REDUCED CHEMICAL KINETICS MECHANISM FOR COMPLEX MIXTURES OF HYDROCARBON/SULFUR/AMMONIA GASES

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Abstract. *Predicting turbulent flow field in industrial incineration equipments requires that simplified chemical reaction mechanisms be developed in a case-by-case basis. In the present paper, reduced chemical kinetic mechanisms are developed, with the objective of capturing part of the time scales involved in a detailed mechanism for a mixture of hydrocarbon, sulfur and ammonia gases. This development is made using a perfectly stirred reactor and an adiabatic thermal explosion (Semenov explosion) model. All representative species involved in the process are considered and different operating conditions are investigated. The computational results highlight the shortcomings and the advantages of the two reduced schemes by comparing with the initial detailed mechanism.*

Keywords: *combustion, perfectly stirred reactor, Semenov explosion*

1. Introduction

Besides from being a major source of energy for the industry, combustion may also be used as means of transforming undesirable, or even toxic, substances in less harmful gases. Predicting pollutant formation is a crucial task of designers of combustion equipment, in the current times of increasingly strict environmental legislation. Industrial furnaces for burning waste gases – containing ammonia and sulfur components, for instance – often involve combustible mixtures of several substances in reactors of complex geometrical configuration. The chemical kinetic mechanism for such mixtures, which are consumed while burning some hydrocarbon with air, is only now being assessed (Hughes et al., 2001a; Hughes et al., 2001b), and the interaction between various intermediate chemical species are subject to controversy. To the best of our knowledge, the accuracy to which the detailed chemical kinetic mechanism of complex mixtures of gases involving hydrocarbon, sulfur and ammonia components (which amount to hundreds of elementary chemical species and several hundred elementary steps) is restricted. Moreover, the complex turbulent flow that arises within industrial burners is, by itself, a difficult modeling subject, since recirculation zones may arise which introduce large scale, sometimes periodic, motions within the combustor. Also, if one of the components is introduced in liquid phase, droplet formation and depletion must be considered, introducing further complications. Even if proper models could be derived for the physical and chemical process involved, the detailed numerical simulation of such equipments is beyond the range of the available computer power in the foreseeable future. As a consequence, predicting the reactive flow in such incineration equipment requires that models be introduced which simplify both the description of the turbulent process and the chemical kinetic mechanism. This works deals with the simplification of chemical reaction mechanism for a mixture of hydrocarbon, sulfur and ammonia gases.

Global reaction schemes (Zel'dovich et al., 1985; Westbrook and Dryer, 1984; Jones and Lindsted, 1988) have been developed by matching values of flame velocities, obtained with Arrhenius-type expressions for the reaction rate, with either experimental or computed results, the latter calculated using detailed chemical reaction mechanisms. These global schemes, which were developed for single reactant mixtures, lack the general nature required for the application in complex mixtures. With the recognition that some of the species present may be in steady state and also that some of the elementary reaction steps may be in equilibrium (Peters, 1985; Peters and Williams, 1987; Peters and Kee, 1987; Sheshadri et al., 1998), several reduced chemical reaction mechanisms were developed for hydrocarbon-air combustion. Also, sensitivity analysis (Brown et al., 1980; Saito and Scriven, 1981), in which critical reaction steps and species are identified, is used in these reduction procedures. However, the complexity of the reduction procedure, which requires the identification of species that are in steady state and reactions that are in equilibrium, increases both with the number of elementary reactions and species involved. This cumbersome procedure has limited application to very large, multi-component, reaction systems. A more general procedure, based on dynamical systems approach, has been developed, which is based on the fact that, once perturbed, a chemically reacting system involving many degrees of freedom rapidly returns to a common trajectory (or atractor), which may be described by a small number of state variables (Maas and

Pope, 1992b; Maas and Pope, 1992a). The "Intrinsically Low-Dimensional Manifolds" seems to be the most popular technique today for performing cost-effective reductions of complex reaction mechanisms, since it offers a general theoretical framework . This technique lacks, however, the ability to detect possible oscilatory modes embedded within the chemical reaction schemes. To cope with this, "Computational Singular Perturbation" methods are currently being developed and applied to various reacting systems (Lu et al., 2001; Sung et al., 2001). These methods, that have been applied to some generic combustion problems, namely the perfectly stirred reactor and the adiabatic flame, involving mixtures of hydrocarbons and air, seem the most promising avenue for the formal reduction of large, multi-component, chemical kinetic mechanisms.

