Coarse-grained state analysis of methane combustion mechanism

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ABSTRACT

This work introduces the coarse graining idea into the analysis of detailed combustion models to determine the key reaction steps that drive macroscopic combustion characteristics. A novel method that combines network community detection and parametric bifurcation techniques is proposed. The effectiveness of the method is demonstrated in a methane fueled combustion system, in which the coarse-grained states are identified during the pyrolysis and oxidation processes under wide temperature and pressure conditions. It is revealed that the evolution process represented by the coarse-grained states not only can distinctively separate the pyrolysis from oxidation processes, but it is also capable of effectively identifying commonalities of the states over a wide range of parameters. In addition, the method allows the identification of important reactions based on identified coarse-grained states; and the results obtained agree well with previous related studies.

1 Introduction

A combustion reaction mechanism can be regarded as an intricate reaction network, whose structure and properties depend on the fuel properties and external factors such as temperature and pressure[1]. The construction and analysis of combustion mechanism models are essential for systematically understanding the influence of microscopic interactions among chemical species on macroscopic combustion characteristics, but the size of the models increases with the size of the fuel molecule, roughly in an exponential trend [2]. For macromolecular fuels, the detailed mechanism is prohibitively large, thus, reduced mechanisms that have similar combustion characteristics must be used in practical applications in computational fluid dynamics [3]. In recent years, methods that directly construct reduced models for macromolecular fuels or surrogate fuel mechanisms have been proposed [4-7].

In the field investigating other complex reaction systems such as biochemical reaction networks, there are studies utilizing the Markov state model method [8] or the hierarchical or modularity

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properties[9] of the network, to explore the phenomenological reaction mechanism by dissecting the assemblies of species and their synergistic effects. For combustion processes, it is proved that the rate-limiting processes or the driving reactions could not be a single reaction, but are the synergistic effect of a number of closely coupled species [10]. In our previous work [11], a coarse-grained method is employed to represent the driving kinetics for the global reactive character based on the identification of functional groups of species that have dense inner connections and their synergistic effects.

In this work, our previously proposed coarse graining method for combustion reactions [11] is further developed by combining with the bifurcation techniques to identify the dominant mechanism of ignition. The methane combustion system is described by the GRI-3.0 mechanism. In a two-parameter diagram of temperature and pressure at a fixed flux rate, the exact ignition and extinction conditions are determined by a bifurcation analysis module based on a predictor-corrector continuation algorithm [12]. Accordingly, the diagram is divided into three kinetic regions, the ignition region, the non-ignition region, and the bistable region. Species communities that have dense inner connections are then identified with community detection techniques in each region. The system's regions identified by different community partitions are defined as different coarse-grained states, i.e., the system is divided into different communities. By analyzing the distribution of these coarse-grained states in a specific kinetic region, their stability, the composition of the communities with high occurrence probability, and the differences in stable coarse-grained states identified at each side of the critical bifurcation conditions, the dominant mechanisms for ignition/extinction, are identified.

2 Method

A species community represents a group of species densely connected within the community and loosely connected to species belonging to the other communities. In a specific condition the local evolution of the system defined by the model equations of the specific reactor type, determines a reorganization of the species communities that therefore, conversely, identify working condition with structural similarities. The communities investigated are those arising from a mapping of both the steady state solutions of Eq. (1) (the states $\bar{X}$ that are solutions of the equation $F(\bar{X},\alpha)+S(\bar{X},\alpha)=0$) and the dynamic solution $X(t)$, for different values of the parameters T_{in} and P. Clearly, for each value of α, we can, therefore, recognize the structure of the communities that will identify a coarse-grained state for the network defined by the reaction mechanism.

$$\frac{dX}{dt}=F(X(t),\alpha)+S(X(t),\alpha) \tag{1}$$

Here X represents the whole set of state variables (Y,T), being Y the variable vector of species mass fractions and T the temperature, and α the vector of all the system parameters, including the pressure P, the inlet temperature T_{in}, and the residence time τ.

2.1 Coarse-grained states identification.

The concept of coarse-grained state arises from the analysis of the community partitions resulting in different values of the system parameters α and time t. It can be defined as an immutable structure of the community partition. In this work, we define two different levels of "coarse-grained" states: community states and milestone states. As shown in Fig. 1c, a community state refers to all the system states X with the same community partition for the entire species mechanism network, which may be related to the concept of pre-equilibria in chemical kinetics [13]. The concept of betweenness centrality [11] of a reaction network are used to identify important species and then define the milestone states (Fig. 1d). For the current analysis, the 8 species that highly ranked in the value of betweenness are adopted to define the milestone states, which can be regarded as a further aggregation of community states.

