2
Literature Review

In this chapter is presented a literature review concerning the existing techniques to reduce the size of a reaction mechanism and efficiently solve models for turbulent chemically reactive flows with detailed combustion thermochemistry. This review follows a historical perspective on the development of reduction techniques.

2.1
Introduction to the Reduction Approaches

According to Ren (2006) [76], among the existing methodologies to reduce the complexity of turbulent chemically reactive flows models with detailed combustion thermochemistry, three types of approaches have been shown to be particularly fruitful: (i) the reduction to skeletal mechanisms; (ii) dimension reduction; and (iii) storage and retrieval techniques. Combinations of these techniques are also reported in the literature.

In order to illustrate the possible interplay between the different techniques, Figure 2.1 presents a diagram with three sets, each one corresponding to reduction technique approach, namely: *reduction to skeletal mechanism* (S/M); *dimension reduction* (D/R); and *storage/retrieval* (S/R). The regions where there is an intersection between the sets correspond to the hybrid approaches. In the sense of this diagram the ideal approach would be the one which could combine the advantages of the three techniques without the associated shortcomings. The following sections review these approaches from this point of view.

2.2
Reduction to Skeleton Mechanisms

The reduction of a detailed reaction mechanism, through a process which involves eliminating species and reactions that have a negligible influence on the combustion process results in the so-called skeletal mechanism. Due to the nature of the reduction process, such mechanisms are simpler than the original mechanism (Law, 2006) [45].

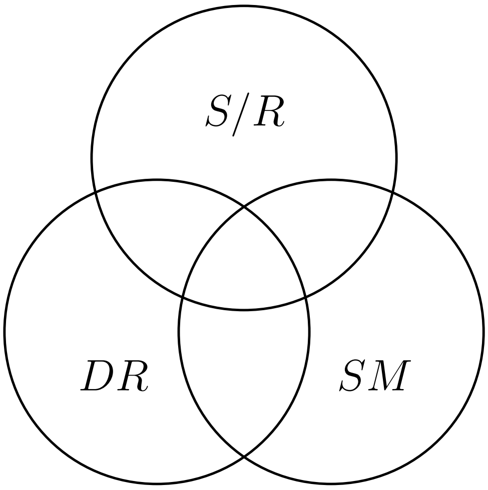

Figure 2.1: Illustration of the classification of the different approaches. S/M: reduction to skeletal mechanism; D/R: dimension reduction; S/R: storage and retrieval.

Skeletal mechanisms need to have quantified the resulting accuracy with respect to the original one. Such a measure could be given by comparing the calculated responses of system properties, such as mass fractions, temperature, etc., obtained from the skeletal mechanism to those issued from the detailed reaction mechanism.

2.2.1
Sensitivity Analysis

The procedure of *sensitivity analysis* (SA) is similar to that adopted in stability analysis, which is used in the nonlinear dynamical systems theory to interpret the bifurcation phenomena and to forecast the existence of oscillations. The basic underlying principle of sensitivity analysis is to determine the local behavior of the system subject to small disturbances in the phase space, i.e., to quantify how the system responds to variations on each of the controlling rate constants at a given set of conditions. The sensitivity coefficient, defined for a particular rate constant, is a measure of the importance for the system behavior of a particular reaction. A small — or even null — sensitivity to a perturbation is indicative that a specific reaction is redundant and could be removed from the reaction mechanism without affecting the overall accuracy (Griffiths, 1995) [25]. A complete overview on the sensitivity analysis technique is provided by Rabitz et al. (1983) [74].

This technique is a local approach — note that a global approach is also possible — with a rigorous mathematical foundation that allows eliminating all the reactions that exhibit low sensitivity to a given set of conditions. Although considerable reductions of reaction mechanisms can be achieved, it is possible that the reduced reaction mechanism generated in this way still has too many chemical species, making an associated numerical solution expensive, from the point of view of computational costs (Griffiths, 1995) [25].

Müller et al. (1992) [61] use the sensitivity analysis technique to reduce a detailed reaction mechanism for heptane with 1011 elementary reactions and 171 species to 79 elementary reactions and 40 species, which represents a reduction of approximately 77% of the number of species involved. As a consequence, the number of balance equations required to be solved in order to predict the system evolution is decreased accordingly.

2.2.2
Proper Orthogonal Decomposition

The technique of *proper orthogonal decomposition* (POD), also known as Karhunen-Loève decomposition or principal components analysis, involves a mathematical procedure which allows the transformation of a number of possibly correlated variables into a smaller number of uncorrelated variables, called principal components. This technique is an important complement to the sensitivity analysis in the context of skeleton mechanisms, since the last one is known to yield vast amounts of data, from which it may be difficult to determine the relative importance in complex systems (Jolliffe, 2002) [33].

The POD provides an absolute measure of how significant is part of the reaction mechanism. Thus, this analysis may be used to provide an objective criterion for selecting a reduced reaction mechanism. The analysis is based on the spectral decomposition (eigenvalues and eigenvectors) of the auto-correlation tensor, obtained from measurements, theoretical considerations or computer simulations. In the context of reaction mechanisms reduction, this tensor is represented, in an appropriate basis, by a data matrix in which the columns are the sensitivity coefficients. Its eigenvectors represent sets of reactions that are coupled and the relative magnitude of the vector components give relative contributions of it. The eigenvector components also contain information about the connections between the reactions. Thus, it is possible to determine which groups of reactions could be eliminated by establishing limits for the significant eigenvalue and eigenvector components (Griffiths, 1995) [25].

2.2.3
Directed Relation Graph

The technique called *directed relation graph* (DRG) proposed by Lu & Law (2005) [52] is an automatic general procedure to generate skeletal mechanisms from detailed thermochemistry. It consists on creating a relation graph where each node corresponds to a chemical species from the detailed reaction mechanism and the valued-orientated-edges express the dependence of a specific species in the rate of production of other species. Given an initial set of significant chemical species, the graph is recursively transversed until it is obtained a set with the minimum number of species that correctly describe the rate of production of the initial species. Then, the elementary reactions of the detailed reaction mechanism which do not include any of the species of the minimum set are eliminated. The skeletal mechanism is obtained by the union of the species in the minium set and the remaining reactions.