In this paper a simpler reduction technique is considered. Departing from a full mechanism for methane, sulfur and ammonia, species and their associated reactions are eliminated on a result oriented approach. In this approach, the results obtained with the full mechanism for two model reactive systems, the perfectly stirred reactor and the adiabatic homogeneous thermal explosion, are compared with those computed with progressive smaller reaction sets. The elimination of species and reactions is halted when important discrepancies occur in the computed temperatures and reaction times. This procedure results in two different sets of species and reactions, each well adapted for a specific reactive problem. The comparisons performed here evidence the limitations of this approach which, nevertheless, may be used as a starting point for computing reactive turbulent flows.

2. Mathematical Formulation

In this work two elementary combustion problems are considered (Zel'dovich et al., 1985): the perfectly stirred (or homogeneous) reactor (PSR) and the adiabatic, constant pressure, thermal explosion, which is also known as the Semenov explosion.

The first of these systems involves a reactor which is continuously fed by a mixture of fresh unburned gases that immediately mixes with the burnt gases present upon entering the PSR. In the PSR the mixing time is much smaller than the residence time of the combustible mixture (τ). Therefore, the composition of the mixture within the PSR is identical to the one at the reactor outlet and can be directly related to the residence time – or the flow rate of the mixture. The balance equations of species mass are

$$\frac{1}{\tau}(Y_k - Y_k^0) = \frac{\dot{\omega}_k W_k}{\rho} \qquad k = 1,\ldots,K. \tag{1}$$

In this equation, Y_k, $\dot{\omega}_k$ and W_k are, respectively, the mass fraction, the molar production rate and the molecular weight of species k, while K is the total number of species present. The superscript 0 denotes the inflow conditions and ρ is the density of the mixture. Note that, since the PSR is adiabatic, the enthalpy h of the mixture is constant throughout the PSR. Also, the residence time τ is connected to the volume V of the reactor and the mass flow rate $\dot{m}$:

$$\tau = \frac{\rho V}{\dot{m}}. \tag{2}$$

Equation (1) must be supplement by the equation of state

$$\rho = \frac{p}{RT}\left(\sum_{k=1}^{K}\frac{Y_k}{W_k}\right)^{-1}, \tag{3}$$

where p is the pressure (which is constant), R is the universal gas constant, and T is the temperature, which may be computed recalling that

$$h = h^0 = \sum_{k=1}^{K} Y_k \left(\int_0^T c_{pk}dT + h_k^f\right). \tag{4}$$

In this equation, c_{pk} is the specific heat at constant pressure and h_k^f is the heat of formation at 0 K of species k. The actual solution of the PSR involves an equation for the balance of temperature within the reactor derived from Eq. (4). The expressions for c_{pk} and $\dot{\omega}_k$ are calculated using the Chemkin-II package (Kee et al., 1991).

In the Semenov explosion (SE) a vessel containing a homogeneous combustible mixture evolves from an initial state of given temperature, composition an pressure $(T, Y_k, p)^0$ at time $t = 0$ to a final state at time $t = t_f$. In the present work we consider an adiabatic SE only, such that the governing equation for species mass fraction is

$$\frac{dY_k}{dt} = \frac{\dot{\omega}_k W_k}{\rho} \qquad k = 1,\ldots,K, \tag{5}$$

This equation is supplemented by Eqs. (3) and (4).

