

# Construction of global reduced mechanisms by using the CSP method

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## SUMMARY

*The simulation of the combustion processes is rather complex when detailed mechanisms are used. The reduced mechanisms of reaction with a restricted number of reactions are thus of significant importance. These reduced mechanisms are composed of some steps, which imply a limited number of chemical species. In this paper, the method of CSP [1, 2] was applied to reduce a detailed mechanism GRI-3.0 [3]. To identify the species in stationary state and the fastest elementary reactions, this technique requires as an input the detailed mechanism and the flame model. Based on an algorithm of CSP, several reduced mechanisms with various steps were given. The mechanism with 5-stages is regarded as a base of the other mechanisms with more reactions.*

**Key words:** CSP method, combustion processes, reduced mechanism, flame model.

## 1. INTRODUCTION

The simulation of combustion in internal combustion engines is important in order to make computer-aided design possible as well as to be able to predict pollutant formation and to gain a better understanding of the coupling between the various physical and chemical processes. Accurate simulations of Diesel engines require models for the various processes, such as spray dynamics, ignition, chemistry, heat transfer, etc. as well as the interactions between them, such as chemistry-turbulence interactions, etc. This simulation by using detailed mechanism required very long CPU times and reached the limits of available memory [4]. Thus, the usefulness of reduced mechanisms ranges from decreasing the computational time all the way to making the simulations feasible.

These reduced mechanisms consist of a few steps, involving only a small number of chemical species and the corresponding rates are linear relations among the elementary rates.

The construction of a reduced mechanism requires (i) the identification of the steady state species and the linearly independent elementary reactions that consume the fastest of these species and (ii) simple linear algebra calculations. In the past, constructing a valid reduced mechanism was a tedious and time consuming process, it was made a little easier with the appearance of computer codes being able to handle the linear algebra calculations [5]. These difficulties were surpassed with the development of the algorithmic procedure implemented in the S-STEP algorithm, which is based on CSP and produces reduced mechanisms of arbitrary size [6, 7]. The algorithm is fully automatic, it identifies

the steady state species and fast elementary reactions requiring as an input a simply detailed kinetic mechanism, a reference of numerical solution of the flame and the desired number of global steps in the reduced mechanism. Reduced mechanisms constructed with S-STEP were shown to be very accurate in a wide range of operating conditions [6, 7].

A crucial decision in the construction of a reduced mechanism is the choice of the number of steps included. Of course, the large number of steps in the reduced mechanism gives a higher its accuracy, which can only be tested a posteriori. For practical purposes a good a priori estimate of whether the size of the mechanism provides sufficient accuracy, can be obtained by inspecting the degree by which the chemical process responsible for the fuel breakdown, the heat release and pollutant formation is properly represented [5].

The chemical process represented in the reduced mechanism relates to the slowest chemical time scales. Inspection of the additional chemical process introduced by increasing the steps in the reduced mechanism will reveal additional dynamics of the flame [5].

In this work, we reduced the detailed mechanism of the methane combustion in air (GRI-3.0) by using the method of CSP. The discussion will be based on a number of reduced mechanisms for laminar premixed methane-air flame produced with S-STEP. In the following, reduced mechanisms of different sizes (involving 5 to 10 steps) will be presented and discussed.

## 2. PREMIXED FLAME EQUATIONS

Upon neglecting viscous effects, body forces, radiative heat transfer, and the diffusion of heat due to the concentration gradients, the equations governing steady, isobaric, one-dimensional flame propagation may be written as follows [8]:

Continuity equation:

$$\dot{M} = \rho u A \quad (1)$$

Energy equation:

$$\begin{aligned} \dot{M} \frac{dT}{dx} - \frac{1}{C_p} \frac{d}{dx} \left( \lambda A \frac{dT}{dx} \right) + \\ + \frac{A}{C_p} \sum_{k=1}^K \rho Y_k V_k C_{pk} \frac{dT}{dx} + \frac{A}{C_p} \sum_{k=1}^K \dot{\omega}_k h_k W_k = 0 \end{aligned} \quad (2)$$

