

Investigation and reduction of two methane combustion mechanisms

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Analyses of two methane oxidation mechanisms, the GRI mechanism (version 3.0) and the Leeds Methane Oxidation Mechanism (version 1.4), are reported here. Laminar premixed flames were simulated using program PREMIX, and redundant species and the redundant reactions were identified by program KINALC. Two series of reductions were carried out, where the aims were (i) the reproduction of flame speed, flame temperature and major species concentrations and (ii) the reproduction of also the concentrations of radicals that play an important role in NO_x production. The two mechanisms were investigated at fuel lean, stoichiometric and rich conditions. More than one hundred reactions could be eliminated in each case. Simulation results obtained by the reduced mechanisms differ by a few percent only from that calculated by the original mechanisms.

1. Introduction

Oxidation of methane is maybe the most important combustion reaction, because the main component of natural gas is methane and its combustion is of great economical importance. Several reaction mechanisms have been developed for the description of methane combustion. In this work, analyses of two methane oxidation mechanisms, the GRI mechanism (version 3.0) [1] and the Leeds Methane Oxidation Mechanism (version 1.4) [2, 3] are reported. These mechanisms are very large (36 species and 422 reactions and 37 species and 351 reactions, respectively) and are able to reproduce a wide range of experimental data with similarly good accuracy. Most reaction steps in these mechanisms are identical, but the temperature and pressure dependence of rate coefficients are usually described by very different parameters [3] and also a part of

the reaction steps are different. Since similar simulation results are given by different mechanisms, a parallel analysis of the two mechanisms is expected to reveal seminal information on methane combustion.

2. Methods and aims of the mechanism reduction

Concentration-time curves in spatially homogeneous chemical kinetic systems can be calculated by solving the following initial value problem:

$$dc/dr = f(c, k); \quad c(0) = c_0,$$

where c is the vector of concentrations, k is the vector of parameters and f is the right hand side of the system of kinetic differential equations. In partial differential equations describing flames or other spatially inhomogeneous systems, f is the chemical source term.

Almost all published reaction mechanisms contain species, called redundant species, which can be eliminated from the mechanism without any change of the calculated concentration profiles of important species. The modeller has to define which species are considered to be important. In our analysis, redundant species were identified by the exploration of kinetic connections [4] between species via the study of the Jacobian

$$J = (\partial f / \partial c).$$

Principal component analysis of matrix

$$F = (\partial f / \partial k)$$

was used for the identification of the redundant reactions [4]. All mechanism analysis and reduction calculations were based on program KINALC [5].

Two series of reductions were carried out, where the aims were (i) the reproduction of flame speed, flame temperature and major species concentrations and (ii) the reproduction of also the concentrations of radicals that play an important role in NO_x production. In the first case the reduced mechanism was called the 'first level' mechanism, in the second case the 'second level' mechanism. The important species were on the 1st level CH_4 , O_2 , H_2O , CO_2 , and CO , and on the 2nd level the previous list was complemented by species OH , CH and CH_2 .

The reaction mechanisms were investigated without NO_x chemistry to study the pure methane oxidation kinetics. The Leeds Methane Oxidation Mechanism contains the methane oxidation reactions only and the nitrogen reactions are provided in a separate block. The GRI 3.0 mechanism contains also nitrogen chemistry species and reactions, and they were eliminated by using program MECHMOD [6].

The reduced mechanisms were required to reproduce the full mechanism results with the following accuracy: 5% deviation was allowed for the mole fractions of species, 2% deviation for flame velocity and 10 K deviation for the calculated temperature.

Laminar premixed flames of lean, stoichiometric and rich methane/air mixtures were simulated using program PREMIX [7] of the CHEMKIN package [8]. The fuel-to-air ratios were 0.619, 1.0 and 1.35, respectively. Mechanism analysis was carried out at concentration sets belonging to several temperatures, from the start of chemical changes to maximum flame temperatures, at each fuel-to-air ratio. Reactions, important at each temperature, provided the list of reactions important at a given fuel-to-air ratio. Reactions, important at all fuel-to-air ratios, were considered to be important for methane flame simulations. The Leeds Mechanism does not reproduce well [3] the experimental flame velocity if the fuel-to-air ratio is higher than 1.2, therefore analysis of this mechanism at $\phi = 1.35$ was omitted.

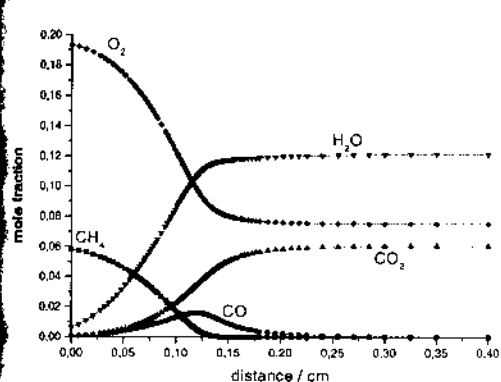


Fig. 1. Mole fraction vs. distance curves of the important species (Leeds Mechanism, 2nd level).

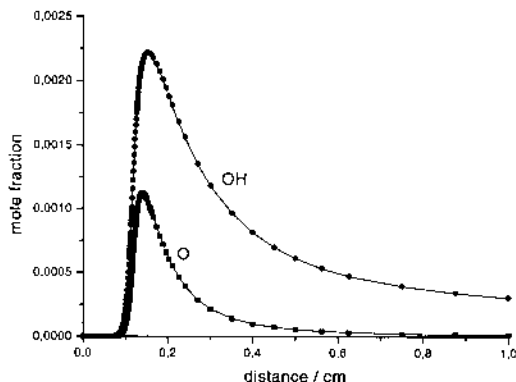


Fig. 2. Mole fraction vs. distance curves of two important radicals (Leeds Mechanism, 2nd level).