Table 1: Chemical species involved in the detailed methane/sulfur/ammonia mechanism.

H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_6	C_4H_2	O_2	H_2O
H_2O_2	CO	CO_2	CH_2O	CH_2CO	C	H	CH	CH_2	$CH_2(S)$
CH_3	C_2H	C_2H_3	C_2H_5	C_3H_2	H_2CCCH	H_2CCCCH	O	OH	HO_2
HCO	CH_3O	CH_2OH	HCCO	CH_2HCO	N_2	Ar	CN	HCN	N
NH	NO	HNO	NH_2	H_2NO	NCO	N_2O	NO_2	N_2H_2	HOCN
H_2CN	NNH	NH_3	N_2H_3	C_2N_2	HNCO	S	SH	H_2S	SO
SO_2	SO_3	HSO_2	HOSO	$HOSO_2$	SN	S_2	CS	COS	HSNO
HSO	HOS	HSOH	H_2SO	HOSHO	HS_2	H_2S_2	SO_2^*		

Table 2: Chemical species involved in the reduced methane/sulfur/ammonia mechanism A.

H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	O_2	H_2O	CO	CO_2	CH_2O
CH_2CO	H	CH_3	O	OH	HO_2	HCO	CH_2OH	N_2	NH_3
H_2S	C_2H_5	CH_3O	CH_2HCO	CH_2					

It should be noted that these two systems, namely the PSR and the SE, may be thought as limiting situations of general combustible systems, as far as turbulent mixing is concerned. Indeed, within the PSR, the turbulent mixing is so intense, i.e., the characteristic time of the turbulent mixing is much smaller than the residence time of the mixture, that the chemical reaction is homogeneously distributed throughout the reactor volume. On the other hand, the SE, for which the time variable may be transformed to a space coordinate, may be interpreted as a plug flow reactor, where reactants are continuously fed through an inlet, but no mixing occurs within the reactor. The analysis of these systems provides relevant information with respect to the chemical species which should be retained when mechanism reduction is performed.

3. Chemical Kinetic Mechanisms

Of interest to this work are combustible mixtures of hydrocarbons, sulfur and ammonia related to the incineration of waste gases in oil plants. The initial detailed mechanism which was used was developed specifically to deal with such mixtures and contain not only elementary reactions specific for each of these three type of components, but also reactions which involve interactions between hydrocarbon radicals and sulfur or ammonia radicals (Hughes et al., 2001a; Hughes et al., 2001b). This "full" detailed mechanism involves 78 chemical species and 467 elementary, reversible reactions. This mechanism is too large to be reproduced here, however, the 78 species (including argon, not relevant to this study) are listed in Tab. 1 for completion.

The first reduced mechanism, heretofore called "mechanism A" is obtained by successive elimination of species and considering, for purpose of comparison with the baseline detailed mechanism, only the temperature variation with the residence time τ of the mixture within the PSR. The 25 species remaining after the elimination procedure are given in Tab. (2). Note that, in this mechanism, hydrogen sulfide and ammonia are inert species, retained only for their role in the composition of the mixture, since they have been shown to contribute negligibly to the heat release. However, higher hydrocarbons are needed in order to correctly predict the temperature of the burnt gases, and were kept in the mechanism.

Reduced mechanism B, whose 22 species are shown in Tab. (3) is the outcome of an elimination procedure which compares the temperature history for the SE for different initial conditions. Some of the sulfur and ammonia reactions were found to play a significant role on the induction period of the SE, which led to the consideration of hydrogen sulfide and ammonia dissociation. However, in contrast to the PSR, higher hydrocarbons are not present in mechanism B, since they are not significant during the induction time, even if they may affect the final temperature of the burned gases.

Table 3: Chemical species involved in the reduced methane/sulfur/ammonia mechanism B.

