

# Model Reduction Techniques for Chemical Mechanisms

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## 1. Introduction

To be able to meet the increasing demands for efficiency in energy producing systems (engines, turbines and furnaces), changes in the geometry of combustion devices or fuel composition are necessary. Such changes should be based on a thorough understanding of both the physical and chemical processes involved. Today, computer simulations are one of the most important tools for research to address these issues. This is increasingly employed for testing and characterizing the many features of the combustion process, along with or sometimes replacing the considerably more expensive experiments. Numerous types of reliable software are available for simulations of car engines, gas turbines, heaters and boilers. However, one limitation in using computer simulations is the degree to which one is forced to rely on the available computer capacity. Since most cases of combustion involve turbulent processes and numerous chemical reactions, this can be a serious drawback if one wishes to carry out a detailed simulation. Codes for turbulent flow situations are developed to account for turbulent motion between small regions, often called cells, where combustion within the cell is assumed to be homogenous. To deal with complex interaction between the physical and chemical processes in reactive systems, it is necessary to find methods that simplify modeling in such a way that it becomes both more comprehensible and practically useful.

The starting point for any reduction of chemical model is the detailed mechanism itself. Detailed chemical mechanisms have been investigated extensively during the history of combustion physics since the chemistry involved plays a key role in the outcome of any combustion process. By understanding the chemistry one can predict the rate of production and consumption of different species and thus also predict the total change in enthalpy during the combustion process. This in turn provides the values for the energy output, the end gas temperature and the emission characteristics allowing one to describe the overall combustion system.

The chemical system consists of a mechanism containing a set of differential equations representing the evolution of the concentrations of the individual species during the combustion process, thus representing the species conservation equation. The system itself is most often described in terms of molar fractions,  $X_i$ , or mass fractions,  $Y_i$ , of the following form:

$$\frac{\partial Y}{\partial t} = P(Y, \mathbf{u}, T) + \omega(Y, T) \quad (1)$$

where  $P(\mathbf{Y}, \mathbf{u}, T)$  represents the spatial differential operator (advection, convection and diffusion; it is thus depending on the velocity field,  $\mathbf{u}$ , and the temperature,  $T$ ) and  $\omega(\mathbf{Y}, T)$  represents the chemical source term, which includes chemical production and consumption of the species.  $\mathbf{Y}$  is the  $N_S$ -dimensional vector of mass fractions of a mechanism containing  $N_S$  species.

A long list of different detailed mechanisms have been presented in literature, ranging from simple hydrogen-oxygen mechanisms (Lewis & von Elbe, 1987); (Li et al., 2004) to complex fuel mechanisms which involve hundreds of species that interact in thousands of reactions (Côme et al., 1996) or even thousand of species reacting in tens of thousands of reactions (Westbrook et al., 2009). Discussions related to the nature of these detailed mechanisms in the literature is dating back to the beginning of combustion science. Some of these mechanisms have been developed and extended by hand, the validation of the detailed mechanism coming through experimental measurements, a very time consuming procedure. One very well known mechanisms for methane kinetics is the GRI-Mech 3.0 mechanism (Bowman et al., 2004). This mechanism is the result of collaboration between several groups and is under constant revision. This mechanism contains 49 species and considers 277 reactions for the  $C_1$  chain only.

Detailed mechanisms can also be obtained through an automatic generation process carried out by computer software. One way to automatically generate detailed mechanisms is described in works by Blurock (Blurock, 1995); (Blurock, 2000). Large and detailed chemical mechanisms including species larger than  $C_{12}$ -hydrocarbons are generated by the use of *reaction classes* associated with the reacting substructure in the species and a set of reaction constants. As Blurock (Blurock, 2000) indicates this "allows for a wide variety of arbitrarily branched and substituted species far beyond straight-chained hydrocarbons". This is an advantage when performing numeric computations of the combustion process, since only the reacting part of a class of species is of importance for the computations. This allows a symbolically generated mechanism to be studied that is substantially larger and more detailed than mechanisms previously carried out by hand. Mechanism generation tools are also freely available, such as the "Reaction Mechanism Generator" (RGM) developed by W. Green and co-workers (Green et al., 2011). This is a very extensive tool which generates mechanisms based on knowledge on how molecules react through elementary reactions.

As much as such tools are needed to develop mechanisms for complex chemical processes such as for e.g. combustion of bio-fuels from various biomass sources, the models become increasingly unmanageable due to their size. The detailed mechanism is therefore the object of different reduction procedures aimed at obtaining smaller mechanisms to be used in more complex simulations of combustion systems. The reduced mechanisms can be and to a large extent have been, worked out by hand on the basis of the total sum of the experience and knowledge available. This can result in compact and accurate mechanisms subsequently validated by experimental data. However, these mechanisms are often restricted to a narrow range of conditions. It is advantageous therefore to find general procedures that can reduce mechanisms automatically by using physical quantities associated with different reactions and species. Through identifying a set of selection criteria it is possible to detect species and reactions that play a minor role in the overall reaction process and can thus be excluded from the mechanism. This can be done by use of *reaction flow* and *sensitivity analysis* or by using *directed relation graph* (DRG) methods, which result in what is hereafter referred to as a skeletal mechanism.

Furthermore, mathematical procedures can be applied to the detailed mechanism or the skeletal mechanism which reduces the mechanism even more. These mathematical procedures do not exclude species, but rather the species concentrations are calculated by the use of simpler and less time-consuming algebraic equations or they are tabulated as functions of a few preselected progress variables. The part of the mechanism that is left for detailed calculations is substantially smaller than the original mechanism. These methods often make use of the wide range of time scales and are thus called *time scale separation methods*. The most common methods are those of (i) *Intrinsic Low Dimensional Manifolds* (ILDM), (ii) *Computational Singular Perturbation*(CSP), and (iii) *level of importance* (LOI) analysis, in which one employs the Quasy Steady State Assumption (QSSA) or a partial equilibrium approximation (e.g. rate-controlled constraints equilibria, RCCE) to treat the steady state or equilibrated species.

In Figure (1) a schematic overview of the different reduction paths is laid out. As can be seen, different paths and possibilities for reducing the mechanisms are possible. Which method is adopted is determined mainly by the nature of the problem to be solved. The starting point is a detailed mechanism generated by hand or by the software available and validated for the current conditions. These mechanisms can contain up to hundreds of active species and thus need to be reduced for practical use. However, smaller detailed mechanisms can successfully be applied in stationary combustion situations, and in situations in which speed-up is of less concern. This could be the development of flamelet libraries or simple zone models, for example. Larger mechanisms are the object of reaction flow and sensitivity analysis in which minor and major pathways of the mechanism are identified. Species that are only involved in the minor paths and do not appear as species sensitive to the governing parameters, are selected for removal from the system. The result is a smaller mechanism containing the major pathways and the sensitive species, termed a skeletal mechanism. This mechanism is complete in the sense that it can be applied in combustion simulations. For reasons of speed-up it is favorable for use in stationary combustion situations. If the mechanism is small enough, it can also be applied in non-stationary situations such as in the calculation of interactive flamelets and transported probability density functions (PDF) for turbulent motion simulations. However, these calculations require very compact mechanisms and in most cases a further reduction through a lifetime analysis is necessary. This reduces the number of active species in the mechanism and accounts for the contributions of the remaining species selected as steady state species. The resulting reduced mechanism can be successfully applied in flow codes, and is applicable in simpler systems for speed-up reasons as well. The lifetime analysis and the resulting reduced mechanism is employed when on-line reduction is carried out, since the number of active species involved can change during the computational run.

In the following, reaction flow analysis, sensitivity analysis and the directed relation graph method will be presented as static and dynamic reduction procedures. Thereafter will the main features of ILDM (including extensions such as flamelet generated manifolds (FGM) and reaction-diffusion manifolds (REDIM)), CSP and the LOI be discussed, including the fundamentals of the quasi steady state elimination procedure and the rate-controlled constrained equilibria (RCCE) approach.

## 2. Static and dynamic analysis tools

The static and dynamic analysis tools available provide important information that is useful for reduction procedures and includes reaction flow and sensitivity analysis procedures. Reaction flow analysis detects minor and major flows in the reaction system, where the species involved in the minor flows can be neglected in further investigation. Under given physical

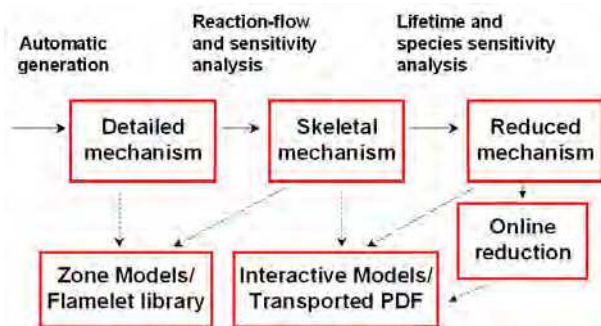


Fig. 1. A figure over the reduction methods and their relations. The dashed lines represent suggested uses of the different mechanisms. As shown in the figure, reduced mechanisms are applicable to both static and dynamic problems. Detailed mechanisms, in contrast, are not practical for dynamic systems.

conditions these will represent static properties of the mechanism. However, some species in the minor flows may exhibit a strong influence on the quantities under investigation and should thus not be neglected. These reactions and species are found through sensitivity analysis, in which the dynamic properties of the system are investigated. This can be formalized into one reduction tool called the directed relation graph (DRG) methodology. These three methods will now be discussed below.

## 2.1 Reaction flow analysis

Reaction flow analysis describes the importance of reaction paths in the mechanism under specified conditions. It is performed by calculating the transfer rate of certain atomic species such as C, O, N and H between molecular species. The flow of atoms between the reacting molecules is used as a measure of the relevance of the species in the reaction mechanism. The reaction flow of atomic species  $a$  between species  $i$  and species  $j$  can be described very simply by (Nilsson, 2011)

$$f_{ij}^a = \sum_{k=1}^{N_R} r_k (n_i^a v_{ik}'' - n_j^a v_{jk}'), \quad (2)$$

where the sum is taken over the number of reactions  $N_R$ .  $n_i^a$  and  $n_j^a$  are the numbers of the atom  $a$  in molecule  $i$  and  $j$ , and  $v_{ik}''$  and  $v_{jk}'$  are the stoichiometric coefficients for the molecules  $i$  and  $j$  in reaction  $k$ .  $r_k$  is the reaction rate,  $v_{jk}'$  and  $v_{ik}''$  are the stoichiometric coefficients of the reactants and the products in reaction  $k$ .

A more adequate method of determining the reaction flow, is described in more detail by Soyhan et al. (Soyhan et al., 2001); (Soyhan et al., 2001) and optimized further. In this work, forward and backward reactions are treated separately so as to capture reversible reaction pairs in which the flow of atoms is high in both directions but where the net flow is not necessarily high. This procedure results in the two new flow parameters shown below in which  $f_{ij}^a$  is the normalized flow of atom  $a$  by the formation of species  $i$  from species  $j$  relative

to the total production of species  $i$ , and  $c_{ij}^a$  is the flow of atom  $a$  by the consumption of species  $i$  to species  $j$  relative to the total consumption of species  $i$ :

$$f_{ij}^a = \frac{\sum_{k=1}^{N_R} r_k v'_{jk} v''_{ik} \frac{n_i^a}{\Delta n_k^a}}{\sum_{k=1}^{N_R} r_k v'_{jk}}, \tag{3}$$

$$c_{ij}^a = \frac{\sum_{k=1}^{N_R} r_k v'_{jk} v''_{ik} \frac{n_i^a}{\Delta n_k^a}}{\sum_{k=1}^{N_R} r_k v'_{jk}}. \tag{4}$$

The number of atoms  $n_i^a$  is now normalized to the total number of atoms  $a$  transported in the reaction  $\Delta n_k^a = \sum_{i=1}^{N_S} n_k^a (v''_{ik} - v'_{ik})$ . The flow parameters are normalized to the total formation or consumption rate of species  $i$  in order to achieve a non-dimensional range between 0 and 1 for the flow parameters.

