A partially stirred reactor model for turbulent combustion closure using detailed chemical time scales


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Abstract
The closure of the reaction term in modeling turbulent combustion systems is crucial when dealing with the Reynolds-averaged Navier-Stokes (RANS) approaches. The partially-stirred reactor model (PaSR), that explicitly includes the characteristic chemical time of the system in the expression of the mean reactive term is one of the most commonly used approaches in the description of turbulence-chemistry interaction. The model showed limitations in predicting some key phenomena, such as Nitrogen Oxides (NO\textsubscript{x}), which have distinct characteristic time scales compared to that of the main combustion process. The present study proposes a refined PaSR model with incorporating detailed chemical time scales in the description of the reaction source term closure. A stochastic reactor is used as a representation of the target turbulent combustion system and its results are compared with data given by a perfectly stirred reactor whose reactive term is modeled according to the proposed formulation of PaSR. The model is tested with reaction schemes describing different common kinetic pathways. Overall, good agreement is found between PaSR and the stochastic reactor.

Introduction
The computational simulation of turbulent reacting flows is a challenging problem due to the extremely large number of solution variables and a large spectrum of length and time scales involved. For many engineering applications, the Reynolds-averaged Navier-Stokes (RANS) approach is most commonly used as a means to provide the statistical average behavior of the system. In particular for reacting flows, the proper closure of the mean reaction source terms is a great challenge, due to their strong nonlinearity associated with chemical reactions (with vastly different time scales) and their interaction with turbulent flows which also have a range of flow time scales. The partially-stirred reactor (PaSR) model [1], which has been
widely used in engineering computational fluid dynamic (CFD) simulations, allows a systematic way to account for various chemical and flow time scales. Most existing forms of the implementation of PaSR, however, represent the complex chemical reaction processes with a single characteristic time scale, thus limiting its fidelity in predicting a wide variety of key observables, such as the NO\textsubscript{x} formation. The present study aims to improve on this limitation of the PaSR approach by systematically incorporating key chemical time scales depending on the targeted objectives, by employing the numerical procedure based on the computational singular perturbation (CSP) theory [2]. In the following, the proposed model is described and its implementation into the PaSR model is validated against the stochastic reactor model results, which represent an idealized turbulent combustion system. Results of different test cases are presented and discussed.

The partially-stirred reactor (PaSR) model

The partially-stirred reactor model (PaSR) [1], is based on the assumption that each computational cell can be divided into two fractions: a reactive portion (characterized by a concentration \( c \)) and a non-reactive one where species are characterized by the initial concentration \( c_0 \). Due to the mixing, these two portions interact and exchange mass giving an outlet composition \( c_1 \). It was shown [1] that the mean reactive term can be expressed as:

\[
\Omega(c) = \gamma \Omega(c_1)
\]  

(1)

\[
\gamma = \tau_c / (\tau_c + \tau_{mix})
\]  

(2)

In PaSR model the formation rate of a certain species is then defined according to the \( \gamma \) factor. In fact, when the mixing time \( \tau_{mix} \) is smaller than the chemical characteristic time of the system \( \tau_c \) (\( \tau_{mix} < \tau_c \)), \( \gamma \) is close to unity, meaning that mixing is efficient, and the final composition is mainly determined by chemistry. Contrarily, when \( \tau_c < \tau_{mix} \), \( \gamma \) is close to zero and mixing controls the system. The model is then able to well correlate the chemical phenomena with the mixing one due to turbulence. The chemical characteristic time is related to a reference species and can be calculated from the eigenvalues of the Jacobian matrix. Generally, the largest chemical time is selected because it is supposed to be most limiting one. However, this is the main limitation of the model, and makes it unable to describe systems where chemical times are very different from each other (e.g. formation of thermal NO\textsubscript{x} in combustion systems). In order to take into account for all the chemical time scales, a different approach should be used, and it is the focus of this work. To this purpose, reactions chemical times can be exploited. According to Lam [2] they can be expressed as:
\[ \tau_{c,j} = \frac{1}{\left( \frac{\partial r_j}{\partial c_0} \alpha_j \right)} \]  

(3)

where \( j \) is the number of reactions and \( r_j \) and \( \alpha_j \) are, respectively, the reaction rate and the vector of stoichiometric coefficient of the \( j \)-th reaction. In this way, it is possible to assess a \( \gamma_j \) for each reaction that directly scales the value of the corresponding reaction rate. Then the formation rate of each species \( i \) is computed:

\[ \Omega_i = \sum_{j=1}^{NR} \gamma_j r_j \alpha_{i,j} \]

(4)

**Stochastic reactor**

The validation of the proposed methodology is performed by means of a stochastic reactor [3]. It describes the effects of the partial mixing assuming fluids not perfectly diffusing one into each other at a molecular level but considering mean thermo-chemical properties to be spatially homogeneous. The reactor is then composed of many fluid particles that interact statistically and diffuse into each other according to the imposed mixing. The statistic events are chosen from the stochastic ensemble. Then, the mixing is modeled according to the modified coalescence and dispersion model [4]. The mixing events occur with a frequency which is characteristic of turbulence mixing. If \( \tau_{mix} = 0 \) the stochastic reactor becomes a perfectly stirred reactor (PSR), while if \( \tau_{mix} = \infty \) the particles are completely segregated. Finally, chemistry is solved inside each particle which is treated like a batch reactor. Mass inside the reactor can be assumed constant since the mass entering the reactor is equal to the one at the exit. The stochastic reactor can be then considered like a single cell inside a complex computational domain. It is able to faithfully reproduce the real behavior of the system since the only phenomena which is modeled is the mixing. Its results are compared with those coming from a perfectly stirred reactor whose reactive term is modeled according to the new formulation of PaSR.