NH_3	NH_2	H	H_2	OH	H_2O	O	HNO	HO_2	NO	N_2
O_2	CO	CO_2	CH_3	CH_4	CH_2O	CHO	H_2S	S	SO	SO_2

4. Results and Discussion

4.1. Baseline results obtained with the detailed chemical scheme

The computations performed consider the two above described elementary systems, namely the perfectly stirred reactor (PSR) and the Semenov explosion (SE), for which are varied the temperature and pressure of the unburned gases for a given composition. The chosen composition, which represents a typical inflow of a methane-rich driven incinerator, is, in volume (or mole) percentage, (CH_4/12.4, O_2/14.4, N_2/54.3, H_2O/16.7, H_2S/1.28, H_2/0.72, CO_2/0.10, NH_3/0.10). The chosen pressure range is $1 < p < 3$bar, while the temperature ranges for the PSR and the SE are $300 < T_0 < 400$K and $1100 < T_0 < 1300$K, respectively. Note that, in the case of the SE, pre-heating of the fresh mixture is needed in order to lead to reasonable reaction times.

In Fig. 1 are given the temperature and the mass fraction of some selected species, computed both for the PSR and for the SE. In the former system, the results are given as functions of the residence time within the reactor, τ, while, in the latter one, the time history of the mixture is given. Note that these are usual representations of these systems (Zel'dovich et al., 1985). Considering first the temperature, this figure shows
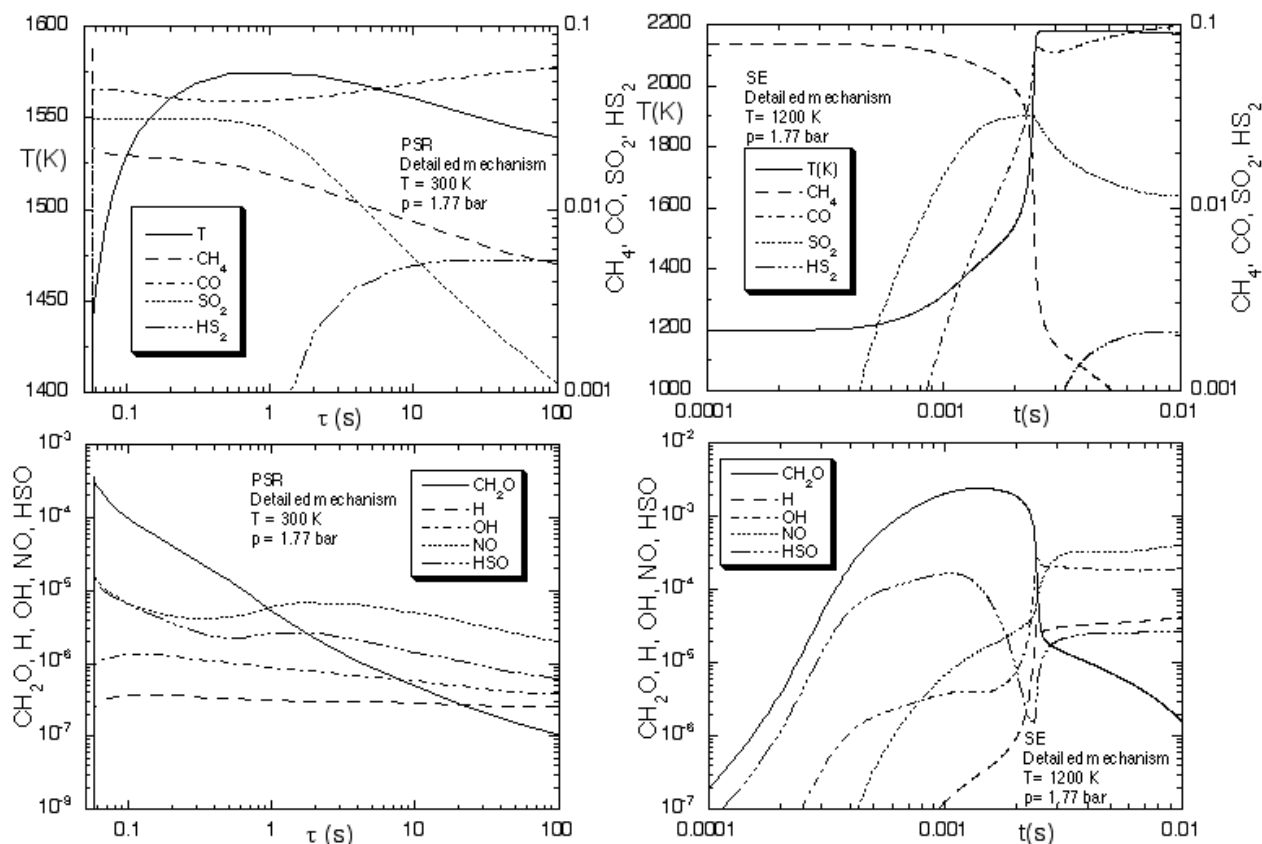