An example of the scheme of such an analysis is given in Figure (2) which shows the flow of C atoms in a reaction mechanism for a CH<sub>4</sub>-fueled homogeneous reactor. This analysis was performed under specific conditions in which the engine speed was set to 1400 revolutions per minute (RPM), the fuel-air ratio was set to 0.412 and the compression ratio was set to 17.30. In the figure, the major reaction flows are marked by thick arrows and the minor flows by thinner arrows.

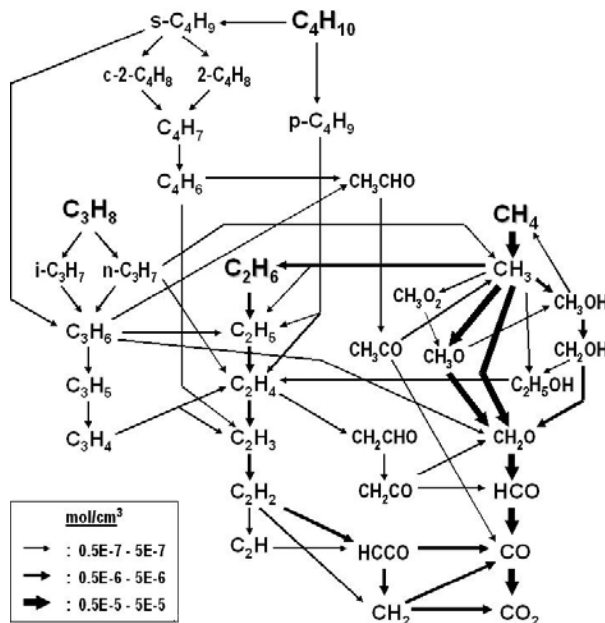


Fig. 2. Reaction flows of C atoms in a natural-gas mechanism for CH<sub>4</sub> as fuel in a homogeneous reactor (Nilsson, 2011).

Figure (2) shows that the major paths represents the high-temperature hydrocarbon oxidation of  $\text{CH}_4$  through the relatively stable radicals  $\text{C}_2\text{H}_5$  and  $\text{CH}_3$  shown in the lower right corner of the figure. Flows with a lower transport rate than  $5 \times 10^{-7} \text{ mol/cm}^3$  can be considered minor flows. These are shown for the most part in the upper left corner of Figure (2). These flows can thus be neglected in further calculations. Note that the situation is different if natural gas is used as a fuel, in which some of the fuel components may be selected for removal. Thus some of the species involved in minor flows may be important for the desired results and should be retained in the reaction mechanism. These are selected by the sensitivity analysis, as described below.

## 2.2 Sensitivity analysis

Sensitivity analysis involves investigating the change in a quantity of interest due to small changes in the controlling parameters. Investigating this is of interest in itself for gaining insight into the reaction model. In addition, it is a very useful tool for reduction of reaction mechanisms. After the minor flows have been detected by reaction flow analysis, it is important to ensure that the species involved in the minor flows do not influence the result significantly, in which case they should not be excluded in the further calculations. In local sensitivity analysis, this is described by the partial derivative of the investigated quantity with respect to the controlling parameters. Emanating from Equation (1), investigation of how the concentration of a species  $i$  is influenced by a perturbation  $\Delta k$  of the rate coefficient  $k$  can be expressed by differentiating the original set of chemical differential equations with respect to  $k_j$  and expanding the right hand side giving

$$\frac{d}{dt} \frac{\partial \mathbf{Y}}{\partial k_j} = \frac{\partial \mathbf{P}}{\partial \mathbf{Y}} \frac{\partial \mathbf{Y}}{\partial k_j} + \frac{\partial \mathbf{P}}{\partial k_j} + \frac{\partial \omega(t)}{\partial \mathbf{Y}} + \frac{\partial \mathbf{Y}}{\partial k_j} \frac{\partial \omega(t)}{\partial k_j}, \quad j = 1, \dots, N_S. \quad (5)$$

If considering a homogeneous reaction system,  $\mathbf{P} \equiv 0$ , the equation above results in the following expression:

$$\frac{d}{dt} \frac{\partial \mathbf{Y}}{\partial k_j} = \mathbf{J}(t) \frac{\partial \mathbf{Y}}{\partial k_j} + \frac{\partial \omega(t)}{\partial k_j}, \quad j = 1, \dots, N_S, \quad (6)$$

where  $\mathbf{J}(t) = \partial \omega(t) / \partial \mathbf{Y}$  is recognized as the Jacobian matrix and the initial condition for  $\partial \mathbf{Y} / \partial k_j$  (recognized as the sensitivity matrix) is a vector containing only zeros (Tomlin et al., 1997). In order to solve Equation (6), the concentrations in the original set of equations must be known, which is not always the case. The most efficient way of overcoming this problem is to solve the two systems in succession. This method is called the decoupled direct method. It first takes one step in solving Equation (1) and then performs an equal step in solving Equation (6). This can be done since both sets of differential equations have the same Jacobian matrix  $\mathbf{J}$  (Tomlin et al., 1997).

The same method can be applied to investigate the sensitivities of such parameters of the system as the flame temperature for premixed flames or the ignition timing in such ignition systems as in engine simulations as outlined below. The information obtained through this analysis is the basis for reduction of the mechanism. After the sensitivity analysis, the next step is to order the species and select those that are redundant. Tomlin et al. (Tomlin et al., 1997) classifies the species involved in a mechanism into three categories. The *important species* are those needed for the current investigation, such as the reaction products when investigating pollution or the initial reactants defining the fuels. The *necessary species* are those needed to provide for an accurate calculation of the concentration profiles of the important

species, of temperature profiles and of other important features. The remaining species are the *redundant species* that are candidates for removal from the mechanisms without loss of important information. Tomlin et al. eliminated a reaction from the mechanisms if the redundant species played simply the role of being reactants in the reaction, since only the reactants are present in the equation for the rate of change of species concentrations. Even if a particular reaction needs to be retained in the mechanism the redundant species can be eliminated from the list of products if it does not violate the conservation of atoms and mass in the calculations.

The approach to finding redundant species described by Tomlin et al. (Tomlin et al., 1997) is to investigate the matrix  $\mathbf{J}(t) = \partial\omega(t)/\partial\mathbf{Y}$  (for homogeneous systems;  $\mathbf{P} \equiv 0$ ), where the element  $\partial\omega_i/\partial Y_j$  describes the change of the rate of production of species  $i$  caused by a change of concentration of species  $j$ . A species is considered redundant if a change in its concentration does not affect the rate of production of important species significantly. A slightly different approach is taken by Soyhan et al. who let the sensitivities being transported through the mechanism in the sense that a species is rated according to its own importance and its involvement in producing or consuming important species (Soyhan et al., 1999); (Soyhan et al., 2001). Thus, the method can be considered as representing a simultaneous reaction flow and sensitivity analysis, called *necessity analysis*. First the reaction sensitivity represents a variable  $\psi$ 's sensitivity towards a chosen reaction coefficient  $A_k$  in reaction  $k$  is changed by a factor  $x$  (e.g. 1 percent):

$$S_{\psi k}^r = \frac{\partial\psi}{\partial A_k} A_k x \quad (7)$$

The species sensitivity can be taken either as the sum of the reaction sensitivities in which the species are involved, or can be derived directly in the same manner as the reaction sensitivity; investigating how much a variable  $\psi$  is changed when the concentration of species  $i$  is changed by a small factor  $\epsilon_i$  (again e.g. 1 percent):

$$S_{\psi i}^s = \frac{1}{c_i} \frac{\partial\psi}{\partial \alpha_i} \quad (8)$$

where  $S_{\psi i}^s$  contains the information on how sensitive a chosen target variable,  $\psi$ , such as the mass fraction of a particular species or temperature, is to the species  $i$ . The factor in which the concentrations are allowed to change is small and  $\alpha_i = 1 + \epsilon_i$  where  $\epsilon_i$  is e.g. 1 percent. Therefore,  $\alpha_i$  can be considered an error term for the concentrations which become  $c_i^* = c_i \alpha_i$ .

A species is assigned a relative necessity index which represents how important the species is for changes in variable  $\psi$  in relation to the other species. The redundancy index is based on the species sensitivity in the following way:

$$I_i = \max \left( \frac{S_{\psi i}^s}{\max_{k=1, N_s} (S_{\psi k}^s)}, Z_i \right) \quad (9)$$

where  $Z_i$  takes the value 1 or 0 depending on whether the species has been preselected as an important species (fuel, oxidant etc.). Even if a species has a low necessity it can be assigned a high overall necessity index if there is a significant flow of atoms to or from an important

species. The overall necessity is determined as follows:

$$\bar{I}_i = \max \left( I_j f_{ij}^a, I_j c_{ij}^a, I_i; j = 1, N_s, a = 1, N_a \right) \quad (10)$$

where  $f_{ij}^a$  and  $c_{ij}^a$ , as defined previously, are the flow of atom  $a$  by formation or consumption of species  $i$  from or to species  $j$ . This equation needs to be solved iteratively with a preset value of  $\bar{I}_i$ . Species with a low overall  $\bar{I}_i$  are considered to be redundant. This procedure has been used extensively to perform reduction on large hydrocarbon mechanisms, e.g. up to C-8 reaction chains where together with a lumping procedure the mechanism was reduced from about 246 species to 47 (Zeuch et al., 2008). Also, this reduction procedure is been made available in reaction kinetics simulation tools such as DARS (DARS, 2011) where the reduction is performed entirely automatically. The computed necessity index ranks the species accordingly, and a user set cut-off limit will generate a skeletal mechanism according to desired accuracy of the resulting skeletal mechanism; i.e. the more species which are excluded from the mechanism the less accurate the mechanism will be to predict the combustion process.

### 2.3 Directed relation graph methodology

The step wise reduction procedure described above can be automated by the use of the Directed Relation Graph method (Lu and Law, 2005);(Lu and Law, 2006). This procedure quantifies the coupling between species, and assigns an "pair wise" error which contains the information of how much error is introduced to a species  $A$  by elimination of a species  $B$ :

$$r_{AB} \equiv \frac{\max |v_{Ai}\omega_i\delta_{Bi}|}{\max |v_{Ai}\omega_i|}, \delta_{Bi} = \begin{cases} 1 & \text{if the } i\text{th reaction involves } B. \\ 0 & \text{otherwise.} \end{cases} \quad (11)$$

Note that the denominator contains the maximum reaction rate contributing to the production of  $A$ , whereas the numerator contains the maximum reaction rate contributing to the production of  $A$  that also involves species  $B$ . The original formulation used a summation over *all* reactions which did not prove to be efficient when e.g. dealing with larger isomergroups (Luo et al., 2010). This formalism is not unsimilar to Equation (9). However, both the reaction flow and an error estimate are included when the species dependence is expressed in the following *graph* notation:

$$A \rightarrow B \text{ if } r_{AB} > \epsilon. \quad (12)$$

Species  $A$  is thereby connected to species  $B$  only if the pair wise error is above a user set error threshold. The starting point if the directed relation graph would be one of the important species, such as the fuel species. When species with low connectivity (below the threshold) is eliminated the result will be a skeletal mechanism similar to what is obtained by a necessity analysis.

This procedure will not be discussed further here, but the DRG methodology has proven to be easy to implement and to fully automate. Hence, it has become very popular to use for reduction of larger mechanisms. In its simplest form DRG has however proved to have some limitations. These have been addressed in extended versions of the procedure. This includes DRG with error propagation (DRGEP) (Pepiot-Desjardins & Pitsch, 2008), DRG aided sensitivity analysis (DRGASA) (Zheng et al., 2007) and DRGEP and sensitivity analysis (Niemeyer et al., 2010). The reader is referred to these works for further discussion.