The DRG method has two great advantages, when compared with the sensitivity analysis: (i) easy implementation; (ii) it is more efficient from the computational point of view, since the time of processing is linearly proportional to the number of species in the reaction mechanism (Lu & Law, 2005) [52].

Lu & Law (2005) [52] test the DRG technique to the reduction of a detailed reaction mechanism for ethylene oxidation with 70 species and 463 elementary reactions. DRG allows to obtain a skeletal mechanism with 33 species and 205 elementary reactions. This skeletal mechanism shows good agreement when compared to the detailed one for the calculations of a laminar flame speed and nonpremixed counterflow ignition for a wide range of pressure, temperature and equivalence ratio.

Lu & Law (2006a) [53] improved the capability of the DRG technique applying a new algorithm for the graph generation which is linear in the number of reactions. The new version of the DRG technique is applied to a n-heptane detailed reaction mechanism with 561 species and an iso-octane detailed reaction mechanism with 857 species, obtaining skeletal mechanisms with 188 and 233 species, respectively.

Pepiot-Desjardins & Pitsch (2008) [66] propose a variant of the DRG technique that uses a different strategy to quantify the interdependence of the chemical species. This new strategy allows one to generate more accurately the minimum sets of species. A test case is performed generating a skeletal mechanism for iso-octane with 195 species from a detailed one with 850 species.

2.3
Dimension Reduction

The dimension reduction approach is based on the assumption that a high-dimensional dynamical system can be parametrized in a low-dimensional subset of the original phase space. Some of the techniques that are part of this category consist on mathematical oriented approaches, mostly based on the theory of dynamical systems. Another possibility involves a large physical insight, which explores the restrictions imposed, for instance, by the second principle of thermodynamics in order to simplify the description of the system. A description of the dimension reduction techniques found in the literature that are relevant to the present study is given below.

2.3.1
Reaction Lumping

One early reduction technique involves the order reduction by lumping of variables. This approach is based on the transformation of the reaction vector to a lower dimensional vector of lumped-species (Okino & Mavrovouniotis, 1998) [64].

The reactive systems which present a number of chemical species tending to infinity and the decaying of the species following the same reaction order allow one to treat the reacting mixture as a continuous distribution. The technique of reaction lumping applied to these systems — known as *continuum lumping* — combines all the reactants into a single lump and tracks its disappearance. This method has the advantage of demanding only a small set of experimental data to fit the parameters of the reduced reaction mechanism, since specific reactions and components concentrations do not need to be known. This last characteristic is also a weakness, when the technique is applied to problems that require information about concentrations or reaction types, since such information is not easily extracted from or inserted into the continuum lumping (Okino & Mavrovouniotis, 1998) [64].

The application of the reaction lumping technique to reactive system for what a reaction mechanism is known — called *discrete lumping* — creates lumped models from the set of equations that govern the evolution of the reactive system. This technique presents, as positive points, the reduction of the chemical species number and the possibility of estimating the error introduced. As drawback, the reduced reaction mechanism generated by the discrete lumping may still contain multiple time scales and the technique limitates the information that can be extracted about a specific chemical species within a certain reaction structure (Okino & Mavrovouniotis, 1998) [64].

The technique of reaction lumping is discussed in Chen (1987) [9] where its application for hydrogen/air, methane/air and methyl radical/air combustion is illustrated. In this work a computer program is developed to construct reduced reaction mechanisms from detailed reaction mechanisms containing a large number of chemical species and elementary reactions. Reduced reaction mechanisms for methane/air and methyl radical/air combustion are obtained, making use (or not) of the steady state assumption for the hydrogen atom. A reduced reaction mechanism for lean air combustion, without C_2 chain reactions, is also obtained, leading to the conclusion that these reactions do not change neither the number nor the stoichiometry of the global reactions in the reduced reaction mechanism for methane, but changes reaction rates for the C_2 chain. Additionally, that study shows that the assumption of steady state for hydrogen atom alters the reduced reaction mechanism into a different form, i.e., the number and the stoichiometry of the global reactions are changed as well as their reaction rates.

2.3.2
Quasi-Steady State Approximation

The technique of *quasi-steady state approximation* (QSSA) is perhaps the oldest one concerning the reduction of reaction mechanisms. This technique was first developed by Bodenstein & Lind (1907) [6] and Bodenstein & Lütkemeyer (1924) [7] in the framework of the process of formation of hydrogen bromide.

The general formulation of the QSSA, independent of particular features of the system considered, given a general treatment for the error introduced by the QSSA is developed by Frank-Kamenetskii (1940) [19], see also Turányi & Tóth (1992) [93] and Turányi et al. (1993) [92].

The main idea of the QSSA technique is described as follows. Some chemical reactions present the formation of highly reactive intermediate species. After an initial buildup in concentration, these intermediate components are formed as rapidly as they are consumed, so that the rate of formation and the rate of consumption equilibrate. Due to this equilibrium, the rate of reaction of these species are negligible and, therefore, these species can be assumed as being in steady state. The steady state hypothesis allows the replacement of an ordinary differential equation (ODE) by an algebraic equation in the system of equations that describes the dynamical behavior of the chemical reaction. The use of the steady state assumption for several species provides a considerable simplification on the system dynamics (Turányi et al., 1993) [92].