Figure 1: Comparison between the results obtained with the detailed chemical kinetic mechanism for the PSR (left) and for the SE (right), for $p = 1.77$bar and $T_0 = 300$K (PSR) and 1200K (SE).

that both systems exhibit a non monotonous behavior with either τ or t. In both systems, the temperature first increases then decreases to its final equilibrium values with τ or t. Such a fact precludes the use of a global Arrhenius law to describe the chemical heat release, since this simple expression of the chemical transformation leads to temperatures which increase monotonically with the times (τ and t). It could be possible to derive multi-step global reaction schemes to describe the chemical transformation (Jones and Lindsted, 1988). However, such schemes have a limited range of application and require numerous adjustments of the reaction rates coefficients. Moreover, global reaction schemes would be unable to capture the evolution of important chemical species, as far as pollution is concerned, e.g., NO, CO and SO_2. Indeed, the variation of the mass fraction of these species does not have a direct dependence on the temperature of the gases, since it is linked with the various elementary chemical processes they participate in. Understanding the detailed behavior of the pollutant species would require a specific study.

In the case of the SE, it can be noted that the time required for the burned gases to achieve chemical equilibrium is several times larger than the characteristic time of the onset of the exothermic chemical reactions.

Indeed, the temperature begins to increase around $t = 1$ms, however, at $t = 10$ms the temperature is still 2170K, above the equilibrium value of 2160K. This decrease of the burned gases temperature, which occurs after an initial phase of strong chemical heat release, is accompanied by chemical transformations, as can be noted in Fig. 1. As noted above a similar trend of decreasing temperature with increasing residence times (τ) occurs for the PSR, also with a substantial change of minor species mass fractions, even for values of τ of the order of 100s. This slow evolution of the state of the burned mixture could be relevant to the study of pollutant formation, since it is highly likely that in many commercial reactors the burning gases would leave the combustor before attaining the equilibrium conditions, thus leading to further reaction with air.