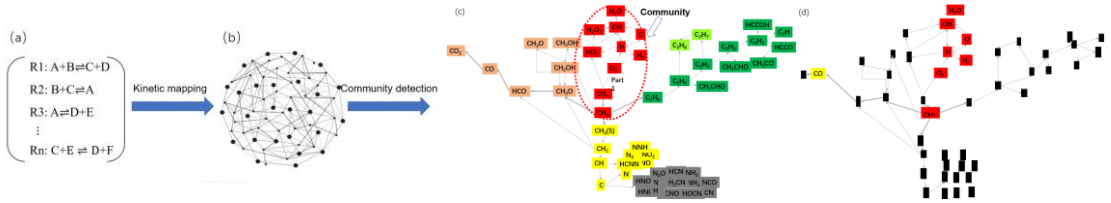

Fig 1: Identification of coarse-grained state in a combustion reaction system. (a) Detailed elementary reaction steps (b) Reaction mechanism network (c) a community state of the mechanism (d) a milestone states of the mechanism

2.2 Coarse-grained-states based mechanism analysis

For the mechanism analysis of the dynamical state transitions such as ignition or oscillation, identifying coarse-grained states near critical bifurcation points would be very helpful to highlight different dominant mechanisms at work, especially for complex and large systems. Since bifurcation defines the boundary where a dynamical state change occurs while coarse-grained states will exhibit the significant mechanism state difference beneath it. To do this, it is necessary to first determine the critical condition on the parameter diagram of interest according to the bifurcation analysis[12] (Fig. 2e and 2f) .

2.2.1 State persistence evaluation

To quantify the significance of the coarse-grained states (CS) in different regions of the $T_{in} - P$ diagram, we define the cumulative probability of the CS:

$$PR^{reg}_{\xi_{(CSi)}} = \sum_1^{\xi_{(CSi)}} P^{reg}_{\xi_{(CSi)}} = \frac{\Sigma_1^{\xi_{(CSi)}} N^{reg}_{\xi_{(CSi)}}}{N_{total}} \quad (2)$$

where $N^{reg}_{\xi_{(CSi)}}$ represents the number of $T_{in} - P$ selected conditions that the CS $\xi_{(CSi)}$ is recognized in a certain region. N_{total} is the total number of $T_{in} - P$ conditions selected in the certain region. In this work, N_{total} is fixed as 500 in both regions. Further increasing the number of points does not lead to a change in the results. Discussion in later sections will focus on states whose $PR^{reg}_{\xi_{(CSi)}}$ is greater than 0.7, and call them significant CS.

2.2.2 Community persistence evaluation

Please note that $PR^{reg}_{\xi_{(CSi)}}$ represents the significance of the CS, Therefore, an additional index is introduced, called Community identification probability $P^{reg}_{(Ci)}$. It is defined, to quantify the number of occurrences of a certain community, as follows:

$$P^{reg}_{(Ci)} = \frac{N^{reg}_{(Ci)}}{N_{total}} \quad (3)$$

where $N^{reg}_{(Ci)}$ represents the number of $T_{in} - P$ condition points that produce community C_i in a certain region. N_{total} is same Eq (2).

2.2.3 Coarse-grained-state based cross-bifurcation condition dominant mechanism identification

Based on the significant coarse-grained states identified at each side of the critical bifurcation conditions, the dominant pathway is determined by searching whether species A and B are in the same community. And then dominant reactions r participated in pathway $A - B$ are identified by Eq.5 and 6. The Reaction repetition probability, $PR^{reg}_{r_j^{A-B}}$, is defined to quantitatively distinguish the significance of

the reaction:

$$P_r^{A-\mathrm{B}} = \frac{\dot{\mathcal{F}}_r^{A-B}}{\sum_{r(r\in A-B)} \dot{\mathcal{F}}_r^{A-B}} \tag{4}$$

$$PR_{r_j^{A-B}}^{reg} = \frac{n_{r_j^{A-\mathrm{B}}}^{reg}}{n_{total}} \tag{5}$$

where $\dot{\mathcal{F}}_r^{A-B}$ represents the reaction flux of reaction r in the A – B pathway. $n_{r_j^{A-\mathrm{B}}}^{reg}$ represents the number of $T_{in} - P$ selected conditions where r_j is recognized as the reaction with the highest $P_r^{A-\mathrm{B}}$ in a certain region. n_{total} is the total number of $T_{in} - P$ selected conditions used in the certain region of the range, as shown in Fig. 3a. In this work, n_{total} is fixed as 200 in both regions.