### 3. Time scale separation methods

In the following section the methods based on time scale separation analysis will be discussed. Employing these methods relies on the fact that the chemical system consists of a number of species that react with each other on time scales that range over several orders of magnitude. Thus, some of the reactions can be considered as being fast compared with the physical processes involved, such as diffusion, turbulence and other reactions that are considered slow. This is illustrated in Figure (3).

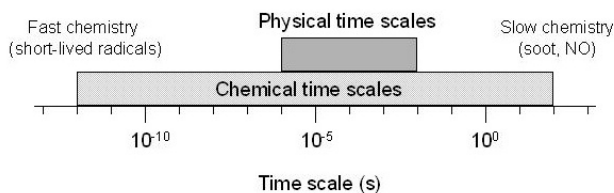


Fig. 3. Comparison of typical chemical and physical time scales. The chemical time scales span several orders of magnitude (Nilsson, 2011).

A time scale separation method makes use of the fact that the physical and chemical time scales have only a limited range of overlap. The time scales of some of the more rapid chemical processes can thus be decoupled and be described in approximate ways by the Quasi Steady State Assumption (QSSA) or partial equilibrium approximations for the selected species. This reduces the species list to only the species left in the set of differential equations. Also, eliminating the fastest time scales in the system solves the numerical stiffness problem that these time scales introduce. Numerical stiffness arises when the iteration over the differential equations need very small steps as some of the terms lead to rapid variations of the solution, typically terms involving the fastest time scales.

Three time-scale separation methods will be described below. These are the Intrinsic Low Dimensional Manifold method (ILDM), Computational Singular Perturbation (CSP), and the lifetime analysis based on the Level Of Importance (LOI).

Since the methods are all concerned with determining the processes involved on the shortest time scales, they have many similarities. Although it could be argued that they in reality are virtually the same, they have different coatings and different ways of presenting the solutions. In the overall picture here one can describe the differences as follows: the key difference between ILDM and CSP is the sub-space created to describe the new manifold. ILDM employs partial equilibrium approximations for the species selected and creates a species sub-space. CSP employs steady state approximations and creates a reaction sub-space. It does not indicate a preference for QSSA as to opposed to partial equilibrium approximation. Including the partial equilibrium approximation in selecting the "steady state" species represents a more general criterion than using only the QSSA (Goussis, 1996). However, this introduces all the species in the stoichiometry vector, often making the algorithm more complicated. The difference between CSP and lifetime analysis is that CSP includes coupled time scales, whereas lifetime analysis assumes that on a short time scale no coupling is significant, it is thus operating with a diagonal Jacobian. Details of this are described below.

Once the "fast" and the "slow" components are identified, several of these methods use the quasi-steady state assumption (QSSA) as the basis for reduction. Together with a

chemical equilibrium assumption or as an alternative to it, this procedure makes it possible to mathematically eliminate species from the set of differential equations. They are treated separately through use of approximative algebraic relations. Their concentrations still contribute to the reaction rates of the non-reduced species. The basic idea of developing reduced chemical mechanisms by introducing the assumption of a steady state is not new and has, in fact, been used in chemistry since the 1950s (See (Peters, 1990)) and further references therein). However, not until the early 1990s was this strategy for solving complex chemical problems introduced in combustion physics.

Until rather recently, these reduced schemes were mainly developed by hand using QSSA and an à priori definition of which species were to be considered in steady state, a particularly time-consuming procedure. Before presenting the various time scale separation methods, the basic steps of the QSSA reduction procedure will be presented in the subsection below followed by the theory rate-controlled constraints equilibria (RCCE). Thereafter are the time scale separation methods outlined.

### 3.1 Manual reduction by means of QSSA

The underlying assumption for QSSA is that some species can be treated as being in steady state. This means that, if one ignores physical terms as convection and diffusion, their concentrations remain constant. It follows then from Equation (1) that the change in species concentration of species  $i$  is

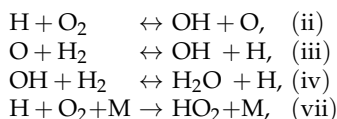
$$\frac{dX_i}{dt} = \sum_{k=1}^r v_{i,k} r_k = \omega_i = 0, \quad (13)$$

where  $\omega_i$  is the chemical source term and the summation is over all reactions of the product  $v_{i,k} r_k$ . This equation corresponds to Equation (1) for chemical treatment only, where the reaction rate  $r_k$  can be expressed by the following general definition:

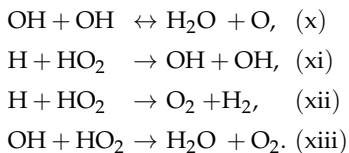
$$r_k = k_k \prod_{j=1}^n X_j^{v_j^k}, \quad (14)$$

and the net stoichiometric coefficient being  $v_i = v_i'' - v_i'$ . The physical meaning of this assumption is that the reactions that consume the species are very much faster than the reactions producing the species. Thus, the concentration remain low just as their time derivative.

The H<sub>2</sub>-O<sub>2</sub> system will be used as an example (Peters, 1990);(Peters et al., 1993). The reactions needed for the present analysis are (following the numbering in the original mechanism)



where the backward reactions are treated as being separate reactions. Additional reactions in the H<sub>2</sub>-O<sub>2</sub> reaction system are also included in the present example:



Equation (13) indicated that the time derivatives of all the species concentrations can be expressed in terms of the concentrations of species that consume and that produce that particular species. As noted above, the derivatives not only contain a chemistry-term, but in the case of inhomogeneous systems, can also contain diffusive and convective terms, often being denoted in such cases by the L-operator. Here, only the chemical contribution is included, resulting in the following set of equations:

$$\begin{aligned} \omega_H &= -r_{ii} + r_{iii} + r_{iv} - r_{vii} - r_{xi} - r_{xii}, \\ 0 = \omega_{OH} &= r_{ii} + r_{iii} - r_{iv} - 2r_x + 2r_{xi} - r_{xiii}, \\ 0 = \omega_O &= r_{ii} - r_{iii} + r_x, \\ \omega_{H_2} &= -r_{iii} - r_{iv} + r_{xii}, \\ \omega_{O_2} &= -r_{ii} - r_{vii} + r_{xii} + r_{xiii}, \\ \omega_{H_2O} &= r_{iv} + r_x + r_{xiii}, \\ 0 = \omega_{HO_2} &= r_{vii} - r_{xi} - r_{xii} - \omega_{xiii}. \end{aligned} \quad (15)$$

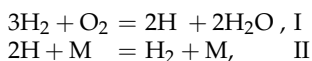
where OH, O and HO<sub>2</sub> are all set to steady state and their derivatives are set equal to zero, transforming the corresponding differential equations conveniently into algebraic relations. Since the system is already reduced, the steady state concentrations can be found. However, in obtaining a set of global reactions and optimizing the reduction, the corresponding number of reaction rates can be eliminated from the system. A rule of thumb is for each species to eliminate the fastest reaction rates at which this species is consumed. This is  $r_{iv}$  for OH,  $r_{iii}$  for O and  $r_{xii}$  for HO<sub>2</sub>, them being placed on the right-hand side of the equations and expressed in terms of the remaining reaction rates on the left-hand side (Peters, 1990). However, the reaction rates that are eliminated from the system are arbitrary and result in the same global reactions. After some algebra, the system is as follows:

$$\begin{aligned} \omega_H &= 2r_{ii} - 2r_{vii} + 2r_{xi}, \\ \omega_{H_2} &= -3r_{ii} + r_{vii} - 3r_{xi}, \\ \omega_{O_2} &= -r_{ii} - r_{xi}, \\ \omega_{H_2O} &= 2r_{ii} - 2r_{xi}. \end{aligned} \quad (16)$$

By arranging the right-hand side so that rates with the same stoichiometric coefficients are added together one obtains

$$\begin{aligned} \omega_H &= 2(r_{ii} + r_{xi}) - 2r_{vii}, \\ \omega_{H_2} &= -3(r_{ii} + r_{xi}) + r_{vii}, \\ \omega_{O_2} &= -(r_{ii} + r_{xi}), \\ \omega_{H_2O} &= 2(r_{ii} + r_{xi}), \end{aligned} \quad (17)$$

resulting in the following global reactions:



with the reaction rates being  $r_I = (r_{ii} + r_{xi})$  and  $r_{II} = r_{vii}$ . This procedure shows how a set of eight elementary reactions can be reduced to just two global reactions and two corresponding reaction rates, which are sufficient to describe the system. The resulting system is also called a two-step mechanism.

The computations above are quite straightforward once a choice is made of which species are to be considered to be in steady state. In the  $H_2-O_2$  system, the three species OH, O and  $HO_2$  are conveniently set to steady state. Although, in the manual reduction procedure the choice of steady state species often stems simply from the experience of which species can be approximately calculated. However, the choice is often based on an analysis of the intermediate species' mole fraction. The argument is that no species at high concentration, and no reactant or product species either, can be a steady state candidate. The algorithm is such that the conservation equations are dealt with only for the species included in detail in the mechanism. The steady state species only appear through their contribution to the reaction rates determining the non-steady state species. Thus, species of high concentrations or high enthalpy content need to be kept in the mechanism so as to not violate the conservation of mass fraction and enthalpy. In the case of the methane-air mechanism that was reduced by Peters (Peters, 1990), the computation of mole fractions in a premixed stoichiometric methane-air flame was the basis for defining the steady state species.

In the flame calculations accounting for the physical processes diffusive and convective terms must also be small in order for the differentials to be set equal to zero. Nevertheless, in the reactive inner layer of the flames, the diffusive terms turn out to be dominant as compared with the convective terms. Consequently, since the species concentrations are strongly influenced by the diffusion, obtaining an order-of-magnitude estimate for selection of the steady state species requires that the mole fractions be weighted to the molecular weight of the inert species  $N_2$ ,  $W_{N_2}$ , the resulting weighting factor being

$$\sqrt{W_{N_2}/W_{i,N_2}} \quad (18)$$

where  $W_{i,N_2}$  is given by

$$W_{i,N_2} = \frac{2W_i W_{N_2}}{W_i + W_{N_2}}. \quad (19)$$

The H radical, for example, diffuses through the flame quickly and displays a low concentration profile. However, it is not a species in steady state and it is highly sensitive to the desired result. The species for the methane-air flame fall into two distinct groups: those in which the corresponding weighted mole fraction has a value well below 1% and those in which the corresponding weighted mole fraction has a value well above 1%. Thus, the choice is clear, the first group being selected as steady state species candidates.

The final step is to calculate the values of the reaction rates for the species and to then determine their concentrations. The reaction rates are expressed in the form of rate constants, stoichiometric coefficients and concentrations, as defined in Equation (13) and (14). However, the reaction rates also contain concentrations of the steady state species. As shown in Equation (13), these can be calculated from their balance equation with  $\omega_i = 0$ . The concentration of OH, for example, can be calculated as follows:

$$0 = r_{ii} + r_{iii} - r_{iv} - 2r_x + 2r_{xi} - r_{xiii}, \quad (20)$$

where  $r_{iv}$ ,  $r_{ii}$  and  $r_{iii}$  all include both forward and backward reactions. The equation can be solved by setting  $r_{iv}$ , for example, on the left-hand side and inserting all the rate constants and concentrations.

A very powerful and important step in the reduction process is the *truncation of the steady state relations*, such as that shown in Equation (20). By investigating the reaction rates, both the forward and the backward rates, for a stoichiometric flame over the typical physical range of calculations one can track down the one or two reaction rates that are dominant. Peters (Peters, 1990) could show that in the case of OH only  $r_{iv}$  is dominant, allowing the other reaction rates to be neglected in the further calculations. The advantage of performing truncation is that the most rapid reaction rates are excluded from the system, reducing the stiffness of the problem considerably and enhancing the accuracy. Thus, Equation (20) can easily be solved, the resulting [OH] being found to be

$$[\text{OH}] = \frac{k_{ivb}[\text{H}_2\text{O}][\text{H}]}{k_{ivf}[\text{H}_2]} \quad (21)$$

Similar calculations for the other steady state species need to be performed. In the next step then these relations are used to calculate the remaining set of differential equations which govern the non-steady state species. The overall reaction rate for each remaining species is thus determined by means of an *inner iteration loop*, a simple fixed-point iteration procedure is often employed. The remaining set of differential equations can be solved in different ways, and several numerical solvers for stiff differential equations are freely available.