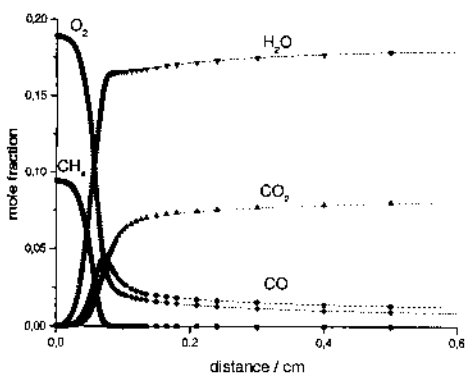


Fig. 3. Mole fraction vs. distance curves of the important species (GRI 3.0 Mechanism, 1st level).

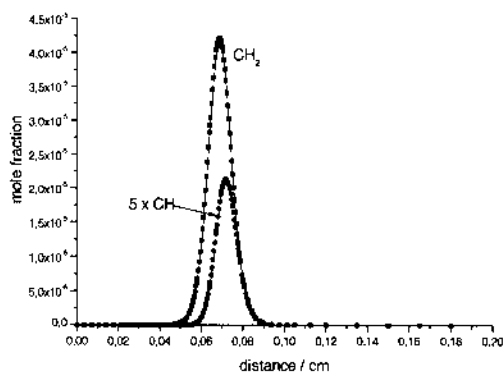


Fig. 4. Mole fraction vs. distance curves of two important radicals (GRI 3.0 Mechanism, 2nd level).

Table 1

Summary of results for the GRI 3.0 mechanism reduction.

mechanism	number of species	number of irreversible reactions	maximum deviation		
			T, ν_i	important species	important radicals
Original GRI 3.0 Mechanism	36	422	-	-	-
1 st level reduced, $\Phi=0.619$	29	125	1K, 0.4%	identical	-
1 st level reduced, $\Phi=1.0$	29	181	7K, 0.9%	CO 6%	-
1 st level reduced, $\Phi=1.35$	28	172	1K, 2.0%	CH ₄ 5%	-
1 st level reduced, united	29	221	-	-	-
2 nd level reduced, $\Phi=0.619$	29	164	0K, 0.5%	identical	O 0.5%, OH 2.0%, CH 3.2%, CH ₂ 1.0%
2 nd level reduced, $\Phi=1.0$	36	256	3K, 0.5%	CO 1.8%, CO ₂ 0.2%	O 3.9%, OH 1.7%, CH 0.7%, CH ₂ 1.9%
2 nd level reduced, $\Phi=1.35$	36	250	1K, 0.9%	H ₂ O 0.2%, CO 0.8%, CO ₂ 1.0%	O 2.2%, OH 1.7%, CH 3.0%, CH ₂ 3.1%
2 nd level reduced, united	36	302	-	-	-

Table 2

Summary of results for the Leeds Mechanism reduction.

mechanism	number of species	number of irreversible reactions	maximum deviation		
			T, ν_i	important species	important radicals
Original Leeds Mechanism v.1.4	37	351	-	-	-
1 st level reduced, $\Phi=0.619$	29	171	1K, 1.0%	CO 0.4%	-
1 st level reduced, $\Phi=1.0$	29	123	1K, 1.5%	H ₂ O 0.2%, CO 1.5%, CO ₂ 0.3%	-
1 st level reduced, united	29	178	-	-	-
2 nd level reduced, $\Phi=0.619$	34	200	0K, 0.1%	identical	O 0.6%, OH 1.8%, CH 3.5%, CH ₂ 0.8%
2 nd level reduced, $\Phi=1.0$	33	180	0K, 1.5%	CO 1.4%, CO ₂ 1.3%	O 16.0%, OH 7.0%, CH 6.2%, CH ₂ 0.4%
2 nd level reduced, united	34	213	-	-	-

3. Mechanism reduction results

Simulation results for the full (lines) and the corresponding reduced mechanisms (symbols) are compared in Figures 1 to 4. These figures demonstrate that there is always an excellent agreement between the two mechanisms.

Tables 1 and 2 show the mechanism reduction results for GRI 3.0 mechanism and Leeds mechanism, respectively. The last three columns of the tables contain the maximum deviation of the reduced mechanisms with respect to the calculated temperature, and to the concentrations of important major species and important radicals. Redundant species could be eliminated from both mechanisms at the 1st level reduction, but such species were found at the 2nd level reduction in Leeds mechanism only. In case of both mechanisms, almost half of the reactions could be eliminated without significant change of flame speed, flame temperature and important species concentrations. Reduced mechanisms that were able to calculate NO_x production accurately were much larger, but still more than one hundred reactions could be eliminated from both mechanisms.

4. Conclusions

Two recently created, up-to-date methane oxidation mechanisms were analysed. Both mechanisms were found to contain a large number of redundant species and reactions. The reduced mechanisms contained less than half number of reactions, but provided almost identical simulation results compared to the original mechanisms. Presence of redundant species and reactions in reaction mechanisms increase the computational burden and obscure the chemical understanding, therefore systematic mechanism reduction should always be the final step of the creation of detailed reaction mechanisms.

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