On Transport-Chemistry Interaction in Laminar Premixed CH$_4$-Air Flames

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ABSTRACT

A laminar premixed CH$_4$-Air flame is analyzed with tools from the Computational Singular Perturbation method. The analysis focuses on the transport-chemistry interaction in the flame zone, considering lean, stoichiometric and rich mixtures. It is shown that transport has no influence in the directions in the phase space along which act the fastest chemical time scales. Diffusion starts becoming important in the directions along which act the intermediate chemical time scales, while along the slowest directions both diffusion and convection dominate. It is also demonstrated that the stoichiometry of the mixture has no significant effect on the dynamics along the fastest chemical directions, influencing the slow ones. In particular, the fast chemical time scales are not affected as the flammability limits are approached, the slow ones becoming slower in the lean/rich flames than in the stoichiometric. The identification of the transport-free chemically fastest directions is crucial for the simplification of the governing equations.

INTRODUCTION

Traditional methods for the analysis of flow-chemistry interaction range from inspection of mole fraction profiles and net formation rates, to reaction path analysis, sensitivity analysis and paper and pencil asymptotic expansion methods.

Here, the algorithmic Computational Singular Perturbation (CSP) analysis [1], will be employed, which has been applied to a wide range of combustion problems [e.g., 2-4]. CSP is based on the realisation that the solution of the species equation follows a trajectory, which lies on a low dimensional manifold in the mass fraction space. This manifold is created by the equilibration of the “fast” part of chemistry, due to the action of fast chemical time scales acting perpendicular to the manifold; directions along which the effect of diffusion and convection time scales is negligible. The “slow” part of chemistry and the other physical processes present, such as convection and diffusion, are responsible for moving the solution along the manifold.

CSP will be employed here to study the interaction of chemistry and transport in laminar premixed CH$_4$-Air flames. The aim of this study is to investigate the extent to which transport couples with chemistry and the physical mechanism by which such a coupling is possible. In addition, a methodology will be presented for the identification of the fastest part of chemistry which is not coupled to transport and is thus allowed to equilibrate. Here, results will be displayed for the main reaction zone, where the most intense chemical activity occurs.

The structure of the manuscript is as follows. First, a brief presentation of the CSP tools is given. Then, one-dimensional, premixed CH$_4$-Air flames are analysed for three different stoichiometries, $\phi$=0.6, 1.0 and 1.5; the lean and rich cases being close to the experimentally determined flammability limits [5]. Finally, the chemistry-transport interaction in the flame zone is discussed.

THE CSP TOOLS

Consider a kinetic mechanism consisting of N species, E elements and K elementary reactions (forward and backward counted separately). The species equations is:

$$\frac{dy}{dt} = L_c(y) + L_d(y) + \frac{1}{\rho} W \left[ S_1 R_1(y) + \ldots + S_K R_K(y) \right]$$

(1)
where, $y$ is the vector of the species mass fractions, $L_c$ and $L_d$ are the convective and diffusive spatial vector differential operators, $\rho$ is the mixture density, $W$ is a diagonal matrix with the species’ molecular weights as entries, $S_k$ is the stoichiometric vector of the $k$-th elementary reaction and $R^k$ is the $k$-th reaction rate. Equation (1) can be cast as:

$$\frac{dy}{dt} = a_1 h^1 + \ldots + a_N h^N$$  \hfill (2)

where

$$h^i = b^i \cdot L_c(y) + b^i \cdot L_d(y) + \frac{1}{\rho} f^i$$  \hfill (3)

$$b^i \cdot L_c(y) = \sum_{n=1}^{N} b^i_n L^c_n, \quad b^i \cdot L_d(y) = \sum_{n=1}^{N} b^i_n L^d_n, \quad f^i = \sum_{k=1}^{K} (b^i \cdot WS_k) R^k$$  \hfill (4a-c)