4.2. Comparisons between the different chemical schemes

The results obtained with both reduced chemical kinetic mechanisms A and B are now compared to those computed with the detailed scheme. Figure 2 gives both the temperature as a function of the residence time within the PSR and the time evolution of the SE, for three different values of pressure and initial temperature, 1, 1.77 and 3bar, 300, 350 and 400K (PSR), and 1200, 1300 and 1400K (SE), respectively. As far as the PSR
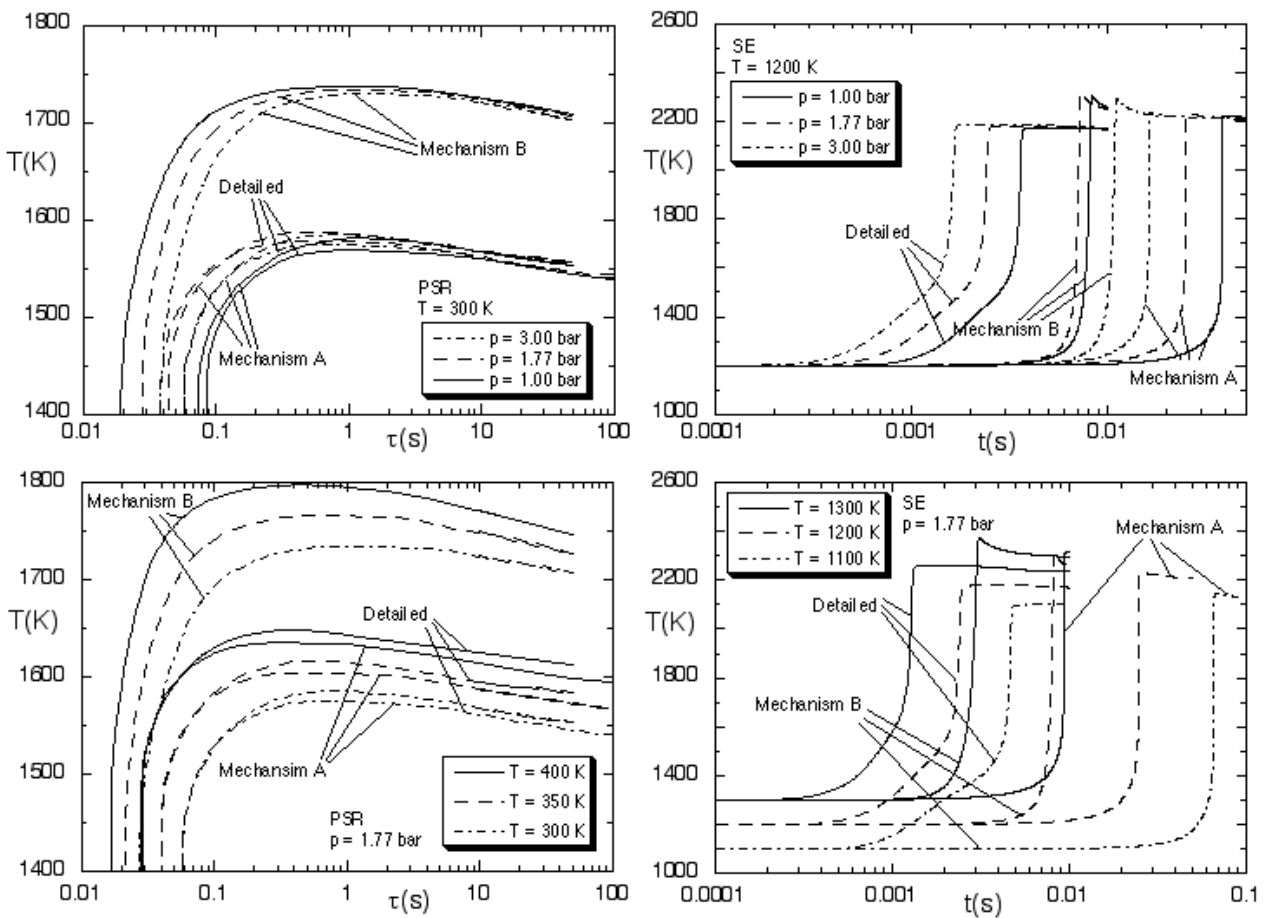

Figure 2: Comparison between the temperatures obtained for the PSR (left) and SE (right), for different chemical kinetic mechanisms, and for different values of pressure and temperature.

is concerned, this figure shows that an excellent agreement is obtained between the reduced mechanism A and the detailed chemical scheme. Indeed this reduced mechanism closely matches (i) the critical residence time τ_{cr} for which the PSR extinction is obtained, (ii) the maximum value of temperature observed for intermediate values of τ and (iii) the temperature at the limit $\tau \to \infty$, all of them with discrepancies smaller than 1%. On the contrary, mechanism B computed temperatures which are more than 10% higher than those obtained with the detailed mechanism, and τ_{cr} is smaller by a factor of 2. It should be emphasized that mechanism A was specifically derived in order to match the PSR detailed scheme results. Therefore, mechanism A retains higher hydrocarbon species as C_2H_2, C_2H_4, C_2H_5, C_2H_6, which play a leading role on the chemical equilibrium (at least for this methane rich mixture), and thus on the behavior of the PSR as $\tau \to \infty$, and the associated elementary reactions. In addition, in order to correctly reproduce the PSR evolution near extinction, species HCO, CH_2O, CH_2OH and CH_3O are required. Mechanism B, which was tailored to match the SE results, does

not contains those species, which explains the poor results obtained.

