5. Reduced Kinetic Mechanisms for Premixed Methane–Air Flames

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5.1 Introduction

Methane-air flames have served as the first example for the development of a strategy to systematically reduce kinetic mechanisms. Premixed methane-air flames were first considered in [5.1] and [5.2], methane-air diffusion flames in [5.3]. At last, an entire book, from which further references may be taken, was devoted to the subject of “Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames” [5.4]. The idea there was to use a relatively short kinetic mechanism containing only 25 reactions of the C1-chain, and to analyse not only different approximations for reduced mechanisms of methane-air flames, but asymptotic formulations as well.

It may at first be surprising that reduced mechanisms were first derived for methane rather than for the kinetically simpler hydrogen flames. The reason is that the radical level in methane flames is lower than in hydrogen flames and that therefore steady state relations are better justified. It is lower because the chain from methane that leads to CH3, CH2O, CHO and eventually CO consumes radicals. This part of the mechanism therefore is chain-breaking. A consequence of this chain-breaking effect of the fuel reactions is that the preheat zone in a premixed methane-air flame is chemically inert. Fuel and radicals cannot coexist there, radicals disappear in a thin layer downstream of the preheat zone, the radical consumption zone [5.5]. This effect also simplifies the asymptotic analysis of methane flames.

In this paper, differently from the previous formulations, we will include the C2-chain in deriving a reduced mechanism for methane-air flames. The first 61 reactions in Table 1, Chap. 1, but without reactions 17 and 48 will be used as the starting mechanism for the reduction procedure. Reaction 17 was excluded since it plays a negligible role in methane-air flames. Because it involves the square of the O-concentration it would have complicated the derivation of an explicit algebraic steady state relation for the O-radical. Reaction 48 was excluded because it leads to the C3-hydrocarbons. This reaction
is important for the soot formation mechanism which will not be considered here.

The oxidation of methane proceeds through the fast reactions

\[
\begin{align*}
38 & \quad CH_4 + H &\rightarrow& \quad CH_3 + H_2 \\
35 & \quad CH_3 + O &\rightarrow& \quad CH_2O + H \\
29 & \quad CH_2O + H &\rightarrow& \quad CHO + H_2 \\
24 & \quad CHO + M' &\rightarrow& \quad CO + H + M' \\
\end{align*}
\]  
(5.1)

representing the main chain of the \( C_1 \) mechanism. A side chain through the \( C_2 \) mechanism proceeds as

\[
\begin{align*}
36 & \quad CH_3 + CH_3 + M &\rightarrow& \quad C_2H_6 + M \\
59 & \quad C_2H_6 + H &\rightarrow& \quad C_2H_5 + H_2 \\
58 & \quad C_2H_5 + M &\rightarrow& \quad C_2H_4 + H + M \\
52 & \quad C_2H_4 + H &\rightarrow& \quad C_2H_3 + H_2 \\
51 & \quad C_2H_3 + M &\rightarrow& \quad C_2H_2 + H + M \\
45 & \quad C_2H_2 + O &\rightarrow& \quad CH_2 + CO \\
25 & \quad CH_2 + H &\rightarrow& \quad CH + H_2 \\
19 & \quad CH + O_2 &\rightarrow& \quad CHO + O \\
24 & \quad CHO + M' &\rightarrow& \quad CO + H + M' \\
\end{align*}
\]  
(5.2)

Assuming the intermediates in steady state and adding up these reactions leads to the global step

\[
2 CH_3 + O_2 \rightarrow 2 CO + 3 H_2 .
\]  
(5.3)

The latter step states that the oxidation of \( CH_3 \) via the \( C_2 \)-chain essentially does not produce nor consume radicals if the reactions above are the fastest side reactions to be considered. This global step has to be compared to the one resulting from the \( C_1 \)-chain. Adding to the last three reactions in (5.1) the fast shuffling reactions

\[
\begin{align*}
2b & \quad OH + H &\rightarrow& \quad H_2 + O \\
3b & \quad H_2O + H &\rightarrow& \quad H_2 + OH \\
\end{align*}
\]  
(5.4)

one obtains the global step (taken twice)

\[
2 CH_3 + 2 H_2O + 2 H \rightarrow 2 CO + 6 H_2 .
\]  
(5.5)

Here, two \( H \) radicals are consumed. Therefore, when the \( C_2 \) chain is added to the methane mechanism, its overall effect is to reduce the chain breaking effect of the \( C_1 \) chain. This, of course, is triggered by the relative importance of reactions 35 and 36. For lean methane flames the amount of \( O \)-radicals present is always high enough to make reaction 35 dominate over reaction 36. For rich flames, however, this is no longer the case and the \( C_2 \) chain becomes important. Because reaction 36 is trimolecular the influence of the \( C_2 \)-chain shifts with increasing pressure to lean flames.

Figure 5.1 shows the burning velocity over the equivalence ratio calculated with the starting mechanism with and without \( C_2 \)-species, as compared