$a_i$ and $b_i$ are the N-dim. CSP basis vectors ($b^i a_k = \delta^i_k$), $h^i$ are the related amplitudes, $b^i_n$ is the $n$-th component of $b^i$ and $L^c_n$ and $L^d_n$ are the $n$-th components of $L_c$ and $L_d$ [6]. The signs of $b^i$ and $a_i$ are adjusted so that $f^i > 0$ for $i=1,N-E$. $f^i \equiv 0$ for $i=(N-E+1),N$ due to the conservation of elements in each elementary reaction. The CSP-modes $a_i h^i$ are ordered in eq. (2) according to the magnitude of the chemical time scales they relate to; i.e. the $i=1$ term relates to the fastest scale $\tau_{chem,1}$, etc. Here, the CSP basis vectors $a_i$ and $b_i$ are approximated by their leading order term: the right and left, respectively, eigenvectors of the Jacobian of the source term in eq. (1) [3, 6]. The chemical time scales are defined as $\tau_{chem,i} = 1/ | \lambda_i |$, where $\lambda_i$ is the $i$-th eigenvalue acting along the direction $a_i$. Equation (1) can also be cast as:

$$\frac{dy}{dt} = \frac{1}{\rho} W \left[ \tilde{a}_1 \tilde{h}^1 + \ldots + \tilde{a}_N \tilde{h}^N \right]$$  \hfill (5)

where $\tilde{a}_i = W^{-1} a_i$ and $\tilde{h}^i = \rho h^i$, so that $K$ elementary reactions, convection and diffusion in eq. (1) can all be replaced by $N$ non-physical reactions, the stoichiometric vector and rate of which are $\tilde{a}_i$ and $\tilde{h}^i$ (CSP reaction and rate). Inspecting the elements in $\tilde{a}_i$ and the major contributors in the expression for $\tilde{h}^i$, valuable information can be extracted regarding the most important chemical paths, which either are in equilibrium or drive the system.

Of course, such an investigation and the expansion of the original RHS of eq. (1) in the $N$ components of the RHS of eq. (5) is meaningful only for the fastest components, in which the effect of transport is negligible. To assess the effects of transport in each component, the $K+2N$ Amplitude Participation Indices for each $\tilde{h}^i$ are introduced as:

$$I_{src,k}^i = \frac{b^i \cdot WS_k R^k}{D}, \quad I_{con,n}^i = \frac{\rho b^i_n L^c_n}{D}, \quad I_{dif,n}^i = \frac{\rho b^i_n L^d_n}{D}$$  \hfill (6a-c)

where

$$D = \sum_{k=1}^{K} | b^i \cdot WS_k R^k | + \rho \sum_{n=1}^{N} | b^i_n L^c_n | + \rho \sum_{n=1}^{N} | b^i_n L^d_n |$$

Since by definition $| I_{src,k}^i | + \ldots + | I_{src,K}^i | + | I_{con,1}^i | + \ldots + | I_{con,N}^i | + | I_{dif,1}^i | + \ldots + | I_{dif,N}^i | = 1$, the closer to unity is the value of $| I_{src,k}^i |$, $| I_{con,n}^i |$ or $| I_{dif,n}^i |$, the largest the contribution of the $k$-th elementary reaction rate and the $n$-th species’ convection or diffusion to $\tilde{h}^i$. Positive values of the indices indicate that the relevant process tends to move the CSP reaction $\tilde{a}_i$ forward, while negative values have the opposite effect.

The species affected the most by the i-th CSP reaction and the corresponding chemical time scale are those on whose axes the vector $a_i$, along which this time scale acts, has non-negligible projections [3]. Furthermore, the species which are found in the reaction rates participating the most in $\tilde{h}^i$ are those whose axes have a non-negligible projection on $a_i$ [3]. The species that possess both these characteristics, i.e. are affected
CHEMISTRY-TRANSPORT INTERACTION

Steady, freely propagating, one-dimensional, laminar, premixed, atmospheric CH₄–Air flames were simulated with the RUN-1DL code [7], using the detailed GRI 3.0 mechanism [8], which incorporates 53 species (N=53), 325 reversible reactions (K=650) and 5 elements (E=5). The inlet mixture temperature was considered at $T_0 = 300K$, while the exit product temperature was computed $T_{\infty} = 1670K$ for $\phi=0.6$, $T_{\infty} = 2231K$ for $\phi=1.0$ and $T_{\infty} = 1909K$ for $\phi=1.5$. Since the problem considered here is steady, all CSP rates $\tilde{h}_i$ are equilibrated:

$$\tilde{h}_i = \rho b^i L_c(y) + \rho b^i L_d(y) + f^i = 0 \quad i=1,N-E \quad (10a)$$

$$\tilde{h}_i = \rho b^i L_c(y) + \rho b^i L_d(y) = 0 \quad i=(N-E+1),N \quad (10b)$$

The N-E eqs. (10a) are projections of the N-dim. system of eqs. (1) on the N-E directions in the phase space, along which chemistry is active and is allowed to interact with transport. The E eqs. (10b) govern the conserved scalars and by definition chemical activity is absent.