When the QSSA technique is employed, the species for which steady state is assumed are called minor species, whereas the others are the major species. Keck (1990) [34] questions whether entropy production is always nonnegative — as required by the thermodynamics second principle — when QSSA is employed. In his work, the thermodynamical system composed by the major and the minor species is considered, and an expression is given for the entropy production of the system composed by two terms, one for the entropy production of the major species and another for minor species. The term associated with the major species is always nonnegative (≥ 0) and the term related to the minor species can be positive or negative. Thus, it is not possible to ensure that entropy production is always nonnegative. However, Ren & Pope (2004) [77] argument that QSSA is employed only when information about the systems major species is of interest, thus selecting only the major species as thermodynamical system is more appropriate than considering the system composed by the major and minor species. Ren & Pope (2004) [77] show that, for a system composed only by the major species, the elements conservation and the nonnegative entropy production are both satisfied.

Variants of the QSSA are developed, for example, by Lu & Law (2006b) [54]. This work involves eliminating part of — or even all — the nonlinearities of the set of algebraic equations obtained by employing the QSSA, resulting in a near-linear — or even linear — system of equations. If the resulting system is not linear, then it is linearized. Such a procedure is justified on the physical argument that the quasi-steady state species generally occur in low concentrations, such that the probability of collision between two minor species is smaller than the probability of collision of the major species. The linear system obtained is, in general, sparse and it is solved using a technique based on graph theory, which takes advantage of the sparse structure of the linear system to speed-up its solution. The technique allows the generation of a 16 species reduced reaction mechanism for a ethylene/air mixture, departing from a detailed reaction mechanism characterized by 70 species. Accurate and efficient results are demonstrated for the simulation of auto-ignition (relative error less than 0.1%) and perfectly stirred reactors (relative error less than 0.01%).

Hughes et al. (2009) [31] combine the use of the QSSA with local sensitivity methods, via reaction lumping, and consider reaction mechanisms for n-heptane and cyclohexane. A detailed reaction mechanism with 358 species and 2411 reactions is used for the n-heptane; whereas the reaction mechanism for the cyclohexane involves 499 species and 2323 reactions. The obtained reduced reaction mechanism for n-heptane has 81 species and 452 reactions and yields an excellent reproduction of the temperatures evolution and prediction of the ignition delay time as a function of temperature, for a stoichiometric n-heptane/air mixtures at 13.5 bar. This reduced reaction mechanism leads to a computational cost which is less than 5% of that of the detailed reaction mechanism. The cyclohexane reduced reaction mechanism involves 26 species and 133 reactions, allowing a final computational cost that is 0.2% of the associated detailed reaction mechanism. The reduced reaction mechanisms also represents accurately the prediction of ignition delays. Both cases also exhibit an impressive speed-up of up to a factor of 500, when compared to the detailed reaction mechanisms, which are found to be proportional to square of the number of species.

2.3.3
Rate-Controlled Constrained Equilibrium

The *rate-controlled constrained equilibrium* (RRCE) technique proposed by Keck & Gillespie (1971) [35] assumes that the evolution of a complex system may be described, with an acceptable accuracy, by a relatively small number of reactions that mainly control the system evolution, the so-called rate-controlling reactions. These reactions establish constrains on the allowed states of the system that are slowly changing. This technique also assumes that the system relaxes to the associated constrained equilibrium state due to the existence of fast reactions. This relaxation occurs in time scales which are fast, when compared to that characteristic of the constraints evolution. Considering the above hypothesis, a thermochemical system in nonequilibrium state tends to relax to its final equilibrium state through a sequence of rate-controlled constrained-equilibrium states, each of which may be determined by maximizing the entropy of the system subject to the instantaneous values of the constraints. An extensive review of the RCCE technique is developed by Keck (1990) [34].

Some advantages that the RCCE technique offers are: (i) a small number of equations is required in order to predict the state of a complex system; (ii) the rate constants are necessary only to the calculation of the faster, rate-controlling, reactions; (iii) the balance principles are automatically satisfied, since they appear explicitly as constraints in the technique formulation; (iv) nonnegative entropy is guaranteed, as is the correct stable state of equilibrium; (v) the accuracy of the technique can be increased with the addition of new constraints, until the exact solution is obtained when the number of independent constraints equals the system's number of degrees of freedom; (vi) the technique is extensible, i.e., different constraints may be included stemming from steady state reactions, body forces, selection rules and diffusion phenomena, for instance; and (vii) the technique is applicable to complex systems and its accuracy increases with the system size. Two obvious disadvantages are: (i) the need of a manual identification of the constraints; and (ii) the requirement for efficient algorithms for integration of the rate of reactions and to compute the conjugate Lagrange multipliers (Keck, 1990) [34].

This technique has been applied to high temperature reactions, for example, the calculation of the nitric oxide and carbon monoxide formation in internal combustion engines or industrial burners. Morr & Heywood (1974) [60] perform a 14 species and 2 constrains RCCE calculation to predict carbon monoxide concentration in a steady state cylindrical burner and compare the results with measured values. The first constrain is the total moles of gas, controlled by a set of four dissociation and recombination reactions. The second one is the carbon monoxide number of moles, controlled by five carbon monoxide oxidation reactions. The results obtained for carbon monoxide concentration using both constraints are slightly lower than the measured values, but lie within the combined uncertainty of the measurements and of the rate constants used. Keck & Gillespie (1971) [35] perform a 14 species and 2 constrains calculation to predict nitric oxide formation and removal in an internal combustion engine. The first constrain is on the fixed nitrogen controlled by a set of five chemical reactions. The second constrain considered is the total number of moles in the system. The results obtained with the 14 species and 2 constrains RCCE calculation are compared to those results obtained from a steady state solution. In the early engine cycle — when nitric oxide is being removed — the nitric oxide concentration obtained from the steady state solution is shown to be lower than nitric oxide concentration obtained from RCCE. The opposite behavior is observed for other cycles.