Figure 2 also shows that the temperature evolution of the SE is much better predicted by mechanism B than by mechanism A. The induction time of the mixture, t_i, which can be loosely defined as the time elapsed from the onset of the computation to the beginning of the temperature rise, is always larger when the reduced mechanisms are used to compute the SE. However, t_i increases by a factor of 2 only when the SE is computed using mechanism B, and by a factor of 10 when chemical scheme A is used. This increase in t_i can be explained by the slower buildup of the radical pool of atomic hydrogen and of radical HO_2. This is illustrated in Fig. 3, which gives, for $p = 1.77$bar and $T_0 = 300$ (PSR) and 1200K (SE), the evolution of selected chemical species. It is clear in this figure that the concentrations of atom H and of HO_2 exhibit the fastest increase, in the case of the SE, for the detailed mechanism and the slowest ones for mechanism A. This is partly due to the
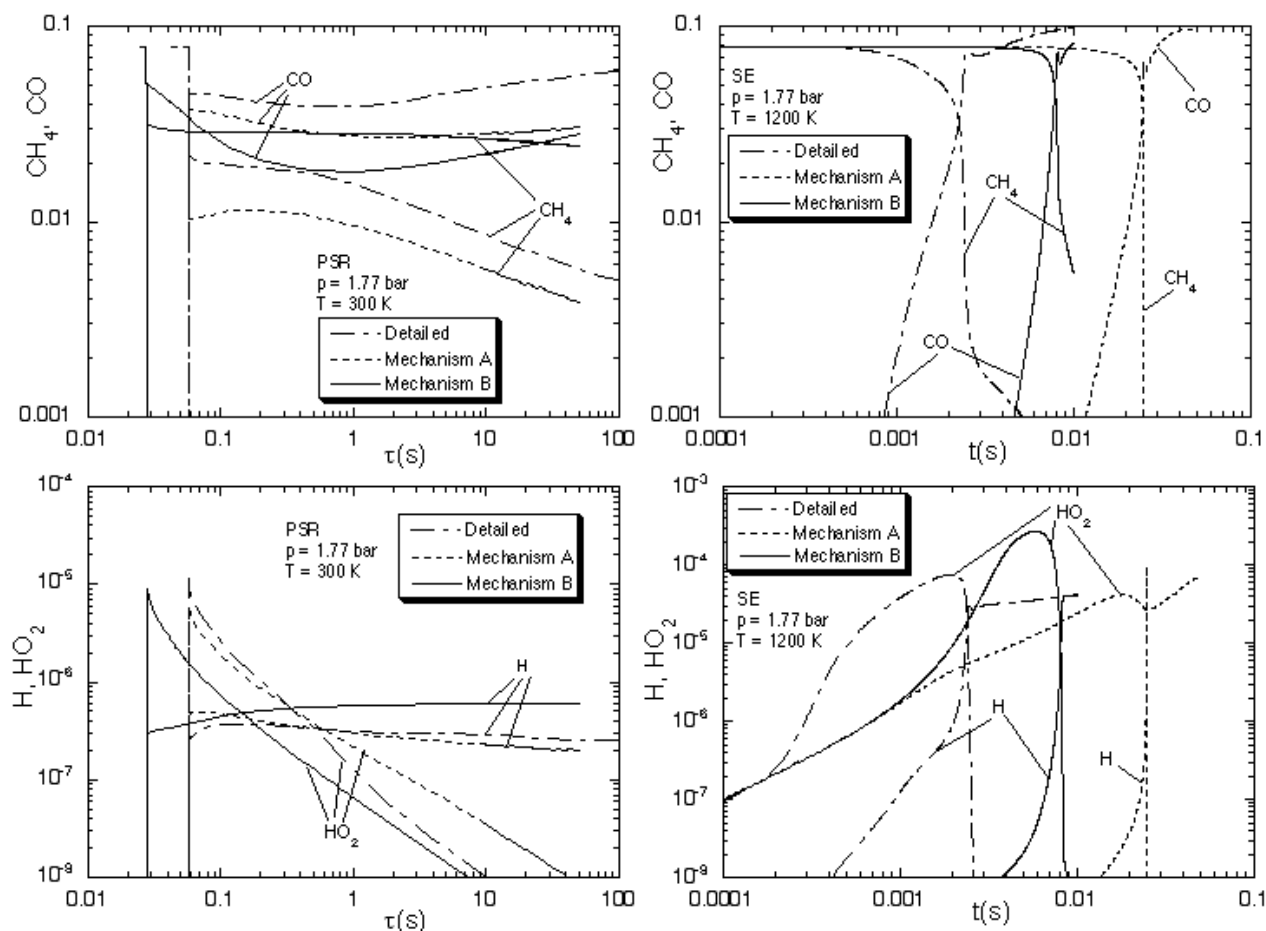