Species equation:

$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0, \quad k = 1, \dots, K \quad (3)$$

Equation of state:

$$\rho = \frac{P \bar{W}}{RT} \quad (4)$$

In these equations,  $x$  denotes the independent spatial coordinate;  $\dot{M}$  is the (constant) mass flow rate;  $T$  is the temperature;  $Y_k$  is the mass fraction of the  $k$ -th species (there are  $K$  species);  $P$  is the pressure;  $u$  is the velocity of the mixture;  $\rho$  is the mass density;  $W_k$  is the molecular weight of the  $k$ -th species;  $\bar{W}$  is the mean molecular weight of the mixture;  $R$  is the universal gas constant;  $\lambda$  is the thermal conductivity;  $c_p$  is the constant pressure heat capacity of the mixture;  $c_{pk}$  is the constant pressure heat capacity of the  $k$ -th species;  $\dot{\omega}_k$  is the molar rate of production by chemical reactions of the  $k$ -th species per unit volume;  $h_k$  is the specific enthalpy of the  $k$ -th species;  $V_k$  is the diffusion velocity of the  $k$ -th species; and  $A$  is the cross-sectional area of the stream tube encompassing the flame. The flame problem is posed on the finite interval  $0 \leq x \leq L$ . The boundary conditions assume fixed values on the left boundary and zero fluxes on the right:

$$T(x=0) = T_b, \quad Y_k(x=0) = \varepsilon_k(0) \quad k = 1, \dots, K \quad (5)$$

$$\left( \frac{dT}{dx} \right)_{x=L} = 0, \quad \left( \frac{dY_k}{dx} \right)_{x=L} = 0 \quad k = 1, \dots, K \quad (6)$$

where  $T_b$  is the temperature of the unburned gas, and the known mass flux fraction of the  $k$ -th species is defined as:

$$\varepsilon_k = Y_k + \frac{\rho Y_k V_k}{\dot{M}} \quad (7)$$

while  $K$  indicates the total number of species implied in the detailed mechanism (GRI-3.0). The problem cannot be resolved analytically, a numerical approach is indispensable.

The results were obtained for the following operating conditions: the pressure is taken equal to the atmospheric pressure (1 atm), the initial temperature is constant and equal to 300K; the fuel is only made of methane. The equivalence ratio  $\phi$  of mixture is considered equal to the unit (stoichiometric mixture).

## 3. DETAILED MECHANISM USED

In this work, the detailed mechanism GRI 3.0 was used as the basis for the construction of the reduced methane combustion [3]. This mechanism has been optimized by experimental data at low and high pressures for ignition delays, perfectly stirred reactors and laminar flames and it is considered to be one of the most up-to-date detailed mechanisms concerning methane combustion and nitrogen oxides formation. This mechanism involves 325 reactions, 53 species and 5 elements (i.e  $K=325$ ,  $N=53$ ,  $E=5$ ), included  $C_2$  species, prompt and thermal  $NO$ , and nitrous oxide chemistry.

#### 4. THE CSP ALGORITHM

The construction of the reduced mechanisms by CSP starts with the choice of the desired number of global steps, say  $S$ , and follows the steps outlined below [7]:

**Step 1:** A numerical solution of the flame structure with a suitable detailed mechanism is obtained, on which the CSP analysis is performed. It is anticipated that the reduced mechanism will be accurate in a range of conditions close to those of the detailed kinetics solution.

**Step 2:** Given the desired number of global steps,  $M=N-S$  steady-state species must be identified, where  $N$  is the total number of species in the detailed mechanism. For this purpose, CSP analysis is performed at each grid point providing the CSP pointer of each species  $i$ ,  $D_i(x)$ , which is a function of space and takes a value between zero and unity. In physical terms, the CSP pointer is a measure of the influence of the  $M$  fastest chemical time scales on each of the species. When  $D_i(x)=1$ , the  $i$ -th species are completely influenced by the fastest scales and are the best candidates to be a steady state. In contrast, when  $D_i(x)=0$ , the fast time scales have no effect on the  $i$ -th species and cannot be identified as a steady state.