This procedure has proven successful, many authors having presented work in which reduced mechanisms resemble detailed mechanisms very closely (See e.g. work presented in (Peters & Rogg, 1993);(Smooke, 1991)). Similarly reduced mechanisms have been produced for a variety of fuels, for example the three-step mechanism for CO-H<sub>2</sub>-N<sub>2</sub>/air diffusion flames by Chen et al. (Chen et al., 1993) and four-step mechanisms for both ethylene/air and ethane/air flames by Wang and Rogg (Wang & Rogg, 1993).

Methane is the simplest of the carbon-containing fuels and extensive investigations of the reduced mechanisms for methane-air flames have been carried out, even before hydrogen flames as the C<sub>1</sub> chain provides a lower radical level, steady state relations thus being easier justified. The first reduced mechanisms for methane-air flame combustion originated from a skeletal mechanism consisting of 25 reactions for the C<sub>1</sub> chain, and 61 reactions including the C<sub>2</sub> chain evolved during the 1970-1980s (Kaufman, 1982);(Mauss & Peters, 1993);(Smooke, 1991);(Turns, 2000). A fully detailed mechanism can contain over 40 species and involve some 300 reactions. An example of such a mechanism is the GRI-Mech 3.0 mechanism obtained from Berkeley University (Bowman et al., 2004). Peters (Peters, 1990) and Mauss et al.(Mauss & Peters, 1993) demonstrated the reduction of the skeletal mechanism for methane-air flame combustion by use of the quasi steady state assumption, validating it for the range of lean to stoichiometric mixtures. The mechanism was reduced to a four-step mechanism containing 7 species, the reduction procedure following exactly the same underlying principles as for the H<sub>2</sub>-O<sub>2</sub> system described above.

The investigation of higher carbon containing fuels such as acetylene for the purpose of reduction is of considerable importance for soot studies. Ring compounds and their growth through acetylene (C<sub>2</sub>H<sub>2</sub>) are important features for formation of soot under fuel-rich conditions (Turns, 2000). Mauss et al. (Mauss & Lindstedt, 1993) presented a 7 step reduced mechanism validated for acetylene-air premixed flames which originates from the skeletal

mechanism described in Peters and Rogg (Peters & Rogg, 1993), including all 87 reactions for up to  $C_3$ -species. With use of the 7 step mechanism, both flame velocities and species concentrations were well predicted as compared to the results for the full mechanism. Some deviations were found in the reaction zone, where a steeper consumption of reactants was obtained for the reduced mechanism. However, this can also result from a steeper temperature profile in the same region, which would enhance the reaction rates. In Lindstedt et al. (Lindstedt & Mauss, 1993) the same mechanism for acetylene formation is applied to a diffusion flame system having 8 additional reaction steps. In the work, a five step reduced mechanism is generated and is validated for the entire range of strain rates up to the extinction point. As in the case of the premixed flame, the temperature profiles and species concentration profiles agree very well with the results of the full mechanism for a selected range of pressures.

Nevertheless, as noted, the calculations above and their validations are time-consuming, and since the demand for larger and more complex mechanisms is very strong from areas related to combustion modeling, automating the procedure is important. This will be discussed in the following section.

### 3.2 Rate-controlled constrained equilibria

The Rate-Controlled constrained equilibria (RCCE) approach incorporates the assumption of time scale separation in reactive systems in much the same way as the QSSA described above. However, in the case of RCCE the analytical expressions are derived from equilibrium assumptions rather than steady state. These equilibrium states are constrained by the leading or main species, hence the terminology of constrained equilibria. It means that if e.g. considering a simple chemical system such as  $CH_4$ - $O_2$ , and  $O_2$  is constrained, then  $O_2$  will occupy all O-atoms in the present form as the amount of  $O_2$  can not change, whereas both H and C atoms may be occupied by whatever CH-molecule are thermodynamically stable in the current state. The constraints are thus linear combinations of the species' concentrations. The RCCE method is in large developed by Jones and Rigopoulos for combustion systems (Jones and Rigopoulos, 2005);(Jones and Rigopoulos, 2007), and only briefly outlined here.

In order to derive the equilibrium states, the RCCE makes use of minimizing the Gibbs free energy subject to conservation of enthalpy, elements and mass for each constraint  $i$ :

$$h = \sum_{j=1}^{N_s} n_j H_j^0(T) \quad (22)$$

$$E_i = \sum_{j=1}^{N_s} a_{ij}^e n_j, \quad (i = 1, \dots, M_e) \quad (23)$$

$$C_i = \sum_{j=1}^{N_s} a_{ij}^c n_j, \quad (i = 1, \dots, M_c) \quad (24)$$

where  $a_{ij}^e$  is the matrix of number of element  $i$  in the  $j$ th species,  $a_{ij}^c$  is the matrix of linear combination of concentration of the  $j$  species making up the  $i$ th constraint, and  $n_j$  is the concentration of the  $j$ th species.

It can be shown that two sets of equations arises when employing minimization of Gibbs free energy (Jones and Rigopoulos, 2005). One set becomes algebraic equations defining the

constraints:

$$\mu_j^0(T) + RT \ln \frac{n_j}{n} + RT \ln \frac{P}{P_0} + \sum_{i=1}^{M_c} \lambda_i^e a_{ij}^e + \sum_{i=1}^{M_c} \lambda_i^c a_{ij}^c = 0, \quad (j = 1, \dots, N_S) \quad (25)$$

where  $N_S$  is the number of species, and  $P_0$  and  $\mu_j^0$  are the pressure and chemical potential in the standard state, where the chemical potential is a given function of temperature. These algebraic equations need to be solved simultaneously to compute the concentrations at the constrained equilibrium state. The second set becomes differential equations for the concentrations of the remaining constrained species where the matrix  $a_{ij}^c$  is now incorporated:

$$\frac{dC_i}{dt} = \sum_{j=1}^{N_S} a_{ij}^c \sum_{k=1}^{N_r} \nu_{jk} r_k(n_1, \dots, n_{N_S}, T, \rho), \quad (i = 1, \dots, M_c) \quad (26)$$

The algebraic-differential equation system is then solved in much the same manner as for the QSSA approach. Because the formulation of Equation (25) yields for all species, the RCCE is particularly attractive in adaptive chemistry systems.

### 3.3 Intrinsic Low Dimensional Manifolds

#### 3.3.1 The standard approach to ILDM

Intrinsic Low Dimensional Manifolds is a method for reducing a chemical system by using *attractors* for the chemical kinetics involved. It is thought that fast reactions quickly bring the composition down to the attracting manifolds, an equilibrium solution space that fast chemical reactions relax towards, slow reactions moving within these manifolds (Maas, 1998); (Schmidt et al., 1998); (Yang & Pope, 1998). This represents a time separation of the fast chemical processes. In the work of Maas et al. (Maas & Pope, 1994) and developed further in Maas (Maas, 1998), the fundamental formalism behind the decoupling of the short time scales by use of ILDM is taken up, and this is to be referred here further.

Reacting flow and its scalar field evolve in time according to an  $N_u$ -dimensional partial differential equation system, where  $N_u$  is the number of unknown chemical and physical variables (See Equation (1) for comparison):

$$\frac{\partial \psi(t)}{\partial t} = \mathbf{P}(\psi, \nabla \psi, \nabla^2 \psi) + \omega(\psi), \quad (27)$$

$\psi$  being the  $N_u$ -dimensional vector of the unknown scalars,  $\omega(\psi)$  the vector of the source terms, including the chemical reaction rates, and  $\mathbf{P}(\psi, \nabla \psi, \nabla^2 \psi)$  being the spatial vector operator that governs the contributions of all other physical processes such as diffusion, convection, advection, etc. The time scales governed by  $\omega(\psi)$  span over a large range. Some of the fastest can be decoupled from the system as desired.

The  $N_u$  variables form an  $N_u$ -dimensional space. A chemical reaction represents a movement along a trajectory from the initial state to the final state for  $t \rightarrow \infty$ . An example is given in Figure (4), which shows the trajectories in a CO-H<sub>2</sub> system as plotted in the CO<sub>2</sub>-H<sub>2</sub>O plane. In Figure (4) several cases involving differing initial conditions are plotted. However, one can clearly see in the figure that the trajectories all move towards an equilibrium condition, in this

case at the far right end point of the main manifold. The equilibrium state can represent the chemical system as one single point if the computations do not include the chemical dynamics.

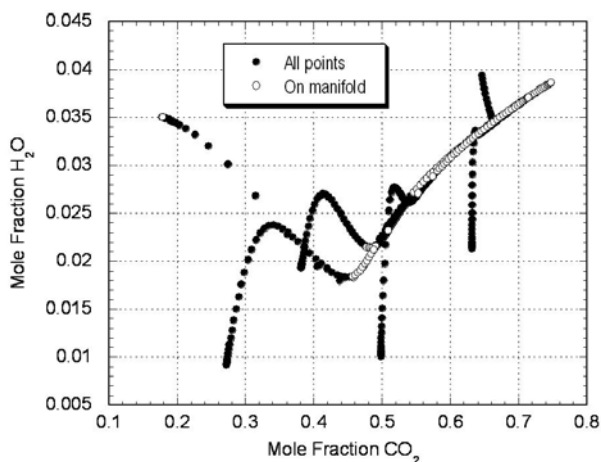


Fig. 4. Trajectories of the chemical reactions progress for a CO-H<sub>2</sub> system and its projection into the CO<sub>2</sub>-H<sub>2</sub>O plane (Nilsson, 2011).

The equilibrium process in this case takes about 5 ms. If the physical processes are slower or have the same order of magnitude, the equilibrium point offers an approximate solution. This corresponds to neglecting chemical dynamics on time scales shorter than 5 ms. By neglecting chemical dynamics that take place on time scales shorter than say 100  $\mu$ s, the solution can be described by a single variable since the main equilibrium curve remains in the state space, which is a one-dimensional manifold. This is shown by the open circles in Figure (4). It is a consequence of the fast relaxation process leading to the reactions being in partial equilibrium and the species involved being in steady state. One can thus conclude that after the relaxation period of 5 ms the system can be described in an approximate way by the equilibrium value, which is a single point. If time scales shorter than 100  $\mu$ s can be neglected, the system can be described by using a single reaction progress variable, a one-dimensional manifold. If even shorter time scales are needed, several additional reaction progresses need to be included, which results in a higher-dimensional manifold.

After identifying the low-dimensional manifolds in the  $N_u$ -dimensional state space that the thermodynamic state of the system has been relaxed to, the reduced system consisting of  $S = N_u - R$  variables ( $R$  is the degree of reduction), can be represented as  $\Phi = (\Phi_1, \dots, \Phi_S)^T$ . Thus the original system  $\psi = \psi(\Phi)$  can be projected onto the  $S$ -dimensional sub-space

$$\frac{\partial \Phi}{\partial t} = \Pi(\Phi, \nabla \Phi, \nabla^2 \Phi) + \Omega(\Phi), \quad (28)$$

where  $\Omega$  and  $\Pi$  are the corresponding  $S$ -dimensional vectors for the source terms and from the other physical processes, respectively. The low-dimensional manifold described by equation (28) represents the chemical system in a further calculation.

