A wide range kinetic modelling study of laminar flame speeds of reference fuels and their mixtures

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Abstract

Aim of this work is to further validate a general detailed mechanism of pyrolysis and oxidation for the high temperature combustion of a large variety of different fuels. The attention is first placed on the validation of the chemical mechanism in respect of the laminar flame speed of H2 and H2/CO mixtures as well as the burning velocity of small hydrocarbon fuels such as methane and C2-C4 species. Alkanes, alkenes and alkynes are considered, together with butadiene. Reference fuels for gasoline and jet fuel surrogates are also analysed. More specifically, three hydrocarbon classes are considered: alkanes (n-heptane: nC7H16 and iso-octane: iC8H18, and higher n-alkanes: nC10H22 and nC12H26), cyclo-alkanes (cyclo-hexane) and aromatics (benzene: C6H6, toluene: C7H8). Finally, burning velocity of C1-C4 alcohols are also compared with experimental data.

1. Introduction

Since several years now, new burners and improved experimental methods produced reliable measurements for the flame speeds [1-2]. Flame speed is one of the key properties which are very useful to validate and optimize chemical reaction mechanisms at high temperatures. Burning velocity of different fuels are compared with experimental measurements, moving from small hydrocarbons up to reference species of gasoline and diesel fuels. Alkanes, alkenes and alkynes are considered, together with butadiene. Flame speeds of cyclo-alkanes and aromatics as well as burning velocity of alcohol fuels are also included in this kinetic study. This work takes advantage of a similar and recent kinetic study of Blanquart et al. [3], used to validate the Stanford high temperature kinetic mechanism. According to the conclusion of Kumar and Sung [4], comparison of experimental and predicted results indicates some deficiencies of the existing mechanisms. Sensitivity analysis shows that the most sensitive reactions pertinent to laminar flame speed are very similar for different hydrocarbons of the same family.

2. Kinetic model

The semi-detailed oxidation mechanism of hydrocarbon fuels up to C16 already discussed elsewhere [5] is here adopted. The overall kinetic scheme is based on hierarchical modularity and is made up of more than 10000 reactions among 350 species. Thermochemical data for most species was obtained from the CHEMKIN thermodynamic database [6]. For those species for which thermodynamic data is not available in the literature, the group additive method was used to estimate these properties. The complete mechanism, with thermodynamic and transport properties, is available in CHEMKIN format [http://www.chem.polimi.it/CRECKModeling].
3. Comparisons of laminar flame speeds and model predictions

The hierarchical structure of the kinetic model of hydrocarbon pyrolysis and combustion suggests analysing laminar flame speeds moving from H\textsubscript{2} and syngas before the investigation of laminar flame speeds of heavier fuel species. Recently, Frassoldati et al. [7] already revised and discussed burning rates of H\textsubscript{2} and syngas mixtures. This work will then sequentially analyse the following systems:

3.1 Flame speed of small hydrocarbon fuels (Akanes, alkanes, alkynes and dienes)
3.2 Flame speed of Heavy hydrocarbon species:
   Linear and branched alkanes (n-heptane, n-decane, n-dodecane and iso-octane);
   Cyclo-alkanes (cyclo-hexane);
   Aromatics.
3.3 Flame speed of alcohols

3.1. Flame speed of small hydrocarbon fuels

3.1.1 Alkanes (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, n-C\textsubscript{4}H\textsubscript{10}, iso-C\textsubscript{4}H\textsubscript{10})

Babushok and Tsang [8] observed strong the similarities amongst alkane/air flames and they also reported the relative sensitivity coefficients for the burning velocity of these flames. For small alkane flames, the kinetic model shows large positive coefficients for the following reactions:

\[
\begin{align*}
  \text{H} + \text{O}_2 &\leftrightarrow \text{OH} + \text{O} \\
  \text{HCO} + [\text{M}] &\leftrightarrow \text{CO} + \text{H} + [\text{M}] \\
  \text{CO} + \text{OH} &\leftrightarrow \text{CO}_2 + \text{H} \\
  \text{CH}_3 + \text{OH} &\leftrightarrow \text{CH}_2\text{S} + \text{H}_2\text{O},
\end{align*}
\]

while a large negative coefficient is shown by the reaction:

\[
\text{H}+\text{OH}+[\text{M}] \leftrightarrow \text{H}_2\text{O} + [\text{M}].
\]

The reaction \(\text{CH}_3 + \text{H} + [\text{M}] \leftrightarrow \text{CH}_4 + [\text{M}]\) indicates a negative coefficient of both \(k_0\) and \(k_\infty\), mainly for methane flame. The reaction \(\text{CH}_3 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_5 + \text{H}\) promotes the reactivity of methane, while has a larger negative impact on ethane flame. Model predictions at stoichiometric conditions, slightly underestimate methane speed, while overestimate ethane burning velocity (see Fig. 1a [1,9-13]). Fig. 1b shows a good agreement between model predictions and experimental measurements of the burning velocities of n- and iso-butane [14, 15]. Model predictions confirm the highest reactivity of ethane, the lowest of methane and also the lower burning rate of branched species when compared to the normal ones.

