reactions. They compose a mathematical architecture designed to retrieve a set of user-defined constraints (temperature, pollutant formation, heat release, *etc.*).

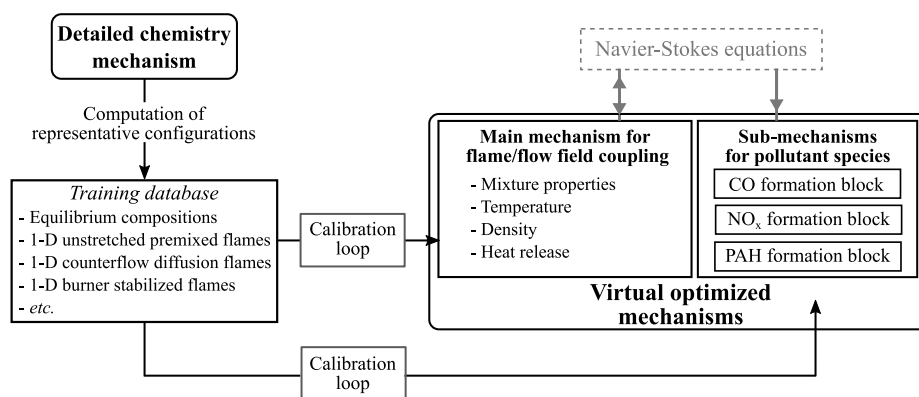


Fig. 2 Virtual mechanisms architecture.

As shown in Fig. 2, the virtual mechanism chemistry architecture is decomposed into independent virtual sub-schemes dedicated to the capture of a given flame property. The main mechanism, modeling the mixture-averaged physical properties as well as the heat released by combustion, retro-acts with the Navier-Stokes solver through species and energy conservation equations. Other satellite sub-schemes are independent and devoted to the prediction of a given pollutant such as CO [100], NO_x, HC_x or soot precursors. As the formation of pollutant involves multiple chemical pathways interacting over a high variability of time scales (see Fig. 1), this solution is more efficient and robust than

including all species in a unique and larger virtual mechanism.

As for tabulated chemistry, the range of validity of the method is controlled by the set of target flames retained to optimize the chemical parameters. For instance, heat losses are well accounted for as soon as non-adiabatic flame elements are included in the learning database [101]. The CO formation is well predicted in multi-flame regimes if both premixed and non-premixed elements are targeted during the optimization step. But, unlike to tabulated chemistry, there is no need to define and to transport *ad-hoc* coordinates.

C. Suitability for turbulent simulation of industrial combustors

Being cost-effective, low-order kinetic schemes have been widely used for LES of practical application. As for reduced and tabulated chemistry, TFLES approach is very popular for coupling low-order empirical schemes to LES. For instance, a one-step irreversible optimized chemical scheme for JP10 combustion has been used to perform the first LES of an ignition sequence in a gas turbine engine [102]. Also combined with TFLES, the two-step BFER mechanism [95] enables the simulation of Flame Transfer Function of a lean swirl-stabilized gas turbine burner [103]. Usually not addressed within then global step chemistry framework, the virtual chemistry concept permit recently the prediction of the CO formation in a gaseous premixed aeronautical combustion chamber [101].

V. Illustrations of chemistry reduction methods in laminar flame configurations

This section aims to compare, on simple 1-D and 2-D laminar flame configurations, the efficiency of the three methods. Despite reduced chemistry intends to compute turbulent flames, canonical laminar flame configurations are of primary interest for comparing reduced chemistry methods on a fair basis. Indeed, laminar solutions are not altered by turbulence and turbulent combustion modeling hypothesis. In addition, a direct evaluation of each method performances is possible as detailed chemistry solutions, which serve as a reference, are affordable on 1-D or 2-D configurations. In order to constitute a representative panel, all laminar configurations have been simulated with a detailed chemical mechanism (GRI 3.0 [104]), an analytical chemical scheme (LU19 [40]), a premixed flamelet tabulated chemistry (FPI [64]) and two optimized mechanisms (BFER [95] and virtual chemistry [100]).