The advantage of the ILDM method is that it requires no information concerning which reactions are to be set in equilibrium or which species are in steady state: "The manifold



method is based on a more intrinsic study of the chemical reaction process happening in combustion" (Yang & Pope, 1998). The use of attractors is sufficient to find a solution. Since computer simulations of combustion processes involving ILDM reduction speed up calculations by a factor of ten, the method is applicable to numerical problems in particular. The results of the calculations of the manifolds are stored and *tabulated* in a preprocessing step. Since the tabulated data consist of the relevant data (such as the reduced reaction rates) the information is assessed through a table look-up during the computational run. This method however requires significant amounts of storage memory, which becomes problematic in higher dimensional manifold calculations. An alternative storage method is proposed by Niemann et al. (Niemann et al., 1996). Whereas the classic approach employs an interpolation procedure within small tabulation cells and a local mesh refinement, Niemann et al. employs a higher order polynomial approximation within large coarse cells. This decreases the storage requirement considerably; for an  $\text{H}_2\text{--O}_2$  laminar flat flame calculation the storage requirements were reduced by a factor 200 (Niemann et al., 1996). However, since the method does not provide a set of rate equations, it cannot be related to a set of global reactions that provide information on the underlying kinetics involved (Tomlin et al., 1997). Furthermore, classic ILDM does not account for transport processes which may be important for diffusion flames. The two next sub-sections will be devoted to methods to account for transport in the ILDM framework.

### 3.3.2 Flamelet Generated Manifolds (FGM)

The Flamelet Generated Manifolds (FGM) approach aims to provide a tool for simplified treatment of the chemical system for flames where also transport in terms of diffusion is important. This is particularly the case for premixed flames where there are also less reactive parts on one side of the flame zone from which radicals diffuse towards the flame zone. The concept is based on two simplification procedures: one is the flamelet approach where a multi-dimensional flame is considered as an ensemble of one-dimensional flames, and another which is the consideration of a low-dimensional manifold in composition space.

van Oijen and co-workers have developed this technique for a set of different flames (van Oijen & de Goey, 2000);(van Oijen & de Goey, 2002). The first approach considers a premixed flame. The technique of FGM make use of premixed flames with detailed chemistry which are pre-calculated and tabulated. Then tables are generated, reflecting the solution of these flamelets as a function of one or more control variables. When solving equations for these control variables by the use of the ILDM, one can use the table of flamelets to retrieve quantities related to the composition that are not known. Since the major part of convection and diffusion processes are included in FGM through the flamelet calculations, the method is more accurate in the low-temperature region of a premixed flame than methods based on local chemical equilibria as the classic ILDM.

### 3.3.3 Reaction-Diffusion Manifolds (REDIM)

The Reaction-Diffusion Manifolds (REDIM) approach represent an extension to the formulation of the standard ILDM. Where the ILDM is in fact a relaxation of a set of ordinary differential equations (ODE's) describing a homogenous system, the REDIM formulation generalizes for a set of partially differential equation (PDE's) where also the coupling between the reaction and diffusion processes are accounted for. Bykov and Maas (Bykov & Maas, 2007) have performed the full derivation of this generalized system in the framework of ILDM and an optimized tabulation procedure of generalized coordinates. They present the method in

three limiting cases: (1) where there is pure mixing and thus no chemical source term, (2) where there is a homogeneous system and thus no transport, and (3) where there is a case of known gradients of the local coordinates. This last limiting case will if the known gradients are found from detailed flame calculations become equivalent to the FGM approach as described in the previous sub section.

It is clear that REDIM represents a generalized form of applying known ideas from invariant manifold theory and have been shown to apply to a wide range of applications from homogeneous systems, premixed flames and diffusion flames (Bykov & Maas, 2009). It is less straight forward to implement, tabulation of the multi-dimensional manifolds need special attention and the interpretation of the results are non-trivial. However, once implemented REDIM represents a very general and powerful reduction tool.

### 3.4 Computational Singular Perturbation method

Computational Singular Perturbation (CSP) is an alternative method employing a time scale separation analysis, thereafter use being made of exhausting modes for the approximate treatment. The core of the technique is to rewrite the set of differential equations that govern the system, using a new set of basis vectors so defined that they represent the fast and the slow sub domains. These vectors thus contain a linear combination of the reaction rates involved in the original mechanism. By employing this method, the problem becomes one of an eigenvalue problem that can help in discarding fast "modes" which involve species that are candidates for steady state. Work on development of the CSP method can be examined in detail in a substantial selection of papers (Lam, 1993);(Lam et al., 1994); (Massias et al., 1999a); (Massias et al., 1999b);(Tomlin et al., 1997).

The method as a whole is described in terms of three major steps (Massias et al., 1999a); (Massias et al., 1999b). The first step concerns as usual identification of the detailed chemical and physical system and setting the limits for reduction. The next step involves finding the steady state species, and constructing the reduced mechanism that involve the simpler algebraic operations. The final step is to optimize the reduced mechanism through truncation of the algebraic relations or of the remaining differential equations and of the resulting global rates. This is done to enhance the computations and also provide a more accurate solution.

The *second* step which is of interest here consists of choosing the number of global steps that are desired for the reduced mechanism, noted here by  $G$ , and determining the *local CSP pointers* for each species. The definition of the size of the reduced mechanism is being based on experience and empirical considerations. A method is yet not presented that can determine the size of the reduced mechanism *a priori* based on the relevant physical situation. The number of steady state species,  $R$ , is given by  $R = N_S - E - G$ , where  $N_S$  is the total number of species in the detailed mechanism and  $E$  is the number of elements in the mechanism, such as C, O, H and N.

The local CSP pointers are generated through representation of the chemical system, Equation (1), by a set of basis vectors,  $\mathbf{a}$ , defined such that (Massias et al., 1999b):

$$\frac{\partial \mathbf{Y}}{\partial t} = \mathbf{a}_r \mathbf{h}^r + \mathbf{a}_s \mathbf{h}^s, \quad (29)$$

where  $\mathbf{a}_r$  is an  $R$ -dimensional vector for the  $R$  reduced species,  $\mathbf{a}_s$  is an  $S$ -dimensional vector for the remaining species, and  $\mathbf{h}^r$  and  $\mathbf{h}^s$  are the corresponding vectors of the form

$$\mathbf{h}^r = \mathbf{b}^r(\mathbf{P} + \omega) \quad \text{and} \quad \mathbf{h}^s = \mathbf{b}^s(\mathbf{P} + \omega), \quad (30)$$

where  $\mathbf{P}$  contains the spatial differential operator,  $\omega$  is the species source term from Equation (1).  $\mathbf{a}_r$  and  $\mathbf{a}_s$  are the stoichiometric vectors for the modified non-physical mechanism, and  $\mathbf{b}^r$  and  $\mathbf{b}^s$  form the corresponding inverse set of basis vectors. According to the definition of the basis vectors, the first term on the right hand side in Equation (29) should be assumed to be insignificant because of the steady state assumption that  $h^i \approx 0$  for  $i = 1, R$ , resulting in the following expression:

$$\frac{\partial \mathbf{Y}}{\partial t} \approx \mathbf{a}_s \mathbf{h}^s. \quad (31)$$

The goal of CSP analysis is thus to find the set of basis vectors that can fulfill this requirement. A CSP analysis is performed on each species at each spatial point, the  $R$  elements to be considered as being in steady state are identified by the  $N_S$  diagonal elements of the CSP pointer,  $D_i, i = 1, N_S$ :

$$\mathbf{D} = \text{diag}[\mathbf{a}_1 \mathbf{b}^1 + \mathbf{a}_2 \mathbf{b}^2 + \dots + \mathbf{a}_R \mathbf{b}^R]. \quad (32)$$

The pointer takes a value between zero and one. It is a function of the space, thus describing the influence of the  $R$  shortest chemical time scales on each of the species  $i$  at this particular point in space. When  $D_i$  takes on a value close to unity, species  $i$  is completely influenced by the shortest time scales and is a candidate for being set to steady state. The opposite occurs when  $D_i$  becomes close to zero, the species in question is not being influenced at all by the shortest chemical time scales and thus not being in steady state.

Some species have local pointers for which the value can go from zero to unity within the range of the calculation. These species are treated wrongly if the local pointer of a certain point in space is the basis of the reduction. Thus, the local pointers are integrated over the computational domain  $L$ . The *third step* involves an integration over the space to find the overall value on the influence on the time scale for each species. These integrated pointers are weighted with the species' mole fraction. This is done so that species at high concentrations are not set to steady state, since the resulting errors in calculating their concentrations as steady state species could affect the results too much.

Massias et. al. (Massias et al., 1999b) propose three different integration procedures for capturing the steady state candidates in the most appropriate way. However, they take the form similar to

$$I^I = \frac{1}{L} \int_0^L D_i \frac{1}{X_i} \frac{q_i}{q_{i,\max}} dx, \quad (33)$$

where  $q_i$  is the production rate of species  $i$ ,  $q_{i,\max}$  is the maximum production rate over the computational range, and  $X_i$  is the mole fraction of the species. Caution is in order as both  $X_i$  and  $q_i$  can take on the value zero (inert species), so that small terms  $\epsilon_1$  and  $\epsilon_2$  are added to the respective denominators so as to avoid numerical problems. The  $R$  species with the highest values for  $I^I$  are selected as steady state species. Note that since for most species  $q_{i,\max}$  is situated in the reaction zone, the largest contribution to the integrated pointer comes from the value in the reaction zone since  $q_i / q_{i,\max}$  there is unity.

The elementary reaction rates are integrated over the space in order to determine the  $R$  fastest elementary reaction rates, which can then be eliminated from the system. The fastest reactions that consumes a steady state species, as identified in the previous step, are selected as to be the "fast reaction". For each steady state species, the fastest reaction consuming the species is

found through use of the integral (Massias et al., 1999b):

$$H_k^i = \frac{1}{L} \int_0^L r_{k,i} \quad (34)$$

where  $r_k$  is the reaction rate of the  $k'$ th reaction. The remaining reactions are considered to be the "slow reactions", their reaction rates being retained in the mechanism. This procedure is carried out in order to optimize the computations when a reduced mechanism is applied. This step is not needed for accuracy.

Finally, the rates of the global reactions and their stoichiometric values are determined. The resulting global reactions consist of the major species found in the previous steps, their rates being determined by a linear combination of the rates of the "slow reactions", which depend both on the steady state species and in the non-steady state species.

Obtaining the solutions to the algebraic equations can still require a significant amount of computational time, and the system can still suffer from stiffness problems. If the result obtained in using the reduced mechanisms is found to be discrepant with the results of the detailed mechanism, a truncation is performed. An importance analysis of the reaction rates then can lead to some reaction rates being omitted. This can be understood as being similar to a reaction flow and reaction sensitivity analysis, where for each species the participation rate,  $\epsilon_P$ , of each elementary reaction and its importance rate,  $\epsilon_I$ , are ordered, the corresponding reaction rates for the elementary steps that produce negligible values of both  $\epsilon_P$  and  $\epsilon_I$  being truncated from the steady state relations. In the work of Massias et al. (Massias et al., 1999a) the number of species that needs to be calculated in greater detail after the CSP analysis is said to be small, often only two or three truncations needing to be carried out.

The advantage of CSP calculations in a simple eigenvalue analysis is that it provides information about which species and reactions are associated with the fastest modes. However, the method does not always represent a computationally efficient technique for repeated reduction, since the time saved by eliminating the slowest modes may be outweighed by the time required for recomputing the basis for each time step (Tomlin et al., 1997). The terminology employed in the CSP method to some extent hides the chemical information if this is not analyzed in detail. Skevis et al. (Skevis et al., 2002) provides an excellent presentation of the physical and chemical meaning of the CSP data. In this paper there are tables that show the contribution of the major elementary reactions to the CSP reactions, the slowest reactions moving the trajectories of the physical processes along the manifold created by the fast reactions. In the work, diffusion and convection processes were also included, demonstrating the CSP methodology being as much a tool for characterization of the combustion process as a tool for reduction of chemical mechanisms.