![Fig. 1 Burning velocity of small alkanes. Fig. 1a – Flame velocity of CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8}](image)

![Fig. 1b – Flame velocity of nC\textsubscript{4}H\textsubscript{10} and isoC\textsubscript{4}H\textsubscript{10}](image)
3.1.2 Alkenes (C$_2$H$_4$, C$_3$H$_6$, 1-C$_4$H$_8$, iso-C$_4$H$_8$)

Contrary to the Stanford model [3], acetylene isomerization into singlet vinylidene C$_2$H$_2$ $\leftrightarrow$ H$_2$CC: and successive reactions with molecular oxygen are not significant in our kinetic model, neither in acetylene nor in ethylene flames. Fig. 2a shows the flame velocity of C$_2$H$_4$ and C$_3$H$_6$. The resonance stability of allyl radicals from propylene explains the lower burning rates of propylene in respect of ethylene. Sensitivity analysis reveals the importance of the reaction of vinyl radical with oxygen CH$_2$CH+O$_2$ $\leftrightarrow$ CH$_2$CHO + O in ethylene flame. As already mentioned, the H and OH abstractions on propylene to form allyl radicals reduce the propylene flame velocity.

Fig. 2b compares the flame velocity of nC$_4$H$_8$ and isoC$_4$H$_8$. Again the model properly reproduces the lower reactivity of branched species. While model predictions are very good in lean conditions, it seems necessary to improve the kinetics in order to increase the reactivity of n-butene in rich conditions, by favouring dehydrogenation reactions of methyl-allyl radicals in respect of the dealkylation ones.

3.1.3 Alkynes and Dienes (C$_2$H$_2$, C$_3$H$_4$, 1-C$_4$H$_6$)

Fig. 3a shows the flame velocity of C$_2$H$_2$, C$_3$H$_4$ and C$_2$H$_6$. The model properly captures the different reactivity of these C2 species. Flame velocity of acetylene is more than the double of the ethylene one and three times the velocity of ethane flame. Similarly, Fig. 3b shows that the flame velocity of 1,3C$_4$H$_6$ is higher than the one of nC$_4$H$_8$. nButane velocity is the lowest. The interest in 1,3-butadiene (C$_4$H$_6$) flames is due to its role in the formation of butadienyl radical and successive aromatic rings. Model predictions well confirm that the reactivity of
unsaturated species is larger than the one of saturated species with the same carbon number.

3.2. Flame speed of Heavy hydrocarbon species

3.2.1 Primary reference fuels (n-heptane and iso-octane)
Babushok and Tsang [8] already studied the burning velocity of n-heptane and they observed that sensitivity of burning velocity to reactions of C5-C7 species is relatively small, while the sensitive reactions are similar to those determining burning velocity of C1-C4 hydrocarbons. Fig. 4 shows that model predictions well agree with the experiments of [14,17], both for n-heptane and iso-octane, further confirming the lower velocities of branched species.

3.2.2 Cyclo-alkanes (cyclo-hexane)
Fig. 5 shows the flame velocity of cyclo-hexane. This comparison of cyclo-alkanes flame velocity clearly confirms not only the very good predictions of the model but also the similar reactivity of cyclo and normal- alkanes.

3.2.3 Heavy normal alkanes (n-decane and n-dodecane)
Fig. 6 shows the comparisons of burning velocities of n-decane and n-dodecane at different initial temperatures [4]. Note that these burning rates of heavy alkanes are very close to the ones of n-heptane, at the same temperature conditions.

3.2.4 Aromatics (benzene and toluene)
Fig. 7 shows the preliminary comparisons with the benzene and toluene flame speeds at 1 and 3 atm and different temperatures [14,18]. Model predictions capture the lower reactivity of toluene, due to benzyl radicals, but the kinetic model requires a further refinement in both the
systems.

![Graph](image)

**Fig. 7** Burning velocity of aromatics at different initial temperatures and pressures

### 3.3. Flame speed of oxygenated hydrocarbon species

The kinetic mechanism of alcohol fuels, from ethanol to butanol isomers, was recently discussed [19-20-21]. Fig 8 shows the very good agreement for all the C1-C4 alcohols. Note that methanol is faster than the remaining alcohols. This is mainly due to the lower propensity of methanol to form methyl radicals. Once again, while ethanol, n-propanol and n-butanol show very similar reactivity, the branched iso-propanol has a lower flame speed.

![Graph](image)

**Fig. 8** Burning velocity of alcohol fuels. Fig. 8a – Flame velocity of methanol and ethanol. Fig. 8b – Flame velocity of n-propanol, iso-propanol and n-butanol (experimental data [2])

### 4. Conclusions

This kinetic study not only contribute to the validation of the kinetic study, but also confirms Davis and Law conclusions [14]. Laminar flame speeds of various fuel hydrocarbons, including alkanes, alkenes, alkynes, aromatics, and alcohols, compared over an extensive range of equivalence ratios, temperatures and pressures, show that the laminar flame speeds of normal alkanes are close in the whole field of operating conditions, except for the lower flame speed of CH₄ and the higher ones of C₂H₆. For fuels with the same carbon number, unsaturated species have higher flame speeds: alkanes < alkenes < alkynes. Branched species show lower burning rates than the corresponding linear components. The flame speed of cyclo-hexane is similar to the one of n-heptane [14]. Fall-out of this kinetic analysis is further validation of the kinetic scheme at high temperature conditions. Future activities will further analyze real fuels mixtures and the effect of high pressure conditions.
5. References