2.3.4
Computational Singular Perturbation

The *computational singular perturbation* (CSP) technique proposed by Lam (1985) [42] and discussed in detail in the works of Lam (1993) [43] and Lam & Goussis (1994) [44], is a general procedure for analysis and reduction of thermochemical systems. This method is a formal mathematical approach that does not only simplify reaction mechanisms but also reduces the set of governing equations of the system. The CSP technique allows one to automatically decouple the system time scales in fast and slow modes. The fast modes are those time scales which are less than a desired time resolution, the others are called slow or active modes. It follows the elimination of the exhausted and dormant modes. The exhausted modes are the time scales that decay due to the competition between consumption and generation of species and are not significant for the behavior of the system after certain period. The dormant modes have no influence on the system dynamics, since they are much slower than the active modes. The technique iteratively identifies a basis of vectors that allows one to decouple the time scales in fast and slow modes.

The main advantages of the CSP technique are: (i) that important reactions can be identified only using data from the reduced system, in opposition to SA, which needs information from the full system; (ii) no *a priori* knowledge about the system dynamics is required; (iii) the method is applicable to problems with multiple time scales. A disadvantage associated to the CSP technique is the impossibility of determining *a priori* the size of the regions which the technique is applicable (Okino & Mavrovouniotis, 1998) [64].

Goussis & Lam (1992) [23] develop a study of the homogeneous oxidation of methanol/air at constant pressure using CSP. A numerical experiment is performed using a fuel-lean (equivalence ratio = 0.6) mixture at a pressure of 1 atm and temperature of 1027 K. A reaction mechanism with 30 species and 173 reactions is used. The reduced system obtained includes 16 species and produces results nearly identical to those of the full reaction mechanism for the hydrogen atom and carbon monoxide mass fractions with error smaller than 1%.

2.3.5
Intrinsic Low-Dimensional Manifold

Maas & Pope (1992a) [58] develop a general procedure for reducing reaction mechanisms called intrinsic low-dimensional manifold (ILDM). This geometrically-based technique is issued from the dynamical systems theory. Based on a local spectral analysis (eigenvalues) of the linearized system of governing equations, the fast time scales of the chemically reacting system are identified. Then, assuming that these fast time scales, which are associated with relaxation processes in chemical reaction, proceed infinitely fast, i.e., that these processes are in local equilibrium, the space state may be globally simplified. This simplification results on a reduced number of parameters, or progress variables, which allows a considerable reduction in the number of differential equations that have to be solved.

In contrast to other techniques, such as the QSSA, no assumption is required about reactions in partial equilibrium or species in steady state. The ILDM is formed upon specification of the desired reduced system dimension only. The simplification procedure is automatic, once it is given the state properties as functions of the reduced parameters, i.e., the coordinates that parametrize the system in the low dimensional manifold. This characteristic is valuable when high dimensional systems are of interest. After the reduction of the system dimension, the reduced system properties are stored in a multi-dimensional table to be recovered *a posteriori* via multi-linear interpolation (Griffiths, 1995) [25].

Maas & Pope (1992a) [58] apply the ILDM technique to the reduction of a reaction mechanism with 13 species and 67 reactions to describe the combustion of carbon monoxide-hydrogen/air in a spatially homogeneous, closed, adiabatic, isobaric reactor. Both one-dimensional and a two-dimensional manifolds have been generated which correctly represent the major and the minor species in the nonequilibrium evolution of the chemical system.

Maas & Pope (1992b) [57] develop a procedure to apply the ILDM technique to reactive systems where molecular transport is present. The study of a perfect stirred reactor model demonstrates that the reduced reaction mechanisms obtained by this technique provide a good description of the detailed evolution in situations where the time scale of the physical process is reasonably slower when compared to the fast, decoupled, time scales. This study also shows that when the time scales difference become too small, the ILDM technique demands a higher dimensional manifold in order to correctly predict the reactive system behavior.

The storage of the reduced information in a multi-dimensional table requires a large amount of memory. In order to overcome this difficult Niemann et al. (1997) [63] propose an ILDM approach which uses orthogonal polynomials to interpolate the stored reduced information obtained from a tabulation step which computes the system properties as function of the progress variables in a corse grid among the system phase space. This procedure allows the decreasing of the ILDM mesh resolution, and thus the storage requirements. For instance, storage is reduced by a factor of 200 when a stoichiometric hydrogen/oxygen system is considered.

König & Maas (2005) [40] introduce a mathematical approach to the calculation of ILDMs sensitivities with respect to kinetic data. This method is applied to a $CO/H_2/O_2/N_2$-system, which consists of 13 species that react in 67 elementary reactions. The temperature of the unburnt gases is 298 K, and the syngas mixture is stoichiometric with a proportion (in volume) for CO:H_2:N_2 equal to 4:3:3. The validity of the technique is demonstrated by a comparison between results obtained via ILDM calculations of a perturbed and an unperturbed reaction mechanism. The study also shows that the behavior of reduced reaction mechanism obtained via this ILDM approach is qualitatively comparable to the behavior of the corresponding detailed reaction mechanism.

König & Maas (2009) [41] develop an technique to generate on demand ILDMs in generalized coordinates extensible to the domain of slow chemistry using a hierarchical concept that progressively increases the original manifold dimension. Also, in this version of the ILDM technique the tabulation of the system properties as function of the reduced variables is made on demand, i.e., only the actually accessed part of the phase space is tabulated allowing to reduce the amount of memory and computational time spent during the ILDM calculations. A syngas/air one-dimensional calculation for a free, adiabatic, premixed, flame in a laminar flow field is used to validate the technique. A reaction mechanism with 13 species and 67 reactions describes the chemical kinetics of this system. The new technique presents an 82% of reduction in memory storage and 22% of reduction in computational time when compared to the classical ILDM approach.

2.3.6
Proper Orthogonal Decomposition

When used as a technique of dimension reduction, POD is used to determine spatial structures that are time applicants called coherent structures. These coherent structures allow the construction of a reduced model in which the dynamical behavior is representative of the original system, since they preserve most of the original system information (Holmes et al., 1998) [30]

The POD procedure can be summarized as follows. Consider a process that varies in time and space and that, after an initial transient, approaches a steady state. Sample discrete data from this process are obtained by following the evolution in time of a set of initial conditions. Then an auto-correlation tensor is computed, where its components are covariances between these discrete data, considering the time average as the ensemble average. The eigenvectors of this auto-correlation tensor are the coherent structures described above and form the basis that maximizes the expectation of information from the original system (Holmes et al., 1998) [30].