### 3.5 Level of importance

The success of the reduced mechanism depends on the reliability of the selection procedure in selecting steady state species. Whereas the CSP method selects species that take part in the fastest reactions, which is done by solving an eigenvalue problem, the level of importance (LOI) method concerns the individual chemical lifetime of a species - or a *function* of its lifetime - as the selection parameter. The line of argument used is that some species are in steady state as a result of that the reactions consuming the species are very much faster than those producing them. The species, when formed, are thus very short lived and are low in concentration. This approach has been developed by Løvås et al. (Løvås et al., 2000)-(Løvås et

al., 2009). However, the method has been adopted into automatic reduction and optimization tools by e.g. Pepiot-Desjardins and Pitsch (Pepiot-Desjardins & Pitsch, 2008) and Shekar et al. (Shekar et al., 2011).

Since a chemical system is strongly non-linear, carrying out a lifetime analysis requires that the system is linearized around a starting point  $\mathbf{Y}_0$ , which results in the following equation, corresponding to Equation (1) where the spatial operator is neglected:

$$\frac{d\mathbf{Y}}{dt} = \omega(\mathbf{Y}) \implies \frac{d}{dt}(\mathbf{Y} - \mathbf{Y}_0) = \omega_0 + \mathbf{J}(\mathbf{Y} - \mathbf{Y}_0) \quad (35)$$

where the limit at which  $\mathbf{Y} - \mathbf{Y}_0 \rightarrow \mathbf{0}$  and  $\mathbf{J}$  is the Jacobian matrix with respect to the source terms in  $\omega$ . The Jacobian matrix holds information regarding the rate of change in the source terms of the species when a change in species concentrations occur. The error introduced by the steady state approximation to a species  $\Delta Y_i$  is calculated as (Tomlin et al., 1997)

$$\Delta Y_i = \frac{1}{J_{ii}} \frac{dY_i}{dt} \quad (36)$$

The fact that the dimensions of  $J_{ii}$  is  $1/t[\text{sec}]$  means that the inverse of the Jacobian elements,  $1/J_{ii}$ , can be interpreted as the characteristic timescale of the species in question. From Equation (36) it can be seen that a short lifetime, i.e. a small  $1/J_{ii}$ , or a slow rate of change for a species, results in a small error in the calculated concentration.

In line with the argumentation above, and expanding the Jacobi elements accordingly, the chemical lifetime can be expressed as

$$\tau_i = 1 / \frac{\partial \omega_i}{\partial c_i} = \frac{c_i}{\sum_{k=1}^{N_R} (v'_{ik} - v''_{ik}) v'_{ik} r'_k} \quad (37)$$

where  $\omega_i$  represents the species source term in terms of concentrations,  $c_i$  is the species concentration,  $v_{ik}$  is the stoichiometric coefficient, the prime denotes the reactant values, the double prime denotes the product values, and  $r_k$  is the reaction rate at which  $k$  is the Arrhenius reaction coefficient. The chemical lifetime can be understood in these terms as being a measure of how fast a particular species is consumed after being produced. Hence the species with the shortest lifetimes can be selected as steady state species alone. However, species with long lifetimes can still be insensitive to the desired result and can thus be approximated by steady state. On the other hand, species with short lifetimes can still be sensitive and should not be set to steady state. In order to capture these species a combined lifetime and species sensitivity measure termed the *level of importance*, LOI, is defined:

$$(\text{LOI})_i = S_{A,i}^S \vartheta_i \quad (38)$$

where  $S_{A,i}^S$  is the relative species sensitivity, as defined in the previous section, of species  $i$  towards some parameter of interest, such as for example the burning velocity  $v$  or the temperature  $T$ .  $\vartheta_i$  can be chemical lifetime itself,  $\tau$ , or a weighted function of the chemical lifetime:

$$\vartheta_i = \frac{\tau_i^{DW}}{\sqrt{(\tau_i^{DW})^2 + (\tau_F)^2}} \quad \text{where} \quad \tau_i^{DW} = \tau_i \frac{D_i}{D_{N_2}} \quad (39)$$

The lifetime is here weighted to both the diffusion time in a manner similar to which is described for the manual reduction procedure by Equation (19), and the flame time,  $\tau_F$  suitable for premixed flames. It can also be weighted to the scalar dissipation rate,  $a$ , in diffusion flames.

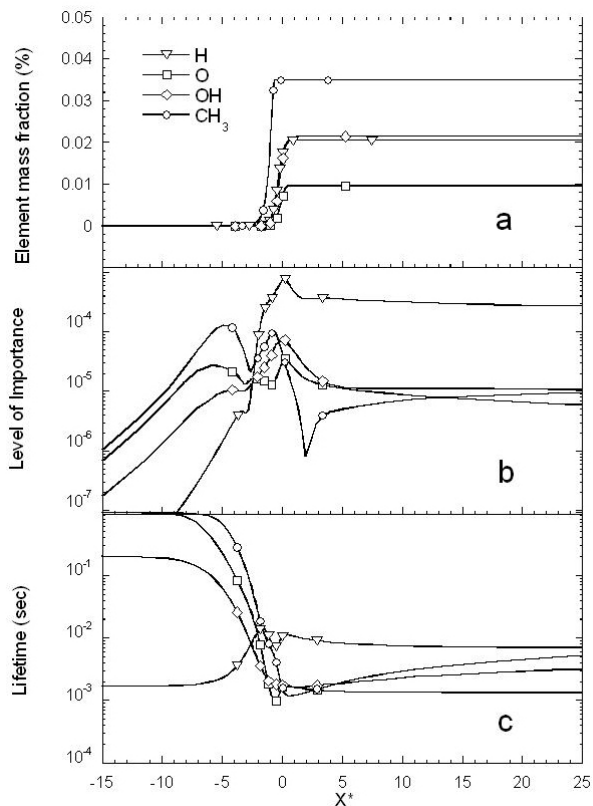


Fig. 5. Selection parameter profiles over the flame zone for a set of species (H, O, OH and  $\text{CH}_3$ ): (a) element mass fraction as a function of the dimensionless flame coordinate  $x^*$ , (b) LOI as a function of the dimensionless flame coordinate  $x^*$ , and (c) weighted lifetime as a function of the dimensionless flame coordinate  $x^*$ . (Løvås et al., 2000)

In Figure (5) the profiles of the selection parameters for various important radicals (H, O, OH and  $\text{CH}_3$ ) in a stoichiometric methane flame have been plotted as functions of the dimensionless flame coordinate  $x^*$  (Løvås et al., 2000). The upper plot shows the element mass fractions as a function of  $x^*$ . After the reaction zone, the species all have high element mass fractions. The threshold limit is most commonly set to 1, leaving only O slightly under the threshold. In the two lower plots, b and c, in Figure (5), the effect of including the sensitivity in the selection procedure is evident. Since during and after the flame zone, the weighted lifetimes are generally short as compared with the cold unburned mixture in which the reactions have not yet started (plot c). An accumulated weighted lifetime over the entire flame zone favors the high values found in the pre-heat zone. However, the sensitivity

contained in the LOI has clearly shown to counteract the high weighted lifetimes found at low temperatures (plot b). The weighted lifetime measure retains the species O, OH and CH<sub>3</sub> as active species, H being set to steady state with a maximum lifetime in the order of 10<sup>-2</sup>. In employing the LOI measure, all the species except H are set to steady state. The high LOI for hydrogen is to a large extent caused by weighting the lifetime to the diffusion. Although H has a relatively high diffusion coefficient as compared with the other species, is nevertheless an important species to retain in the mechanism.

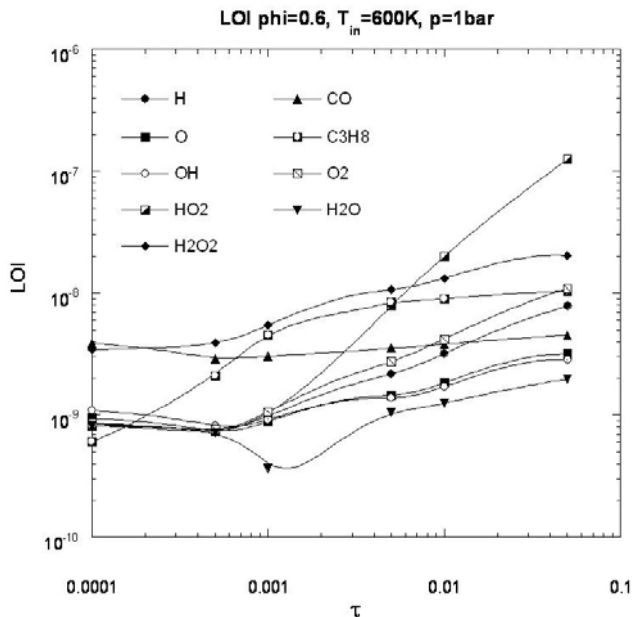


Fig. 6. The evolution of species' LOI as a function of the residence time, shown for certain selected species at a given equivalence ratio in PSR,  $\phi = 0.6$ . (Løvås et al., 2001)

For comparison, Figure 6 shows the evolution of the LOI for an ignition process in a reactor sequence as function of the residence time for a given equivalence ratio in the PSR (Løvås et al., 2001). As the residence time increases, species such as HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and H show a significantly high LOI and are thus retained the mechanism. The effect of the low equivalence ratio is also evident in the dominant role of O. Investigation of the evolution of the LOI as a function of the residence time becomes important when reduced mechanisms are applied in CFD calculations. Many of the CFD simulations model each computational cells as a small perfectly stirred reactor. Thus, the validity of the reduced mechanism needs to be considered over the range set for the CFD calculations. The time scale for the turbulent mixing needs to be included since it affects the chosen residence time for the specific computational cells. Although in the unburned regions, the residence time is much longer than the turbulent mixing times, in the reaction zone the turbulent mixing time is dominant. Thus, varying residence times need to be accounted for when reduced mechanisms are developed for this purpose.

By thorough investigation the optimum conditions for determining the level of importance can be found. For a simple methane flame, the LOI has been calculated from (1) the maximum

accumulated values for the lifetime and the sensitivity, (2) the LOI in the reaction zone and (3) the LOI at the point where the species have a maximum mass fraction. The overall conclusion to be drawn is that the maximum values obtained for the lifetime or for LOI accumulated over the entire range investigated are reliable to some extent, the range involved being over the equivalence ratios, the mixture fractions for the flame calculations, or the time range for the ignition process. However, for the flame calculations a more accurate selection of steady state species is obtained if the values in the reaction zone or the values at maximum species mass fraction are used (Løvås et al., 2009). In ignition situations, the integrated LOI up to the point of ignition, defined as the point of maximum temperature gradient, is found to represent the most appropriate selection parameter (Løvås et al., 2002c). This result is of interest in comparing the LOI with Equation (33), which defines the selection criteria used in the CSP method. The integrated pointers consist of the CSP pointer, a factor weighting it by the species mass fraction and a factor including the production rate of the species. The production rate factor,  $q_i/q_{i,\max}$ , where  $q_i$  is the production rate and  $q_{i,\max}$  is the maximum production rate over the integration range, is unity for most of the species in the reaction zone. Thus, the largest contribution to the integrated CSP pointer comes from that zone, corresponding to the finding that the LOI in the reaction zone is the most appropriate selection parameter.

## 4. Results

In the present section, the results from applications of reduced mechanisms mainly based on skeletal mechanisms and LOI analysis will be presented. For whatever system is chosen the degree of reduction is variable and user defined. It has been found that the strongly reduced mechanisms can be developed for simple premixed flames. Simulating an ignition process however requires a larger set of species in order to predict ignition timing and heat release in an adequate way. If emission rates are of primary concern, however, ignition timing is not necessarily an important feature to investigate. In this section results of developing reduced mechanisms for (i) a diffusion flame configuration, (ii) a reactor sequence for modeling NO emissions and (iii) an ignition process in a SI engine will be presented.