1-D premixed freely propagating and non-premixed counterflow flames have been simulated with the REGATH solver [69]. Spatial evolution of the temperature and CO mass fraction is shown in Fig. 3 for both flamelet archetypes and for all reduced chemistry methods. The CO mass fraction is particularly difficult to predict as its production and consumption are very sensible to the flame regime [67, 74]. Comparison between the detailed chemistry solutions and the profiles obtained with the LU19 scheme shows that the analytically-reduced mechanism reproduces very well the flame temperature and minor species for both premixed and non-premixed flames. As previously discussed, the tabulated-based model is very predictive when applied on the flamelet archetype similar to the one used for table generation. However when used in a diffusion counterflow flame, the FPI premixed-tabulated approach fails to capture minor species formation such as CO. The semi-global mechanism, built to retrieve global flame properties, is not designed to reproduce the local flame structure and CO prediction. Finally, the virtual mechanism predicts reasonably well the temperature and the CO in both premixed and non-premixed flame configurations. This result is consistent as the virtual scheme has been optimized to fit a reference database made of both premixed and non-premixed flamelet archetypes. However, if for instance the non-premixed flamelets were removed from the learning database, then the virtual scheme would fail to tackle the counterflow diffusion flame profiles [100].

Kinetic model predictive capabilities are also assessed on the 2-D partially partially-premixed laminar burner. Details of the configuration and operating conditions are given in [66, 105]. All simulations have been performed with the low-Mach number, unstructured finite volume flow YALES2 solver [106]. Figure 4 (top) displays the temperature field predicted by detailed, analytic, semi-global, tabulated and virtual chemical models. The direct comparison of the temperature 2-D fields demonstrates a qualitative good agreement between all chemistry modeling approaches. All reduced chemical models provide a good reproduction of the temperature levels. A small difference is however noticeable for the global BFER semi-global scheme that over-predicts the temperature in the post-flame zone. A comparison of CO mass fraction fields is provided in Fig. 4 (bottom). As expected from 1-D premixed laminar