The reduced reaction mechanism is obtained by projecting the full reaction mechanism into the subspace spanned by the eigenvectors that correspond to the largest eigenvalues. The nonlinear behavior of the original model is preserved, once the nonlinearity is invariant by projection into a linear of affine space. Also, the method demands only standard matrix operations, which is attractive from the computational point of view (Pinnau, 2008) [68].

Graham & Kevrekidis (1996) [24] propose an alternate approach for the POD technique, in which the sample discrete data is obtained from the short time integration of a large set of initial conditions. This approach is used to study the dynamics of a reaction-diffusion system, using the short time integration of 1000 initial conditions to construct the auto-correlation tensor. The reduced model obtained from the new procedure is shown to contain information about the global dynamics that is not contained in the reduced model obtained from the standard POD approach.

Singer & Green (2009) [86] combine an adaptive strategy for the POD method with an operator splitting technique to study the evolution of a reaction-diffusion system. The technique is applied to an one-dimensional laminar premixed methane/air flame using GRI mechanism version 3.0 [89], with 53 species and 325 reactions. The results of the simulation show that temperature and species mass fractions are predicted with an error smaller than 0.25% when compared with the direct integration of the full reaction mechanism. A speed-up factor of 3.5 is reported, which is related to the fewer evaluations of the source term required to compute the Jacobian matrices.

Berkooz et al. (1993) [4] and Holems (1998) [30] provide a comprehensive review of the POD technique, including the associated mathematical properties. Rathinam & Petzold (2004) [75] discuss other theoretical considerations related to POD technique such as: (i) errors involved in solving a nonlinear ODE initial values problem with POD; (ii) the study of small perturbations in the ensemble of data from which POD reduced model is constructed; (iii) an analysis of computational complexity of solving ODE initial value problem; and (iv) the study of savings obtained by the use of POD technique.

2.3.7
Invariant Constrained Equilibrium Edge Pre-image Curve

The *invariant constrained equilibrium edge pre-image curve* (ICE-PIC) is an automatic dimension reduction technique developed by Ren et al. (2006) [80]. The fundamental idea of ICE-PIC method is the identification of a low-dimensional manifold which is invariant, continuous and piecewise smooth. The reactive system is parametrized in this low-dimensional manifold and when the full composition of the chemical species needs to be locally recovered from the reduced composition in the low-dimensional manifold, the pre-image curve technique proposed by Ren & Pope (2005) [78] is used. The term “locally recovered” means that, for the ICE-PIC technique to reconstruct the species properties from the reduced composition, it is not necessary to reconstruct the whole manifold. The ICE-PIC technique is tested in the simulation of a steady, isobaric, adiabatic, one-dimensional premixed laminar flame of a stoichiometric hydrogen/air mixture with an unburnt temperature of 300 K and pressure of 1 atm. The mixture thermochemistry is described by reaction mechanism of Li et al. (2004) [48] (9 species and 21 reactions). The simulations show that compared to the results obtained with `PREMIX` code by Kee et al. (1985) [36], the ICE-PIC accurately reconstructs the species composition and system temperature (normalized errors smaller than 1.5×10^{-3}). Compared to QSSA and RRCE, ICE-PIC technique yields the smaller maximum error. Considering the ILDM method, it is possible to obtain maximum error smaller than that obtained with ICE-PIC, but ILDM is a technique in which the low-dimensional manifold does not exist for all ranges of temperatures.

Ren et al. (2007) [81] use the ICE-PIC technique to study the autoignition of a homogeneous, adiabatic, isobaric, stoichiometric methane/air mixture at 1500 K and 1 atm, described by GRI mechanism version 1.2 [89] (32 species and 175 reactions). The results of ICE-PIC are shown to be at least 2 orders of magnitude more accurate than QSSA and RCCE techniques. This work also investigates the application of a variant of the ICE-PIC method for an inhomogeneous system: a steady, one-dimensional, adiabatic, isobaric, laminar flame of stoichiometric methane/air mixture also described by GRI 1.2 [89], with an unburnt temperature of 298 K and pressure of 1 atm. The results show that the inclusion of transport coupling in ICE-PIC formulation can reduce the error associated to the reduction of dimension by a factor of a hundred.

The capability of the ICE-PIC technique to treat a combustion system that exhibits a complex dynamics is tested and demonstrated by Ren & Pope (2007a) [79]. In this work, the ICE-PIC technique is applied to the oxidation of a carbon monoxide/hydrogen mixture in a continuously stirred tank reactor at low pressure, the same system described by Brad et al. (2007) [8]. A reaction mechanism with 11 species and 33 reactions is used in the modelling of the reactive mixture. The simulation results show that a reduced description using a low-dimensional manifold of dimension five is able to quantitatively predict the complex dynamics of the continuously stirred tank reactor. This study also shows that the ICE-PIC method is not sensitive to changes in the coordinates (species) that parametrize the reduced system, which is an advantage when compared with QSSA and RCCE methods.

2.4
Storage/Retrieval

The storage/retrieval approach stores the simulation results for *a posteriori* use (retrieval). This approach presents some variants for data storage, such as multi-dimensional tables, binary search trees, etc., but the retrieval is done basically via multi-dimensional interpolation or extrapolation.

2.4.1
Look-Up Table

A *look-up table* (LUT) is a data structure often used to replace an ODE integration with an array indexing operation. The savings, in terms of processing time, can be significant, since retrieving a value from memory is often faster than solving a differential equation. This technique presents a pre-processing step, where direct integration of the governing equations is performed, and the results are tabulated. In the simplest approach, the region of interest in the domain is covered with a regular mesh and the equations are solved for each point of this mesh. Then, *a posteriori* calculations are performed via multi-linear interpolation from tabulated values.