### 4.1 Diffusion flame configuration

In the case of a counterflow diffusion flame, the detailed mechanism in the present example containing 46 species was successfully reduced to 12 species, completely automatically through the LOI and placing restrictions on the element mass fraction, as described above. The chemical kinetic model involves a detailed C<sub>1</sub>-C<sub>2</sub>- mechanism (Bowman et al., 2004). The chemistry of H<sub>2</sub>-O<sub>2</sub>-CO-CO<sub>2</sub> combustion stems from Yetter et al. (Yetter et al., 1991). In the present case, the LOI was based on the values in the reaction zone. The results of applying reduced mechanisms with varying degrees of reduction to the simulation of a counterflow flame in a mixture fraction space of constant scalar dissipation rate and unity Lewis number is shown in Figure (7). According to the upper plot in the figure, the temperature profile over the mixture fraction range is very accurately reproduced. Most species profiles were in close agreement with the detailed mechanism, but some of the C<sub>2</sub>-species showed a discrepancy as a result of all but a few of the C<sub>2</sub>-species being set to steady state. The errors introduced into the computations of these species' concentrations have a knock-on effect on the species that are retained in the mechanism. This is shown in the lower plot in Figure (7). As can be seen for both the temperature profile and the species concentration profiles, the reduced mechanism perform very well as compared with the results from the detailed mechanism.



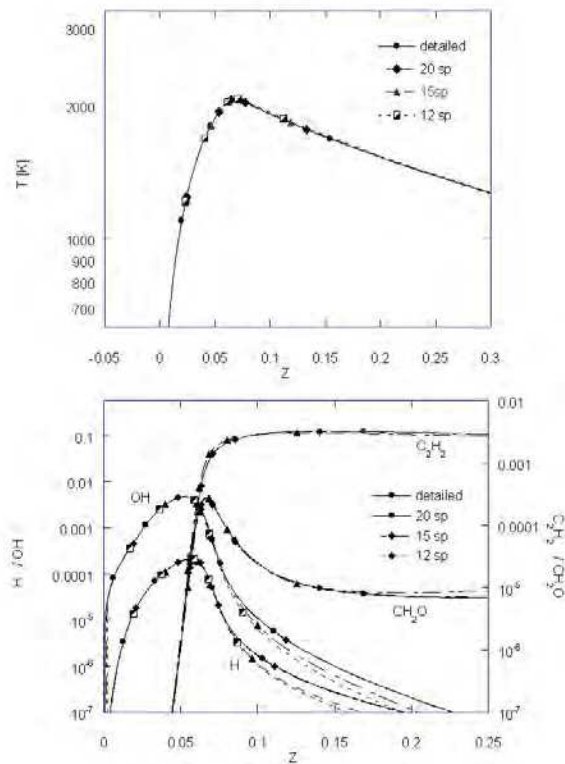


Fig. 7. Results of employing reduced mechanisms for simulating a methane/air counterflow diffusion flame with  $\chi = 0.54$  at 1Bar. The detailed mechanism containing 46 species is reduced to one involving 12 species yet still able to reproduce the features of the flame.

#### 4.2 Reactor sequence

For the simulation of emissions from a staged combustor, the reaction mechanism is extended to include 69 species that interact in 770 different reactions. In order to model NO emissions from such a device, the reactor is fueled with a mixture of ethylene ( $C_2H_4$ ) doped with monomethylamine ( $CH_3NH_2$ ) (Kantak et al., 1997); (Klaus et al., 1997). As stated in the previous section, the steady state species selected varies depending upon whether the lifetime alone or an extended lifetime which includes the species sensitivity is used. A reduction of the mechanism through fully automatic selection in terms of the species' LOI towards NO in the PSR has been carried out and presented by Løvås et al. (Løvås et al., 2001). Figure (8) shows the calculated NO concentrations after the PSR as function of the equivalence ratio. The results were obtained using a reduced mechanism containing as little as 31 of the detailed mechanism, the achieved accuracy of the reduced scheme being within an acceptable level of accuracy as compared with the detailed reaction mechanism. Three of the mechanisms are based on a selection according to chemical lifetime only, whereas the mechanism reduced the most is obtained with the LOI towards NO concentration.

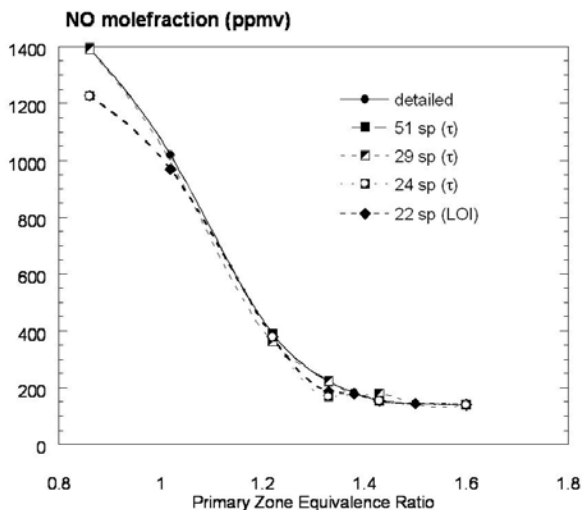


Fig. 8. The NO molefraction as a function of the equivalence ratio in the PSR. Results were obtained for reduced mechanism with increasing degrees of reduction. (Løvås et al., 2001)

### 4.3 SI engine

The degree of reduction depends strongly on the combustion system and on the degree of complexity involved. Ignition processes often require a more detailed mechanism than simple flame configurations. The on-set timing of the ignition is sensitive to the accuracy of species concentrations because of their dependency on the reaction rates.

In Figure (9), temperature and species profile plots obtained in an investigation of autoignition in the end-gas of an SI-engine, known as knock, as presented by Soyhan et al. (Soyhan et al., 2000), are shown. The calculations are obtained in employing a two-zone model (burnt and unburnt zones), the detailed mechanism for iso-octane and n-heptane mixtures being compiled from Chevalier (C<sub>1</sub>-C<sub>4</sub>) (Chavelier, 1993) and Muller (C<sub>5</sub>-C<sub>8</sub>) (Muller et al., 1992), consisting of 75 species and 510 reactions. In the work displayed in the figure, this mechanism was reduced with reaction flow and sensitivity analysis together with LOI. The results obtained with different reduced mechanisms are displayed in the figure, in which they are compared with the results of the detailed mechanism. The skeletal mechanism, obtained on the basis of the reaction flow and sensitivity analysis (denoted "skel" in the figure), was developed prior to the mechanisms from a reduction based on lifetime analysis (denoted "red" in the figure).

In the temperature profile for the end-gas as shown in Figure (9) one can note that at an inlet temperature of 1200K the end gas ignites at around -24 CAD. This is far ahead of the onset of the ignition by the spark plug, and even further ahead of the propagating flame front reaching the wall. Under such conditions, knocking occurs. The presented work concerns the performance of various reduced mechanisms and their performance as compared with the detailed mechanism. The comparison shows that over a large range of physical conditions the profiles of the chemical species and the temperature are the same for the various mechanism, except for changes in the ignition delay times. Thus, the basic characteristics of the detailed mechanism are preserved. The accuracy of the calculation of radicals such as the OH, HO<sub>2</sub>

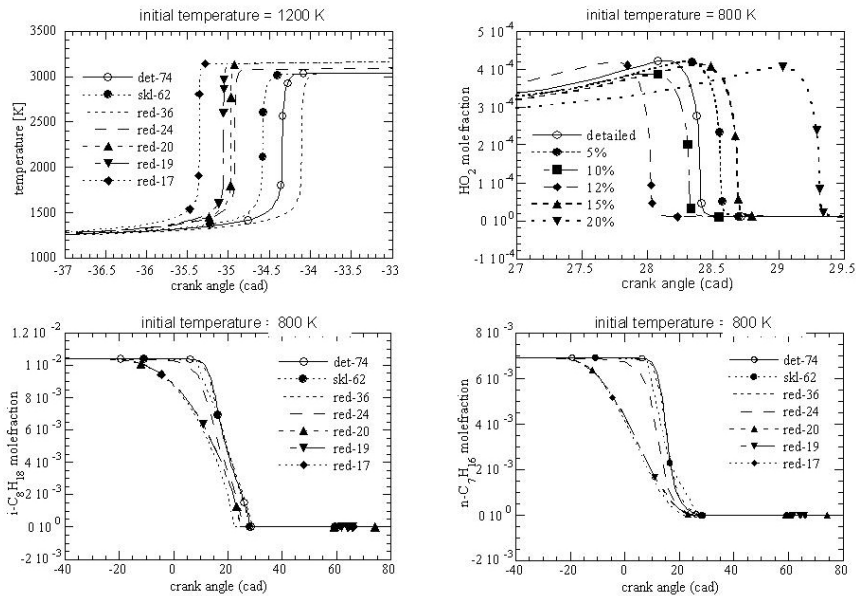


Fig. 9. Calculated temperatures and mole fraction profiles for the end-gas of an SI-engine. Top left: temperature profile, top right:  $\text{HO}_2$  mole fraction representing a radical profile, bottom: fuel profiles, the iso-octane and the n-heptane. Different reduced mechanisms are compared with the detailed and skeletal mechanisms (Soyhan et al., 2000)

and  $\text{CH}_3$  that participate in chain reactions, is important since the formation of  $\text{HO}_2$ , for example, is crucial for the formation of an initial radical pool (Westbrook et al., 1991). The plot at the top left in Figure (9) shows the profiles of  $\text{HO}_2$  that result from employing the skeletal mechanisms as compared with the results from the detailed mechanism for inlet temperatures of 800K. The two lower plots show fuel decomposition as a function of CAD at the same inlet temperature. The plots reveal a close agreement between the reduced and the detailed mechanisms, showing clearly the positive effects on the ignition timing in the end-gas achieved by decreasing the inlet temperature.

The most obvious differences between the various reduced mechanisms in prediction of ignition delay times. Too early an onset of ignition results in both the decomposition of the fuel and the production of the radicals occurring earlier. However, since the errors in the ignition timing are within 1-2 CAD, the mechanisms are seen as performing well within the specified range.

## 5. Application of adaptive kinetics

In contrast to the previously discussed reduction schemes, in which chemical species only are selected if they are in steady state throughout the process, the *adaptive* method allows species to be selected at each operating point or domain separately, generating adaptive chemical kinetics. This is a dynamic reduction procedure that can be employed to ignition systems that are changing over time and to flame systems that change over the flame coordinate. As discussed for the LOI, in some cases the maximum accumulated value over the computational

range was employed, but the values in the reaction zones were found to be a better choice of steady state candidates. However, this means that species that are of importance in the reaction zone are kept throughout the computation, also in regions in which the species may be in steady state. In order to improve the efficiency of the reduction procedure, it is desirable to only consider true steady state species at each point in the calculations. For this reason, methods of reducing the mechanism on-line or adaptively have been developed.

There are two main issues in developing an adaptive reduction procedure. One is the choice of a useful selection criterion for species or reactions to be removed, one that is accurate in selecting the correct species but does not require any considerable amount of CPU time as the analysis is repeated in the course of the computations. For true on-line reduction the selection of steady state species needs to be performed for each operating point or domain, allowing for the fact that species may move in and out of steady state in accordance with their lifetime under the conditions in hand. The second issue is that of implementation into flow codes, the question of how to implement the possibility of a mechanism changing in both size and matter during the simulation.

### 5.1 Selection criteria for adaptive kinetics

The first issue concerning adaptive kinetics is that of the selection criteria. This is rather straight forward for homogeneous ignition scenarios employing adaptive chemistry as only the time evolution of the chemistry needs to be considered. An on-the-fly reduction scheme was proposed by Liang et al. (Liang et al., 2009) for a homogeneous ignition scenario (HCCI), where the basis of the reduction was a modified version of the DRG procedure described earlier. Their procedure removes the locally redundant species from the detailed treatment, and "freezes" their mass fractions in the continuation of the computation. This is performed for each time step through the computation. The DRG analysis is sufficiently efficient that performing this on-line does not outperform the reduction compared to employing the detailed mechanism throughout.