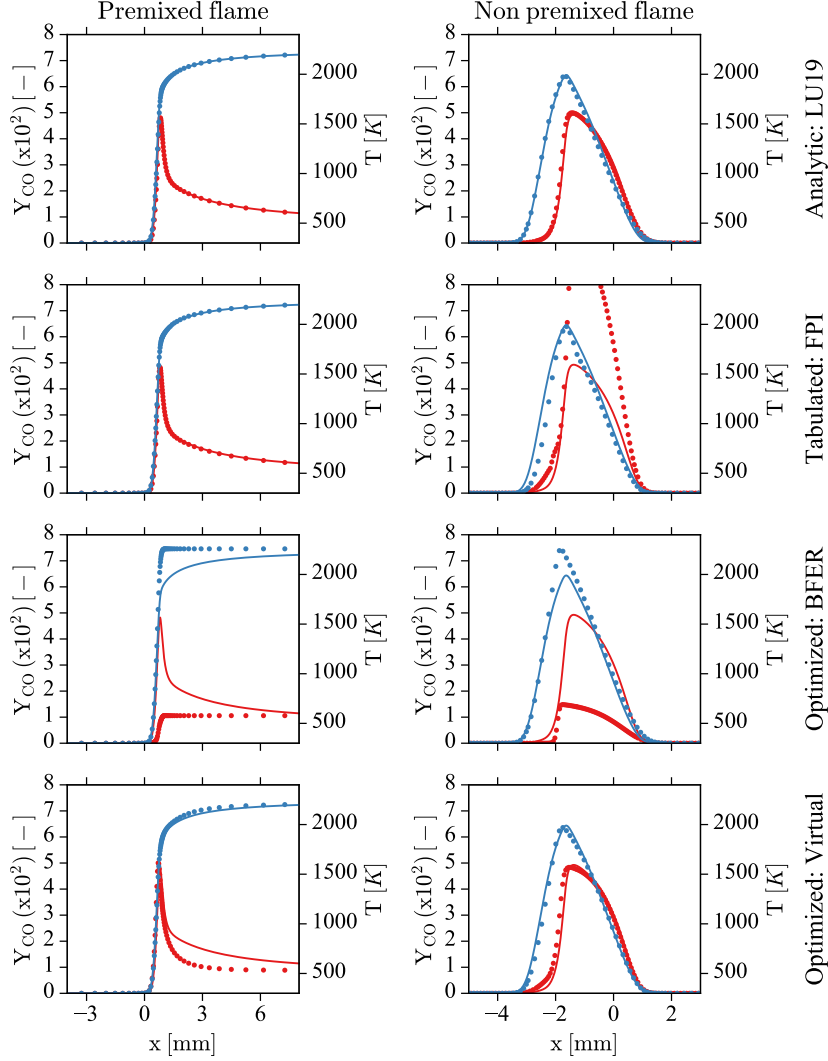


Fig. 3 Spatial evolution of the temperature and CO mass fraction in premixed ($\phi=1.0$) and counterflow diffusion ($a=105 \text{ s}^{-1}$) methane/air flames at fresh gas temperature $T_f = 300 \text{ K}$ and pressure $P = 1 \text{ atm}$. Legend: GRI3.0 detailed chemistry (symbols), reduced chemistry models (line).

comparisons, the semi-global scheme largely under-predicts the CO concentration in the flame region. The satellite sub-scheme dedicated to CO formation matches well the detailed solution. Except a slight overestimation of the CO peak concentration the premixed-based tabulated approach reproduces well the CO field. Eventually, analytically-reduced chemistry is in excellent agreement with the complex GRI3.0 mechanism.

VI. Conclusion

Each one of the three main routes for chemistry reductions illustrated in Fig. 5 has his own advantages drawbacks. Tabulated chemistry has been for a long time the only affordable way to include detailed chemistry effect in practical simulations of reactive systems. It is extremely efficient for conventional combustion systems where the flame regime is identified. However, its extension toward low-temperature and multi-mode combustors requires more coordinates. The introduction of new control variables requires additional modeling assumptions that increase the complexity of the methodology and raise questions with regard to its relevance for the simulations of industrial devices. Thanks to