3 Results and discussion

3.1 Kinetic simulations

Dynamical simulations of the PSR reactor described by Eq.(1) are performed by means of CHEMKIN II software with GRI-mech 3.0[14] under adiabatic, constant pressure, and constant volume conditions. Reactor parameters are set as follows: initial temperature of 1200 K; composition of inlet gas CH_4: O_2: N_2 =1:2:7.52; fixed residence time 1.5×10^{-4} s; equivalence ratio 1.0. The evolutionary end time was fixed to 0.002 s for all simulations, which allowed all reactions in the ignition region to reach a steady state.

3.2 Evolution of coarse-grained states

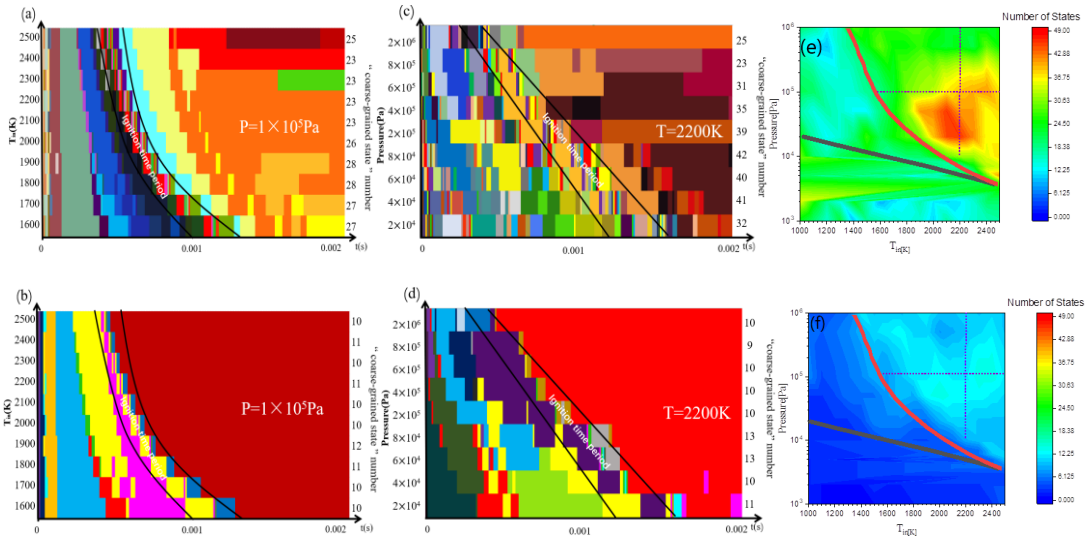

Fig 2: Evolution of coarse-grained states: community states, (a) and (c); milestone states, (b) and (d); Distribution of the number of coarse-grained states: community states(e); milestone states (f).

The evolution of the coarse-grained states during the system evolution is reported in order to analyze the effect of varying the inlet temperature and pressure in Fig. 2a to 2d. It is revealed that the evolution of the community states is quite similar for all the values of T_{in} in Fig. 2a /b. Thus, allowing the identification of the most important reactions/species active during this stage for all the values of T_{in} simulated. A more complex behavior is present at the first stage of ignition that confirms the sensitivity of this stage of the ignition process on T_{in}. The picture appears more complex at varying the

pressure, as reported in Fig. 2c /d, revealing a complex dependency of the reaction network on this parameter. The number of coarse-grained states reported in Fig. 2e /f respectively. Showing the number of coarse-grained states in the ignited region C is higher than in the non-ignition region, reflecting the complex transformations necessary to get the ignited condition starting from the not ignited initial conditions of the inlet mixture. Besides, the gullies in the number of coarse-grained states in Fig. 2e/ f can automatically and efficiently identify the ignited/non-ignition region.