A different approach to a similar problem can be to introduce a separation between vectors for *all* the species, containing specific species data that is kept available in module routines, and dynamic vectors for the *active* species, those being treated in detail. This is the approach proposed by Løvås et al. (Løvås et al., 2002a). The vector of the active species changes during the run according to an array of logicals that hold the information concerning the species' status as steady state. Initially the logicals are assigned their value based on an a priori LOI analysis. The species set to steady state are assigned the logical true such that the species concentrations are to be calculated using algebraic equations instead of the original differential equations. This implies that algebraic equations for *all* the species need to be available in the code for when/if the species is selected to be in steady state. From the list of active species, the source terms are calculated and used to complete the calculations at this point. The combustion process proceeds at each point and the physical conditions change accordingly. This suggests that a new analysis of the species' lifetimes should be performed to allow for modifications in the mechanism so as to account for these changes. The code assesses the new lifetimes based on the inverse of the Jacobian matrix already available; species that has a considerable change in chemical lifetime on the basis of the new conditions being added or removed accordingly. A buffer for numerical inaccuracy needs to be included so as to prevent species with lifetimes very close to the specified threshold limit from systematically going in and out of steady state without adding any accuracy of the computations. Redefining the mechanism at almost every operating point becomes tedious and can mean that the CPU time

saved by applying the reduced mechanism is lost. Figure (10) shows temperature profiles resulting from employing this method of adaptive kinetics with varying threshold limits in selecting steady state species, which result in a greater degree of reduction. The profiles are compared with the corresponding profiles for the detailed mechanism (Løvås et al., 2002a). It is clear that as the level of reduction is increased, the reduced models reproduce the temperature profiles with increasing error. However, it seems to be a very clear cut-off when the reduced adaptive schemes can not reproduce ignition at all.

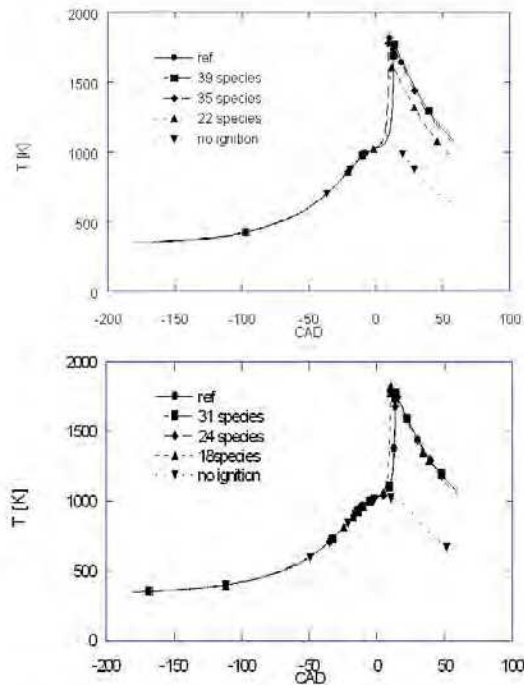


Fig. 10. Temperature profiles of a HCCI engine cycle, employing adaptive kinetics. The upper plot is a result of applying the pure chemical lifetime. The middle plot is a result from applying mass fraction weighted lifetime. The lower plot results from an initial temperature 356K +/- 2K applying mass fraction weighted lifetime. (Løvås et al., 2002a)

For 2D and 3D dynamic simulations such on-line reduction are very computationally costly. A less CPU time intensive approach is to pre-define the combustion domains or zones in which a certain sub-set of the detailed mechanism is used. This is often used for diffusion flame calculations where the domains can be defined by the fuel rich and the fuel lean zones. Hence, schemes that find the smallest chemical sub-set locally in time or space have been proposed e.g. by Schwer et al. (Schwer et al., 2003)). Here each computational cell was assigned a certain sub-mechanism based on a set of physical criteria such as temperature, pressure, species concentrations etc. For highly turbulent flames where these criteria can change rapidly and steeply from cell to cell, this method can be demanding. A single criterion was therefore proposed by Løvås et al. (Løvås et al., 2010), where the sub-mechanism was chosen based on *mixture fraction* alone. This approach will act as example of implementation of adaptive

chemistry into turbulent combustion modeling and will be described in more detailed in the following sub section.

## 5.2 Implementation of adaptive kinetics

When simulation a highly turbulent diffusion flame details regarding both the flow field and the chemical interactions are important. In the present discussion a turbulent ethylene flame is simulated using large eddy simulations (LES). It is not the scope here to discuss the implementation of turbulence models in CFD. However, it can be noted that LES describe the turbulent flow field by resolving the large scales, but employing a sub-grid model for the small unresolved scales. This is a rather CPU intensive approach, and with detailed chemistry the computations becomes cumbersome.

Løvås et al. (Løvås et al., 2010) therefore proposed to combine a hierarchy of methods to simplify the treatment of the chemistry in such large simulations of turbulent combustion. At first it was recognized that the turbulent flow needed a much finer grid than the chemical system. Therefore a coarser "super grid" for the chemistry was imposed onto the spatial CFD grid for which mixing and transport is treated. However, due to the turbulent nature of the flame it was not practical to let the super grid follow the physical 2D or 3D co-ordinates. Instead, the chemistry was solved in the 1D mixture fraction space with the mixture fraction ranging from 0 (pure oxidant) to 1 (pure fuel). The interaction between the turbulent mixing and chemical kinetics are often modeled employing either the flamelet approach (Peters, 1984) or the conditional moment closure (CMC) (Klimenko & Bilger, 1999) method, where the latter was the choice of Løvås et al.

The LES/CMC approach for turbulent reactive flow modeling has already been developed without reduction (Navarro-Martinez et al., 2005). Løvås et al. extended this approach to also include an adaptive chemistry treatment. At first, distinct domains had to be defined using a domain splitting method. In this case the domains were identified in mixture fraction space and the analysis was therefore conveniently limited to one dimension. However, more rigorous automatic domain splitting methods using clustering techniques can be employed (Blurock et al., 2003). Since the choice of selection parameter was the LOI, the mixture fraction space was divided into 4 domains in which the species' LOI was relatively unchanged towards each other. This is illustrated in Figure (11). In this case the cut off limit was chosen such that the number of species was constant throughout the domains. However, the species changed between domains according to the highest ranked species.

Once the domains and the active species within each domain was identified, the RCCE approach described in the previous sub chapter was employed to treat the chemical system. In the LES-CMC code the reduction procedure is implemented on the CMC grid. The adaptive procedure is as follows: the local mixture fraction from the LES-CMC selects the relevant LOI-domain and therefore determines which species are locally leading. The RCCE uses the LOI information to select which species to constrain for a user-given number of constraints and provides a reduced mechanism. Equation (25) is then solved using an iterative Newton solver while non-constrained species are obtained directly from Equation (26). Since concentrations of the non-constrained species are known, the transitions between domains are smooth.

Figure (12) shows the resulting flame simulation based on the LES-CMC LOI-RCCE approach as described above. Employing 4 spatial sub-domains, each with their optimally reduced model for the given conditions (fuel rich, reaction zone, post-reaction zone, and fuel lean)

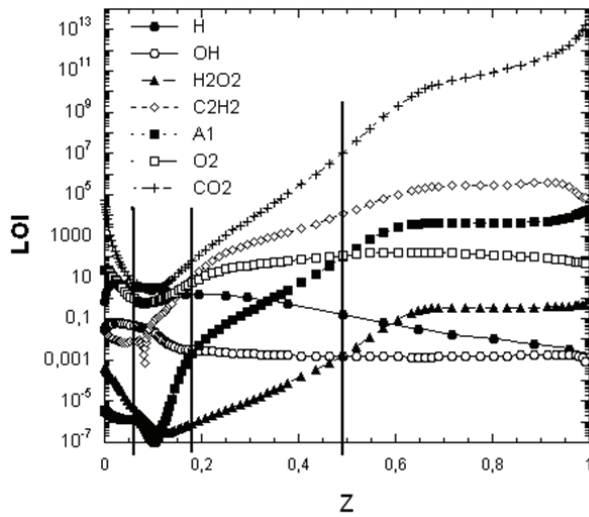


Fig. 11. The LOI profiles for selected species through the flame in mixture fraction space  $Z$ . The vertical lines indicate domain limits. (Løvås et al., 2010)

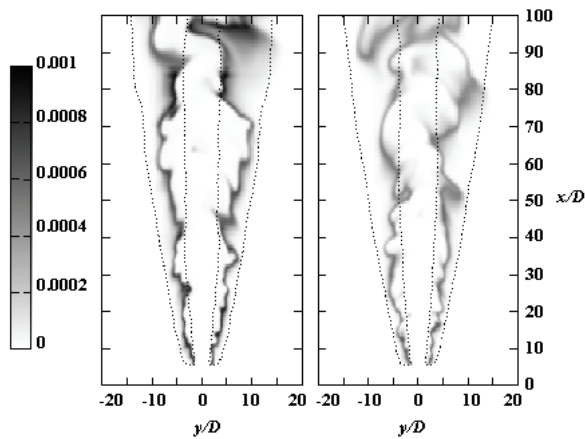


Fig. 12. Instantaneous contour plots of  $H_2$  in a turbulent ethylene diffusion flame resulting from adaptively reduced scheme with 15 species (left) in 4 sub-domains and direct integration of the full mechanism with 75 species (right). Average iso-lines are included to indicate the statistical similarities. (Løvås et al., 2010)

gives excellent correlation to the full treatment. Since these are instantaneous plots, the flame is not identical. However, the averaged values indicated by the stapled lines show clearly the close correlation. It was demonstrated that when adaptive chemistry is employed the number of species that need to be treated in detail is substantially reduced, only true steady state species being selected at each operating point.

## 6. Conclusion

The present chapter intended to outline the main model reduction techniques for chemical systems used in combustion modeling, with the end goal of presenting the recent developments of reducing chemical mechanisms through application of automatic and adaptive procedures. In the past, reduced mechanisms have been used extensively in simulations of combustion processes but they were carried out by hand, which is a tedious process. They were therefore often limited to very specific physical conditions and often represented very simple fuels. However, as chemical models of complex fuels have become very large and detailed, the need for automatic procedures and smart implementation into CFD is evident. These automatic procedures are however based on the ideas of the manual and analytical procedures developed in the past. Although the chapter emphasizes the classic fundamental reduction procedures, it was the goal here to demonstrate the usage of automatic reduction procedures suitable to a wide range of conditions and applicable to realistic multi-component fuels.

It is important to state that this field of research is under constant development, and there are still very promising and interesting techniques being proposed in literature which has not been discussed here. This is not a result of lack of importance, but rather the limitation of space. The reader is therefore encouraged to follow up from here, and based on the current review make a decision in his or her own mind for which approach is the most applicable to the problem in hand.

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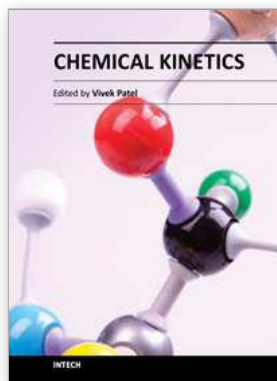


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Chemical Kinetics relates to the rates of chemical reactions and factors such as concentration and temperature, which affects the rates of chemical reactions. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. The book is designed to help the reader, particularly students and researchers of physical science, understand the chemical kinetics mechanics and chemical reactions. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at physical science (mainly chemistry) technologists. Undoubtedly, this book contains "must read" materials for students, engineers, and researchers working in the chemistry and chemical kinetics area. This book provides valuable insight into the mechanisms and chemical reactions. It is written in concise, self-explanatory and informative manner by a world class scientists in the field.

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