The equilibration of each CSP rate $\tilde{h}_i$ is associated with a time scale, the magnitude of which depends on both transport and chemistry. In particular, the time scales characterizing the fastest CSP rates are dominated by the fast components of chemistry only. The time scales of the next CSP rates are influenced by both chemistry and transport; the effect of the latter becoming more important as the time scales become slower, dominating fully those of the E CSP rates, eqs. (10b). In order to relate the above with the different processes contributing in the cancellations in $\tilde{h}_i = 0$, we introduce the quantities:

$$I_{\text{src}}^i = \sum_{k=1,K} |I_{\text{src},k}^i| \quad I_{\text{con}}^i = \sum_{n=1,N} |I_{\text{con},n}^i| \quad I_{\text{dif}}^i = \sum_{n=1,N} |I_{\text{dif},n}^i| \quad (11a-c)$$

which, since $|I_{\text{src}}^i| + |I_{\text{con}}^i| + |I_{\text{dif}}^i| = 1$, are indicative of the chemical, convective and diffusive activity levels taking place in each CSP rate $\tilde{h}_i$. In order to measure the chemical activities among the CSP rates, we introduce the quantity:

$$F^i = \sum_{k=1,K} |b^i \cdot WS_k R^k| \quad (12)$$

While large values of $F^i$ indicate significant chemical activity in $\tilde{h}_i$, the level of chemistry-transport interaction is measured by the value of $f^i$, eq. (4c), which balances transport according to eq. (10a).

The quantities $I_{\text{src}}^i$, $I_{\text{con}}^i$ and $I_{\text{dif}}^i$ for all $i=1,N-E=48$ CSP rates that allow transport-chemistry interaction were computed at a point where temperature attains an average value, $T_a = (T_0 - T_{\infty})/2$, for the three stoichiometries $\phi=0.6$ ($T_a=1000K$), $\phi=1.0$ ($T_a=1286K$) and $\phi=1.5$ ($T_a=1181K$) and are displayed in Fig. 1.
the flame zone of (a) lean ($\phi=0.6$, $T=1000K$), (b) stoichiometric ($\phi=1.0$, $T=1286K$) and (c) rich ($\phi=1.5$, $T=1181K$) flames.

These findings, indicative of what happens throughout the flame zone, allow us to conclude that:

- Along the “fastest” chemical directions, chemistry dominates and transport (mainly diffusion) plays a minor role, being little more effective in the stoichiometric flame than in the lean/rich ones. The corresponding CSP reactions $\tilde{a}_1$ can be thought as in equilibrium, expressed by the relations $f_1^{1} \approx 0$.
- Along the “intermediate” chemical directions the action of diffusion and convection becomes noticeable, with that of diffusion being still more pronounced.
- Along the “slow” chemical directions both diffusion and convection attain equal importance to chemistry, eventually dominating the “slowest” directions, their action being more effective in the lean/rich flames than in the stoichiometric one.

The dominance of chemistry along the chemically “fastest” directions implies that the algebraic relations $f_i^{1} \approx 0$ can safely be employed for the computation of the species affected the most by these fast modes; i.e. the CSP radicals. These species are shown in Table 1 for the 15 chemically “fastest” CSP rates for the conditions of Fig. 1b ($\phi=1.0$, $T=1286K$), along with the ratios $f_i^{1}/F_i^{i}$ which provide a measure of the cancellations in $f_i^{1} \approx 0$. All 15 species are radicals characterized by very small peak concentrations. Note the important C, CH, $^1$CH$_2$ and C$_2$H radicals, which are known to insert very fast to intermediate hydrocarbon fragments leading to molecular growth [e.g., 9], are indeed associated with the four fastest chemical directions involving hydrocarbon species. The CH radical, used to locate the flame zone in both laminar and turbulent flames [e.g., 10], is associated with the third fastest chemical time scale, its chemistry being fully decoupled from convective/diffusive processes. The 15 CSP radicals shown in Table 1 for $\phi=1.0$, are the same for $\phi=0.6$ and $\phi=1.5$, with the exception of H$_2$CN (which falls in the 17-th position, replaced by OH) for $\phi=0.6$ and HCCO (which falls in the 16-th position, replaced by OH) for $\phi=1.5$.