**Results on test cases**

In order to fully understand the effects of the introduction of chemical reaction times, different simple test cases are investigated. All simulations are run with arbitrary, temperature-independent kinetic parameters and fictitious species. The first inlet stream is composed by pure A while the other has B diluted in an inert species I. The molar ratio between B and A is equal to 2. Residence time is fixed equal to 0.1 s. All reactions are elementary and non-reversible.

**Monomolecular reactions**

The sample reaction first considered is:

\( A \rightarrow B \ (k_1 = 10^5 \ [1/(s)]) \)

From Figure 1a it is possible to note that if \( \gamma \) is calculated with the (2), PaSR is not able to reproduce the stochastic results. However, the monomolecular reaction is not
influenced by the mixing, because A converted into B without needing to mix with other species.

**Figure 1:** Mass fraction of A varying with mixing time for (a) a monomolecular and (b) a bimolecular reaction.

Consequently, if \( \gamma \) is fixed equal to one, PaSR gives the same results as the stochastic reactor.

### Bimolecular reaction

The simple, bimolecular reaction investigated is:

\[
A + B \rightarrow C + D \quad (k_1 = 10^5 \left[ \frac{m^3}{s \text{mol}} \right])
\]

Figure 1b shows that the PaSR faithfully reproduces the curve from the stochastic reactor because in this case the mixing is crucial to make species react.

### Bimolecular and monomolecular reactions

According to the results obtained, a kinetic scheme made up of a combination of bimolecular and monomolecular reactions is studied:

\[
A + B \rightarrow C + D \quad (k_1 = 10^5 \left[ \frac{m^3}{s \text{mol}} \right])
\]

\[
C \rightarrow E \quad (k_2 = 10^4 \left[ \frac{1}{s} \right])
\]

\[
D \rightarrow F \quad (k_2 = 10^4 \left[ \frac{1}{s} \right])
\]

Results from Figure 2 confirm that monomolecular reactions have to be treated with a \( \gamma \) which is always unitary, while the reaction rate associated to bimolecular reactions must be properly scaled with the \( \gamma \) calculated as in (2).

### Parallel reactions

The behaviour of PaSR modelling with respect to the following parallel reactions scheme is analyzed:

\[
A + B \rightarrow C + D \quad (k_1 = 10^5 \left[ \frac{m^3}{s \text{mol}} \right])
\]

\[
A + B \rightarrow E + F \quad (k_2 = 10^4 \left[ \frac{m^3}{s \text{mol}} \right])
\]

From Figure 3 it can be noted that the production of species E is largely overestimated by PaSR and also species A and C show consistent discrepancies when \( \gamma_1 \) and \( \gamma_2 \) are computed as in (2). This is due to the fact that once the two reactants mix, their transformation into products is driven only by chemistry. Thus,
The two reactions must be characterized by the same $\gamma$, corresponding to the fastest reaction.

**Figure 3:** Mass fractions of (a) A, C and (b) E varying with the mixing time for parallel reactions.

**Reactions in series**

The following two reactions in series are finally analyzed:

- $A + B \rightarrow C + D \quad (k_1 = 10^5 [m^3/(s \text{ mol})])$
- $C + D \rightarrow E + F \quad (k_2 = 10^4 [m^3/(s \text{ mol})])$

Figure 4 shows that species A is well reproduced by PaSR while differences appear in the curves related to species C and D. This is caused by the fact that C and D are produced from the first reaction, so they are present in the same particle of fluid and then partially mixed. It is easily understandable that the issue is related in general to the premixing of reactants. Reactions may happen not only because reactants are mixed by turbulence but also because they are already in contact (similarly for monomolecular reactions). This suggests that, in order to make the model
comprehensive, the inhomogeneous mixing of premixed reactants has to be considered.

**Figure 4**: Mass fractions of (a) A and (b) C and E varying with the mixing time for series reactions.

**Conclusions and future works**

The new formulation of PaSR that includes chemical reaction times involved in a reactive system shows promising results. Its effectiveness has been investigated by comparing the results of a stochastic reactor and a Perfectly Stirred Reactor whose reactive term has been modeled through the newly introduced algorithm. Several test cases representing common kinetic pathways have been investigated. Overall, PaSR is able to well reproduce the behavior of the system. However, several peculiar aspects have been highlighted. With parallel reactions, the $\gamma_j$ corresponding to the fastest reaction dominates the mixing of the two reactants, thus the process becomes controlled only by kinetics and both reactions must be characterized by the $\gamma_j$ of the faster one. Moreover, premixing of reactants has a strong impact on the final results. For monomolecular reactions it is enough to impose $\gamma = 1$ but bimolecular reactions deserve further attention, because the inhomogeneous mixing of premixed reactants should be considered.

**References**