**Step 3:** The local pointer  $D_i(x)$  is integrated across the flame using the local species net production rate and species mole fraction as a weighted factor, to give an 'integrated CSP pointer' for each species by the following expression [6, 7]:

$$I_i = \frac{1}{L} \int_0^L D_i(x) \frac{|q_i(x)|}{|q_i|_{max} X_i(x)} dx \quad (8)$$

where  $|q_i|$  is the net species production rate,  $|q_i|_{max}$  is the corresponding maximum inside the calculation domain of length  $L$  and  $X_i$  is the species mole fraction. In contrast to the CSP pointers, the scalars  $I_i$  can take any value between zero and infinity. As it was discussed in Ref. [4], the weighting by the mole fraction is consistent with the traditional criterion of taking low-concentration species as the steady state ones. The quantities  $I_i$  for each species are ordered and the  $N-M$  species with the lowest values are taken as major (non-steady-state) species. The  $M$  species with the largest values are identified as steady-state species. The major species for the various sizes of reduced mechanisms were presented in Table 1.

**Step 4:** The rate of each elementary reaction is integrated along the flame. The reactions that consume the steady-state species (step 3) and exhibit the largest integrated rate are selected and deemed the fast reactions (the rest are slow). For  $M$  steady-state species,  $M$  fast reactions are selected.

**Step 5:** Based on the results of steps 3 and 4, the stoichiometry and rates of the global reactions are compiled following Refs. [6, 7]. The reduced

mechanism consists of the global steps involving the major species and the corresponding global rates, which are expressed as linear combinations of the slow elementary rates. These rates depend, of course, on all species, steady state and non-steady state. The former are calculated from the solution of a system of steady-state algebraic relations with the inner iteration procedure.

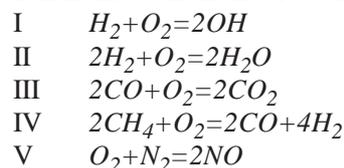
**Step 6:** The accuracy of the reduced mechanism constructed by steps 1-5 might not be the optimum one. Frequently, abnormally high concentrations are encountered for some steady-state species, which might result in low accuracy. This problem is solved by comparing the relative contributions of each elementary reaction to the total production rate of the species from both the reduced and detailed mechanisms. If large discrepancies exist, the corresponding elementary rates are truncated from the steady-state relations. Typically, only two to three truncations are necessary.

Table 1. The major species for  $S=5$  to 10

$S=5$	$S=6$	$S=7$	$S=8$	$S=9$
				<b>HCN</b>
			<b>O</b>	<b>O</b>
		<b>H</b>	<b>H</b>	<b>H</b>
	<b>N<sub>2</sub>O</b>	<b>N<sub>2</sub>O</b>	<b>N<sub>2</sub>O</b>	<b>N<sub>2</sub>O</b>
<b>NO</b>	<b>NO</b>	<b>NO</b>	<b>NO</b>	<b>NO</b>
<b>OH</b>	<b>OH</b>	<b>OH</b>	<b>OH</b>	<b>OH</b>
<b>CH<sub>4</sub></b>	<b>CH<sub>4</sub></b>	<b>CH<sub>4</sub></b>	<b>CH<sub>4</sub></b>	<b>CH<sub>4</sub></b>
<b>H<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>H<sub>2</sub></b>
<b>O<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>O<sub>2</sub></b>
<b>CO</b>	<b>CO</b>	<b>CO</b>	<b>CO</b>	<b>CO</b>
<b>H<sub>2</sub>O</b>	<b>H<sub>2</sub>O</b>	<b>H<sub>2</sub>O</b>	<b>H<sub>2</sub>O</b>	<b>H<sub>2</sub>O</b>
<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>
<b>N<sub>2</sub></b>	<b>N<sub>2</sub></b>	<b>N<sub>2</sub></b>	<b>N<sub>2</sub></b>	<b>N<sub>2</sub></b>
<b>AR</b>	<b>AR</b>	<b>AR</b>	<b>AR</b>	<b>AR</b>