The rising influence of transport along the chemically “slow” directions is the result of the time scales characteristic of transport along these directions in the phase space, catching up with the chemical ones. A demonstration of this coupling is provided by the results shown in Fig. 2, were the chemical time scales for the lean ($\phi=0.6$, $T=1000K$), stoichiometric ($\phi=1.0$, $T=1286K$) and rich ($\phi=1.5$, $T=1181K$) flames are displayed. It is shown that while the mixture composition has no effect on the fastest chemical time scales, the slow ones tend to become slower in lean/rich mixtures than in stoichiometric ones. These findings are in agreement with the results shown in Fig. 1, according to which the increased activity of transport along the chemically “slow” directions is more intense in the lean/rich flames than in the stoichiometric.

<table>
<thead>
<tr>
<th>Mode</th>
<th>CSP Radicals</th>
<th>$f_i^{1}/F_i^{i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NNH</td>
<td>.464e-03</td>
</tr>
<tr>
<td>2</td>
<td>$^1$CH$_2$</td>
<td>.191e-03</td>
</tr>
<tr>
<td>3</td>
<td>CH</td>
<td>.239e-02</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>.511e-02</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H</td>
<td>.823e-02</td>
</tr>
<tr>
<td>6</td>
<td>HCO</td>
<td>.924e-02</td>
</tr>
<tr>
<td>7</td>
<td>HCN</td>
<td>.275e-02</td>
</tr>
<tr>
<td>8</td>
<td>CH$_2$OH</td>
<td>.829e-02</td>
</tr>
<tr>
<td>9</td>
<td>$^3$CH$_2$</td>
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</tr>
<tr>
<td>10</td>
<td>CN</td>
<td>.213e-01</td>
</tr>
<tr>
<td>11</td>
<td>CH$_3$O</td>
<td>.812e-02</td>
</tr>
<tr>
<td>12</td>
<td>C$_2$H$_7$</td>
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<td>13</td>
<td>C$_2$H$_3$</td>
<td>.164e-02</td>
</tr>
<tr>
<td>14</td>
<td>H$_2$CN</td>
<td>.272e-01</td>
</tr>
<tr>
<td>15</td>
<td>HCCO</td>
<td>.320e-01</td>
</tr>
</tbody>
</table>
Table 1  CSP radicals and the ratio $f/F_i$ for the first 15 fastest CSP rates; $\phi=1.0$ at $T=1286K$. 

![CSP Rate vs Time](image.png)

**Fig. 2**  Chemical time scales in the flame zone of lean ($\phi=0.6, T=1000K$), stoichiometric ($\phi=1.0, T=1286K$) and rich ($\phi=1.5, T=1181K$) flames.

**CONCLUSIONS**

The results shown here demonstrate that the dynamics, along the fastest chemical directions in the phase space, of flame structure inside the main reaction zone can be discussed only in chemical kinetic terms. However, along the slower directions chemical kinetics must be examined along with the convective/diffusive processes. The significance of such conclusions has already been recognised by researchers trying to develop very simple reduced kinetics models of high accuracy by including the effects of diffusion [e.g., 11].

Moreover, it was shown that the dynamics of the fastest part of chemistry is unaffected by the stoichiometry of the inlet mixture. This feature has also been observed in flames of different geometries [12]. Apparently, in the problem considered here, the stoichiometry was shown to affect the same slow chemical time scales as those being coupled to the convective/diffusive ones.

The above methodology can also be used to quantify in a fully algorithmic manner other important chemical processes, such as the role of transport-chemistry interaction for the development of flammability limits, the formation of thermal and prompt NO, etc.

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**REFERENCES**