The major advantages of the LUT technique are: (i) the possibility of controlling the interpolation error by refining the mesh; and (ii) the speed-up in the time spent to solve the governing equations. However, the technique has limitations, mainly due to the large amount of memory required to store the table.

Chen et al. (1989 [11] and 1995 [10]) present applications of the LUT technique. The first work uses the LUT technique to efficiently solve the equations corresponding to the probability density function (PDF) modelling of a turbulent nonpremixed methane flame, whereas the second deals with the simulation of a hydrogen flame and prediction of NO_x emissions.

Ribert et al. (2006) [82] propose a technique, called self-similarity flame tabulation, to tabulate turbulent combustion properties using a detailed reaction mechanism. In this technique the species reaction rates and mass fractions are tabulated as function of a limited set of coordinates, such as progress variable, mixture fraction, enthalpy, etc., obtained from the simulations of a one-dimensional laminar premixed flames. The species mass fractions and reaction rates present a self-similar behavior with the progress variable, which is explored in the tabulation technique in order to reduce the size of the tabulation table. This technique has been applied, for a fixed value of initial pressure and temperature, to several adiabatic one-dimensional laminar premixed methane/air flames, for different values of equivalence ratio.

The simulations use the Qin et al. (2000) [73] reaction mechanism, with 34 species and 463 reactions, and the `PREMIX` code by Kee et al. (1985) [36]. The look-up table stores reduced values of species mass fraction and reaction rates as function of the sum of the CO and CO_2 mass fractions and the corresponding scaling relations, which are functions of the mixture equivalence ratio. The simulations using the new technique are verified by comparisons with numerical results obtained using a detailed reaction mechanism, and presented good agreement with the values obtained from a detailed chemistry for several simple hydrocarbon fuels (methane, propane and ethane) and various values of equivalence ratio.

Fiorina et al. (2009) [17] proposed a tabulation strategy that also explores the self-similar properties of tabulated species mean reaction rates in order to decrease the demand for storage memory in the look-up table. A successful application of this technique is reported to a Reynolds Averaged Navier-Stokes (RANS) simulation of a nonpremixed turbulent methane/air flame, the *Sandia Flame D*, experimentally addressed by Barlow & Frank (1998) [2]. A reduction of three orders of magnitude in look-up tables storage memory is obtained with excellent agreement between computations using detailed reaction mechanism and reduced look-up table.

2.4.2
Repro-Modelling

Turányi (1994) [94] proposes the *repro-modelling* (RM) technique, which, for a detailed reaction mechanism, extracts functional relationships between the system properties (species concentration, temperature, etc.) and the species reaction rates. The extracted information is stored in a multivariate polynomial of high order and may be accumulated from a large number of simulations for a specific range of conditions. This data is then used to evaluate the governing equations, a procedure which is faster than to simulate using the detailed reaction mechanism.

Turányi (1994) [94] applies this technique to simulate the ignition of wet carbon monoxide in air. The repro-modelling obtained a speed-up of 24,000 and 11,700, respectively, using two or three variables in comparison to the solution using detailed thermochemistry, given by the `SENKIN` code (Lutz et al., 1987) [56].

2.4.3
Piece-Wise Reusable Implementation of Solution Mapping

The *piece-wise reusable implementation of solution mapping* (PRISM) technique proposed by Tonse et al. (1999) [91], consists in partitioning the chemical phase space into adjacent hypercubes. As the reaction trajectory evolves in composition space, polynomials are calculated for a given hypercube when the trajectory first enters it. From a set of polynomials it is possible to obtain the time evolution of any composition within the hypercube. Then, the hypercube and polynomial information are stored in a particular data structure, which is a combination of a binary tree and a double-linked list, for being reused in future. As the calculations proceed, instead of solving differential equations, only algebraic polynomials evaluations are necessary to predict the system evolution.

The PRISM technique has been applied to three different hydrogen combustion simulations (Tonse et al., 1999) [91], using a reaction mechanism with 9 species and 26 reactions. The simulated cases are: (i) a zero-dimensional, stoichiometric, premixed hydrogen/air mixture with an initial temperature of 1200 K; (ii) a one-dimensional premixed laminar flame, in a 10 mm tube closed in one end and open in the other at atmospheric pressure, filled near the open end with burned gas, while the remaining is filled with stoichiometric hydrogen/air mixture at room temperature; (iii) a nonpremixed two-dimensional turbulent jet with coaxial hydrogen (21 m/s and 300 K) and air (1 m/s and 300 K) inflows. All the simulated cases present an excellent accuracy, the relative error is smaller than 0.2%, for temperature and species mass fraction, and the computational efficiency, compared to the direct integration of the governing equations is increased by a factor of 10.

Najm et al. (2005) [62] propose a novel implementation of the CSP technique combined with the PRISM technique, involving an adaptive tabulation of the basis vectors, which allows fast identification of the reduced chemical model at any point of the phase space. In the new technique, first, the CSP is used to reduce the dimension of the chemical phase space, then, the PRISM technique is applied in order to efficiently compute the system evolution. The key point is that first applying CSP allows the PRISM tabulation procedure to construct low dimensional hypercubes, since the dimension of the new chemical phase space is smaller than the original one. This technique is applied to a four-dimensional system of stiff ODE in order to assess its efficiency, showing a high level of accuracy, relative error less than 2%, and yielding a significant reduction in computational time.

2.4.4
Artificial Neural Network

An *artificial neural network* (ANN) is a computational model inspired by the structure of the brain, in order to provide features similar to human behavior, such as learning, association, generalization and abstraction. The ANN are composed of several processing elements (artificial neurons), highly interconnected, that perform simple operations and send the results to neighboring processors. Due to its structure, the neural networks are very effective in learning patterns from data nonlinear, incomplete, noisy and even composed of contradictory examples. Examples of typical applications are: pattern recognition, time series forecasting and classification, (Gurney, 1997) [26].