3.3.1 Coarse-grained states distribution in $T_{in} - P$ diagram

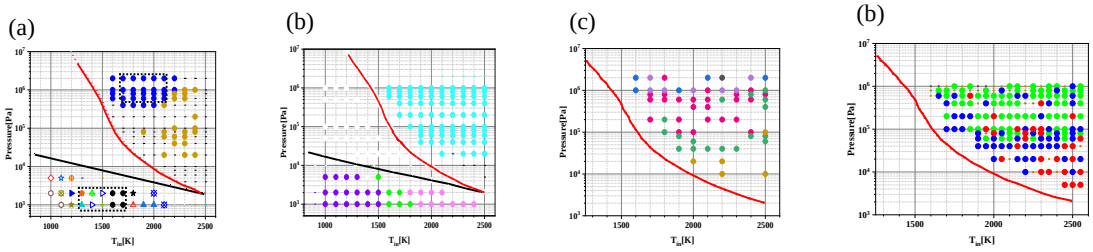

Fig 3: Distribution of significant coarse-grained states on the $T_{in} - P$ bifurcation diagram. Community states: (a), (c); milestone states (b), (d). The same symbol for the same state

We collect the significant coarse-grained states at t=0.002 s in non-ignition and ignition regions; and at ignition time of ignited region solutions, according to Eq.(2). The non-ignition region Fig. 3a shows a poor regularity, indicating the reaction was still not complete in this region at t=0.002 s. Nevertheless, Fig. 3b suggests that the milestone states distinguish the different dominant paths along which the system evolves in different conditions. In the ignition region, Fig.3a and 3b indicates that the reaction in the ignition region reached the steady state by 0.002 s which makes the detected milestone community persistent in the whole region C. In ignition time of ignited region solutions, Fig. 3c and d shows significant coarse-grained states distributions change with the pressure and temperature (some regions share the same coarse grained state) but do not show a clear regularity.

3.3.2 Coarse-grained-states based mechanism analysis

By comparison of the significant CS obtained by Eq.(3) in different conditions, the dominant pathway can be determined. For example, O and OH at both ends of a pathway are in the same community in the coarse-grained state identified at t=0.002 s in the ignition region, while in t=0.002 s in the non-ignition region they are not in the same community, then this red path⑥ O - OH is identified as a dominant pathway in t=0.002 s the ignition region.

Thus we can identify the dominant reaction participated in path⑥ O - OH by Eqs.(4) and (5). The results show that H+O_2⇔O+OH R38 has the highest $PR_{r_j^{A-B}}^{reg}$, R38 reveals to be a key reaction that dominates in the ignition region. OH+CO⇔H+CO_2 R99 and O_2+CO⇔O+CO_2 R31 appear to be two possible termination steps for the production of CO_2 dominating the mechanism in the ignition region at ignition time and at t=0.002 s. Most of the reactions identified by Coarse-grained-states based mechanism analysis, agrees with the findings of Park et al. [15] that discuss the dominant mechanism of methane combustion system.

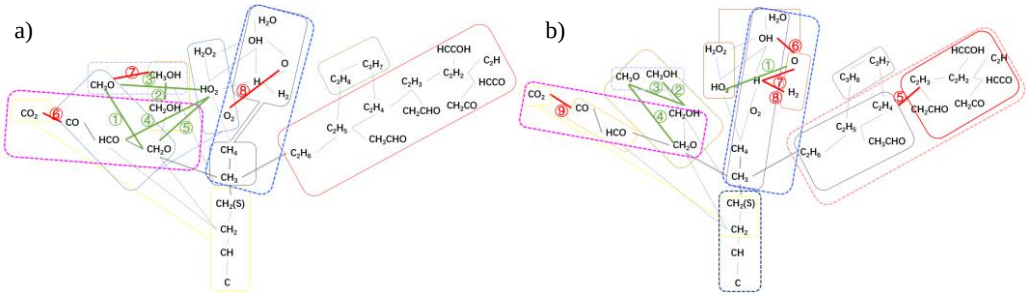

Fig 4: The dominant paths obtained by comparison of significant CS obtained at a) different times (the ignition time: solid line and t=0.002 s ignition region: dotted line); b) different region (t=0.002 s the non-ignition region: solid line and t=0.002 s in the ignition region: dotted line).

4 Summary

This work proposes a novel analysis method that combines the network community detection and bifurcation technique is proposed to study the behavior of chemical mechanisms during state transitions in combustion systems. Coarse-grained states of the reaction system are identified during the pyrolysis and oxidation process and under wide temperature and pressure conditions, according to which the dominant mechanism of dynamic state transition between the different regions detected by bifurcation analysis could be determined. The effectiveness of the method is demonstrated in a methane fueled combustion system. The method here proposed is at an early stage and was applied to a well know system purposely with the aim of validating and identifying its potentiality. It is expected that its further development and its application to new and very complex detailed combustion mechanisms could significantly contribute to the investigation of new generation fuel and hydrogen-based energy carriers.

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