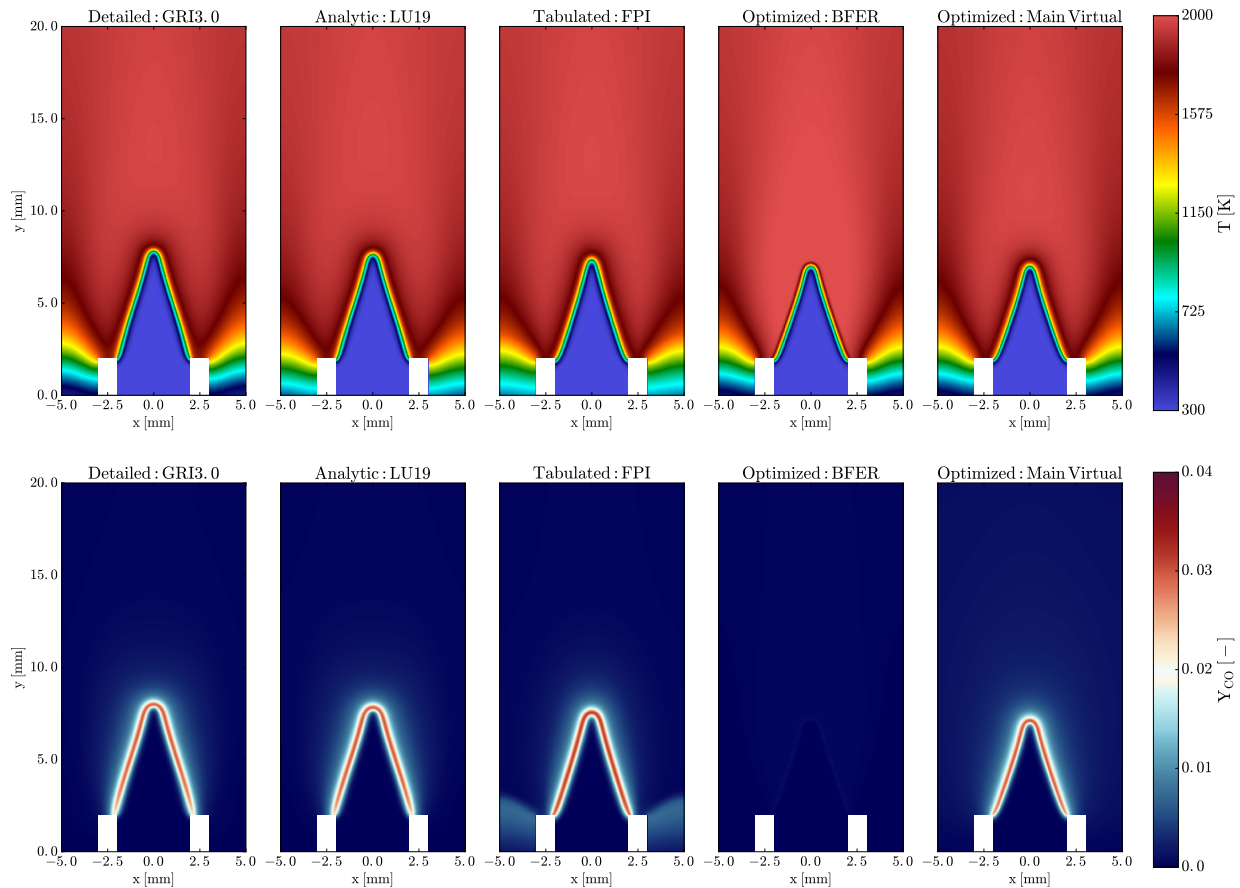


Fig. 4 Temperature and CO mass fraction fields in the laminar partially premixed burner.

the recent progress in computational resources and in the automatization of chemistry reduction techniques, analytical schemes are recently used for the simulation of practical combustion. It enables, in a very accurate way, the numerical investigation of complex combustion phenomena sensitive to detailed chemistry. However, because of the high number of species and the numerical stiffness of the system, the systematic use of analytical scheme in a daily design process of combustion chamber remains too expensive. Optimized schemes have been for a long time being limited to the prediction of global flame properties (heat release, propagation speed, etc.). With the introduction of the virtual chemistry, this route is interesting to follow for predicting pollutant formation. Although today less accurate than analytical chemistry, virtual chemistry may be a good compromise to conduct engineering parametric studies.

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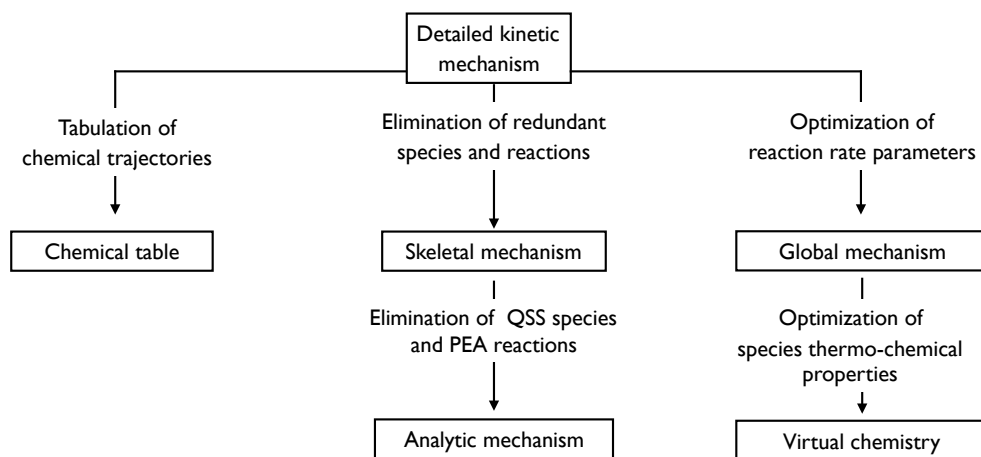


Fig. 5 The three major reduced chemistry routes.

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