Christo et al. (1996) [12] introduce an integrated approach using ANN and joint PDF transport equation for the simulation of turbulent flames. A hydrogen/carbon dioxide turbulent jet diffusion flame is modelled using three step reduced reaction mechanism. The results show good agreement of flame and flow characteristics with those obtained by LUT or direct integration procedures. For small reaction mechanisms, the ANN method does not show significant gains in computational time and memory storage, when compared to LUT and direct integration techniques.

Blasco et al. (1999) [5] introduce an ANN approach which partitionates the computational domain and trains the neural network for each sub-domain. This method allows the increasing of solution accuracy. The method is tested in a methane/air system evolving according to a reduced reaction mechanism with 7 species and 4 reactions. The ANN approach presents a speed-up factor of 2750 times, when compared to the direct integration procedure, and demands 1000 times less memory for storage than the LUT technique. The method also presents an average error of 0.64%.

Ihme et al. (2009) [32] use an optimized ANN approach in the large eddy simulation of Dally et al. (1998) [15] bluff-body swirl-stabilized methane-hydrogen/air flame. The chemically reactive flow field is modelled using a flamelet/progress variable approach. The study shows that the accuracy of the optimized ANN in LES simulations is comparable to the accuracy of the refined structured tables, but with a smaller memory storage cost. Data retrieval from an ANN is shown to be more expensive, when compared to LUT techniques. The integrated approach LES/ANN presents good results when compared to experimental data for the mean and variance of the velocity components, mixture fraction, temperature, H_2O and CO_2 mass fractions. Small discrepancies on CO_2 profiles in the fuel-rich side of the flame are observed, possible due to CO_2 sensibility to changes in the progress variable.

2.4.5
In Situ Adaptive Tabulation

The methodology dubbed *in situ adaptive tabulation* (ISAT), proposed by Pope (1997) [70], consists in progressively creating (*in situ*) a binary search tree which stores in its leaves an initial composition, its time integral value and the corresponding jacobian matrix. A search is performed along this binary search tree whenever the integration of the governing equations is required and a tabulated solution is recovered. If the information recovered from the tree is satisfactory, in the sense that an error tolerance is such that the recovered solution lies inside an ellipsoid of accuracy, a linear extrapolation using the tabulated values issued to provide an adequate approximate solution. This approximate solution has a local error which is second order accurate in time, thus ensuring that the global error is of first order.

The ISAT technique presents an advantage, when compared to LUT techniques, in terms of memory savings. Since the tabulation is performed *in situ* only the compositions that effectively occur in the flow are tabulated, thus leading to large memory savings. This is a significative advantage when dealing with complex reaction mechanisms. Furthermore, the error control allows the usage of a conservative criterion for choosing an error tolerance. However, when a large reaction mechanism is involved and the frequency of additions in the binary search tree is high, the memory usage of the ISAT technique is significant. The major advantage of the ISAT technique, compared to the other storage/retrieval approaches, is the coupling flexibility, which allows ISAT to be used in parallel with practically all of the other methodologies presented herein.

Yang & Pope (1998b) [98] apply the ISAT technique for calculations in the first few principal directions of the composition space — the mixture properties at a given thermodynamical state that present more sensibility to variation on this state — for a premixed pairwise mixing stirred reactor. Two reaction mechanisms are used, a skeletal one (16 species and 40 reactions), for methane/air mixture combustion and the GRI mechanism version 2.11 [89] (49 species and 279 reactions), for natural gas combustion with air. The results show very good accuracy for species mass fraction in both cases, with tabulation error smaller than 4.0×10^{-4} when compared to the direct integration of the governing equations. This variant of ISAT only tabulates the accessed region of the composition space, which allows the ISAT technique to perform few additions and several recoveries in the binary search tree. Thus, the method presents an impressive speed-up factor of 1,655 for methane/air system, when compared to the direct integration of the skeletal mechanism.

Saxena & Pope (1998) [83] model a piloted jet diffusion flame of methane/air using an approach based on the joint PDF. This flame corresponds to the *Flame L* that has been characterized experimentally by Masri et al. (1988) [59]. The domain of calculation consists of a coflow burner, with a central jet of methane (300 K and 41 m/s) with radius equal to 3.6 mm and an outer annulus jet of air (300 K and 15 m/s) with radius equal to 9 mm. The ISAT technique is used to efficiently solve the governing equations for the skeletal mechanism which contains 16 species and 41 reactions. The obtained results of mixture fraction, temperature and species mass fraction are compared to other numerical studies using simpler reaction mechanisms. The results show a better qualitative agreement with the experimental data than other works.

Saxena & Pope (1999) [84] investigate performance, issues such as accuracy, efficiency and storage requirements, in the use of ISAT technique to numerical solve the joint PDF of velocity-frequency-composition in a turbulent chemically reactive flow. To examine the accuracy, the ISAT error control is analyzed in the simulation of a pairwise mixing stirred reactor with a skeletal methane/air mechanism (16 species and 41 reactions). It is shown that minor species incur a larger global error than the major species. The ISAT technique shows to be efficient to solve the joint PDF, with a speed-up of up to 60 over the direct integration of the governing equations. This work also shows that, for 100 stochastic particles, the storage requirements of ISAT for the finest error tolerance (0.0008) is 50 Mbytes, a reasonable value.

Tang & Pope (2002) [90] develop a hybrid methodology for thermochemistry reduction in turbulent reactive flows, combining the dimension reduction of RCCE and tabulation of ISAT. Firstly, the RCCE technique is used to reduce the reaction mechanism size, then, the *in situ* tabulation is performed to efficiently solve the governing equations. Nonpremixed methane/air combustion in a statistically homogeneous turbulent reactor is addressed using GRI mechanism version 1.2 [89] (32 species and 175 reactions). A direct integration of the governing equations with the full reaction mechanism is also performed and considered to be the exact solution. The hybrid technique uses as constraints for RCCE, the four chemical elements conservation, enthalpy conservation and the following chemical species: H_2O, CO_2, O_2, CH_4, CO, H_2, OH, O, CH_3, C_2H_2, and C_2H_4. Thus, the resulting reduced reaction mechanism is 16-dimensional and shows a good agreement with the exact solution, with an error smaller than 3% for density, temperature and major species. The hybrid approach also obtains a speed-up factor of about 500, when compared to the direct integration.