Figure 3: Comparison between CH_4, CO, H and HO_2 mass fractions obtained for the PSR (left) and SE (right), for different chemical kinetic mechanisms, and for $p = 1.77$bar and $T_0 = 300$K (PSR) and 1200K (SE).

possibility, in mechanism B, of the dissociation of ammonia (NH_3), which is absent in mechanism A, and to the aforementioned lack of hydrocarbons in this mechanism which could be formed by using the available atoms of hydrogen. Also, one should bear in mind that the hydrogen atom is highly reactive, and thus is the radical that is responsible for the most efficient breakup of larger molecules, which is materialized by elementary reactions with relatively small activation energies.

Figure 3 also gives the evolution of species CH_4 and CO obtained with the different chemical kinetic mechanisms. In the case of the PSR computations, carbon monoxide mass fractions are underpredicted by both reduced mechanisms by a factor of 1.5 to 2, while CH_4 is, accordingly, overpredicted by mechanism B. Moreover, hydrogen atom mass fractions are overpredicted by a factor of 2-4 when reduced mechanism B is used, since, as discussed above, this mechanism lacks hydrocarbons which could consume part of the H atoms present in the burned gases.

5. Conclusions

Two reduced chemical kinetic mechanisms have been presented, departing from a detailed chemical scheme, for a methane/sulfur/ammonia mixture which is representative of waste gas incineration. The reduced kinet-

ics involves 25 and 22 elementary species, which is significantly less than the original 78 species mechanism. Although not evaluated in this study, such a reduction should, in principle, lead to a factor of 4 in storage requirements and a factor of 16 in computational time in typical combustion programs. The results obtained with the detailed and reduced mechanisms were compared for two simple systems representative of combustion applications, the perfectly stirred reactor (PSR) and the adiabatic thermal explosion (Semenov explosion, SE), using initial conditions for temperature, pressure and composition typical of incineration plants. These results show that the 25 species reduced mechanism is more successful than the 22 species scheme in reproducing the temperature and species computed within the PSR with the detailed mechanism, while the opposite is true for the SE. In particular, discrepancies no larger than 10% are obtained between the temperatures computed within the PSR for the different mechanisms. In the case of the SE, the induction period duration is overestimated by a factor of 2 and 10 by the mechanisms containing 22 and 25 species, respectively. The exact relevance of the results obtained for the computation of the turbulent reactive flows within industrial burners requires a specific study.

6. Acknoledgements

7. References

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