#### 5. GLOBAL REDUCED MECHANISMS OBTAINED

A five-step mechanism, generated on the basis of the full flame domain involves the following steps:



Reaction I describes the formation of the oxyhydrogen pool, while reactions II and III describe the hydrogen to water and carbon monoxide conversions. Reactions IV describe the major fuel breakdown process, in the main reaction zone, to hydrogen and carbon monoxide. Reaction V describes the thermal  $NO$  pathway, which is a dominant  $NO$  formation path, due to the higher temperature involved (see Figure 1). These four steps I, II, III, and IV are almost identical to the four-step mechanism for methane oxidation proposed by Peters in Ref. [9] with

one notable exception. In fact, the  $H$  radical is now assumed to be in a steady-state while  $OH$  is included as a major species [6]. The latter is usually associated with reduced mechanisms for lean flames but its inclusion here is equally justifiable since the detailed kinetic computations show that in the stoichiometric flame  $OH$  radical levels are generally more than an order of magnitude higher than  $H$  radical levels and persist in significant concentrations well into the post-flame zone (see Figure 2).

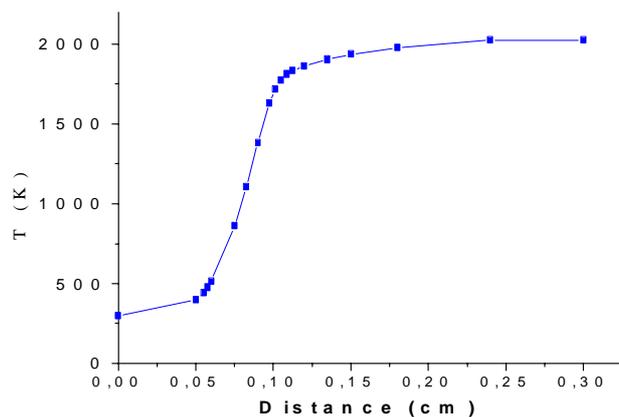


Fig. 1 The temperature vs  $x$ ,  $\phi=1$ ,  $T_u=300$  K, and  $P=1$  atm

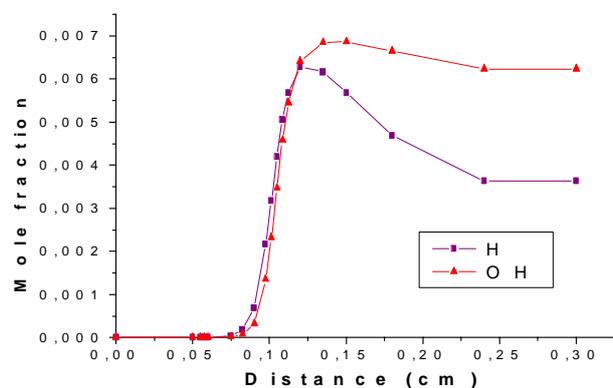
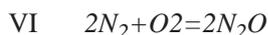
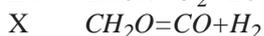
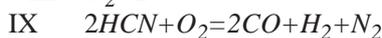


Fig. 2 The mole fractions of  $OH$  and  $H$  vs  $x$ ,  $T=300$  K and  $P=1$  atm

Reduced mechanisms of larger size can readily be constructed by successively adding one more step, related to the slowest of the chemical timescales of the process not represented in the existing reduced mechanism. A six-step mechanism is produced with the inclusion of a nitrous oxide  $N_2O$  pathway:



Seven, eight, nine, and ten-step mechanisms are successively constructed by including steps for the important hydrogen ( $H$ ), oxygen ( $O$ ), hydrocyanic ( $HCN$ ) and formaldehyde ( $CH_2O$ ) respectively:



Analysis of the global reduced mechanism can in particular shed light on differences between various flames with respect to important issues such as the major fuel breakdown process, the generation of the oxyhydrogen pool and  $NO_x$  formation. Thus, in the case of the stoichiometric flame, the fuel breakdown process is solely described by the molecular oxygen attack to methane leading to  $CO$  formation. Intermediate hydrocarbon species are associated with fast time scales due to the large reaction rates characteristic for the high temperature stoichiometric flame and thus their evolution is largely controlled by the chemistry of species associated with slower time scales including the  $H$  and  $OH$  radicals.

## 6. CONCLUSIONS

Reduced mechanisms for methane-air flames are constructed by using CSP and the GRI-3.0 detailed chemistry. Based on the CSP algorithm, the major species for the various sizes of reduced mechanisms were specified by integrating the CSP pointer and after determination of fast reactions corresponding to these major species, the reduced mechanism is constructed.

We conclude that the five-step reduced mechanism contains four-reactions (I, II, III, IV) that are almost identical to the four-step mechanism for methane oxidation proposed by Peters and one Zeldovich reaction (IV). This five-step mechanism is considered as a basis of the other mechanisms (6, 7, 8, 9, 10-step).

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## APPENDIX

List of symbols:

- $A$  - Cross-sectional area of the steam tube encompassing the flame ( $m^2$ )
- $c_p$  - Specific heat at constant pressure of gas mixture ( $J/kgK$ )
- $c_{pk}$  - Specific heat at constant pressure of the  $k$ -th species ( $J/kgK$ )
- $h_k$  - Specific enthalpy of the  $k$ -th species ( $J/kg$ )
- $K$  - Total number of species
- $M$  - number of steady-state species
- $\dot{M}$  - Mass flow rate
- $P$  - Pressure ( $Pa$ )
- $T$  - Temperature ( $K$ )
- $S$  - number of steps in reduced mechanism
- $u$  - Velocity of the fluid mixture ( $m/s$ )
- $V_k$  - Diffusion velocity of the  $k$ -th species ( $m/s$ )
- $\bar{W}_k$  - Molecular weight of the  $k$ -th species ( $kg/mole$ )
- $\bar{W}$  - Mean molecular weight of a mixture ( $kg/mole$ )
- $x$  - Spatial coordinate ( $m$ )
- $X_k$  - Mole fraction of the  $k$ -th species
- $Y_k$  - Mass fraction of the  $k$ -th species
- $\epsilon_k$  - Inlet mass fraction of the  $k$ -th species
- $\lambda$  - Thermal conductivity of the gas mixture ( $W/mK$ )
- $\rho$  - Mass density ( $kg/m^3$ )
- $\dot{\omega}$  - Production rate of the  $k$ -th species ( $mole/m^2s$ )

## KONSTRUIRANJE GLOBALNO REDUCIRANIH MEHANIZAMA POMOĆU CSP METODE

### SAŽETAK

Simulacija procesa sagorijevanja je prilično složena kada se koriste detaljni mehanizmi. Reducirani mehanizmi s ograničenim brojem reakcija su od velike važnosti. Ovi reducirani mehanizmi sastoje se od nekoliko faza koje uključuju ograničen broj kemijskih vrsta. U ovom radu je, za redukciju detaljnog mehanizma GRI-3.0 [3], primijenjena metoda CSP [1, 2]. Za prepoznavanje vrste u nepomičnom stanju i najbrže elementarne reakcije ova tehnika zahtijeva, kao ulazne podatke, detaljni mehanizam i model plamena. U ovom radu pokazano je nekoliko reduciranih mehanizama u različitim fazama, a zasnivaju se na jednom algoritmu CSP metode. Mehanizam s 5 faza smatra se osnovom drugih mehanizama s više reakcija.

**Ključne riječi:** CSP metoda, proces sagorijevanja, reducirani mehanizam, model izgaranja.