Singer & Pope (2004) [87] use the ISAT technique together with a splitting technique to solve a reaction-diffusion equation. The ISAT technique is used to solve pure reaction substep, whereas an implicit Crank-Nicolson finite difference technique is employed for the pure transport substep. The resulting numerical scheme, which is second order accurate in time and space, is applied to the simulation of a stoichiometric premixed hydrogen/air laminar flame using a reaction mechanism with 9 species and 19 reactions. The simulations results show that the numerical scheme is more sensitive to variations on ISAT error tolerance than in the ODE solver absolute error tolerance. This study also shows that ISAT allows to obtain a speed-up of $4.5 - 5$, when compared to the direct integration of the governing equations for the reaction-diffusion model.

Liu & Pope (2005) [49] characterize the local and the global errors of the ISAT technique when used in conjunction with transported PDF methods. The object of study in this work is a nonpremixed turbulent methane/air flame experimentally addressed by Barlow & Frank (1998) [2]. The computational fluid dynamics package `FLUENT` is used to perform RANS simulations of the governing equations, with $k - \epsilon$ turbulence model and ISAT to efficiently solve the thermochemistry described by skeletal mechanism with 16 species and 41 reactions. Their work investigates the ISAT local error through the implementation of three different adaptive strategies, i.e., growth of the ellipsoids of accuracy. The analysis of the cumulative distribution function of local error shows the local error well controlled, but a large error is shown to be possible despite improbable. The global error is quantified and demonstrated to be small, when compared to statistical error, for tolerances values smaller than 10^{-4}. The global error is also shown to vary linearly with the ISAT error tolerance.

Singer et al. (2006) [88] perform the simulation of two-dimensional unsteady laminar reacting flows using ISAT technique. This work presents an operator splitting technique which used ISAT to solve the pure reaction substep and stabilized Runge-Kutta technique for pure transport substep. The numerical scheme is parallelized using a combination of `OpenMP` and `MPI` libraries and applied to the interaction of a laminar premixed methane/air flame with a counter-rotating vortex pair. The reaction mechanism used is the GRI mechanism version 3.0 [89], which has 53 species and 325 reactions. The simulations results show that an overall speed-up factor of approximately $2.5 - 3$ times is achieved by the use of ISAT, when compared to the direct integration of the governing equations.

Lu et al. (2009) [50] develop parallelization strategies for ISAT technique. In essence, these parallelization strategies are smart ways to distribute the calculations tasks among various binary search trees. In a multi-processor environment calculation using parallel ISAT, the computational domain is decomposed into various sub-domains and each one of these are passed to a processor. Each one of these processors has its own binary search tree. Before or after a pure reaction fractional step, particles in one processor may be passed to one or more processors by distribution strategies to be solved there via serial ISAT. Three different distribution strategies have been tested. In the first strategy, there is no message passing, the evolution of each particle at a sub-domain is computed locally via serial ISAT. In the second strategy, all the particles at a group of sub-domains are randomly uniform distributed among the sub-domains of this group via message passing. Then serial ISAT is used to compute their evolution. In the third strategy, the particles of a group of sub-domains present a preference for some processors, e.g., those processors that they have not visited previously. Combinations of these strategies or adaptive strategies of the distribution are also possible. Numerical experiments using different parallelization strategies are performed in a methane/air partially stirred reactor, subject to different parametrical configurations. The adaptive strategy shows good parallel scalability and it is the only that yields a good performance for all parametric configurations tested, achieving a speed-up factor of up to 30 compared to the strategy with no message passing.

Lu & Pope (2009) [51] propose an improved version of the ISAT technique, which includes four search strategies for a query composition: the usual search in the ISAT tree; a list with the most recently used compositions; a list with the most frequently used compositions and the search in a binary search tree which has an ellipsoid associated to each node and leaf. Also, this improved ISAT verifies if a query composition lies inside the ellipsoid of accuracy by using the ellipsoid projection into an affine space. There is also defined an ellipsoid of inaccuracy, which is an upper bound for the region of accuracy. An error checking and correction criterion is introduced and allows the efficiently reduction of ISAT local error. The performance of the improved ISAT technique is compared to that of a previous version for two cases of methane/air combustion in partially stirred reactor. The first case uses a skeletal mechanism (16 species and 41 reactions), whereas the second uses the GRI mechanism version 3.0 [89] (53 species and 325 reactions). The simulation results show that the new algorithm demands less computational time and memory storage than the older version by factors of 2 and 5, respectively.

2.5
The State of the Art

The hybrid methodologies are those which combine two or more existing approaches for reduction reaction mechanisms. These sophisticated techniques envisage the best use of two or more well established techniques in order to achieve performance gains.

Among the different methodologies presented in this review, the hybrid approaches are surely the most promising, since they present excellent results, in terms of accuracy and computational cost. These virtues are associated to the combination of the advantages of well established techniques. The hybrid class can be considered in general as the state of the art in reduction of combustion chemical kinetics. The ICE-PIC technique combined with the ISAT storage/retrieval seems to be the most attractive reduction methodology available.

Pope & Ren (2009) [72] review the state of the art on efficient implementation of combustion thermochemistry in turbulent chemically reactive flows by the Turbulence and Combustion Group at Cornell. This review address the ICE-PIC technique to obtain a reduced models for chemically reactive flows; the coupling between thermochemistry and macroscopic transport in these reduced models; the development of efficient operator splitting schemes for chemically reactive flows; and the recent improvements in ISAT technique.

The remainder of this work is devoted to the presentation and to the study of an ISAT technique. Even if the chosen technique falls short to the state of the art, it is a fist stepping stone in more advanced developments.