Oscillatory Combustion Kinetic Analysis and Reduction through Functional Weight Coefficient

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1 Introduction

The reaction mechanism for undesirable oscillatory combustion is important to understand the origin of the oscillation especially in the diluted combustion systems (MILD, LTC, etc.) when the characteristic kinetic times is relatively longer and the dynamic behavior is chemically controlled. This work focus on the development of efficient method to analysis and reduce the mechanism for oscillatory combustion. Oscillation of species in a reactive network can be regard as the consequence of neighbor species influence [1]. Based on this understanding, a functional weight of species interactions in combustion systems is defined to recognize important reactions and driving loop processes which may contain thermokinetic feedback for the nonlinear dynamics. The method is demonstrated and validated in the methane and propane fueled oscillatory MILD combustion systems.

2 Method

Since species and reactions are two different kinds of nodes that are closely coupled, combustion reaction mechanism with natural pathways are bipartite networks. To clarify the interspecies relationship, the combustion mechanism is first represented as a network where a link between a reactant and a product species node is established. It can be conveniently described by an N × N matrix, where N is the number of species of the system. $a_{XY}(X,Y=1,\ldots,N)$=1 when X (Y) is involved in reaction i ,and 0 otherwise. The key to identify the important process in oscillatory combustion is to define the weight of inter-species edges in network. Figure 1 illustrate the data conversion process from reaction steps to a weighted species network.

From the network aspect, the periodic oscillation of node can be regard as the consequences of the influence coming from its neighboring nodes in the form of reaction flow, whose intensity is affected by the reaction process, we define the functional weight coefficient ω_{ij} as:

$$\omega_{ij} = \frac{1}{T}\int_0^T \dot{\omega}_{ij}\,dt$$

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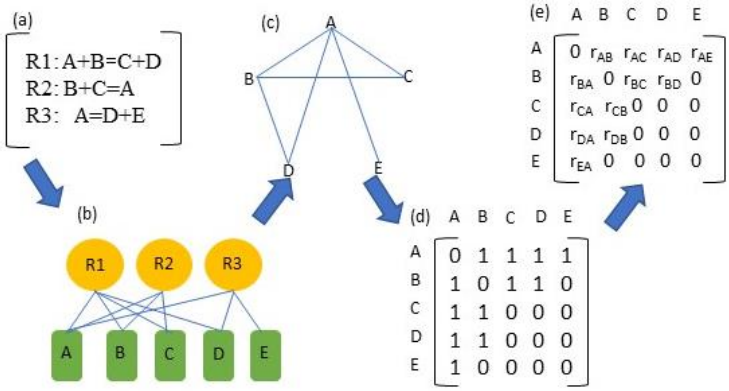

Figure 1. Illustration of data conversion from reaction steps (a) into bipartite network (b)single-vertex network (c) described by an N × N matrix (d) map the kinetic information on the edges to get a weighted matrix of the network(e).

with T is the oscillation period, and $\omega_{ij} = \dot{f_{ij}} / \max\{\dot{f_{11}}, \dots, \dot{f_{ij}}, \dots \dot{f_{ss}}\}$ where $\dot{f_{ij}}$ is the differential form of the total contribution of all neighbor nodes j to the target node i:

$$\dot{f_{ij}} = \sum_{r=1}^{R} \frac{v_i^r}{v_j^r} k_r \delta_{i,j}^r \sum_{r=1}^{R} v_j^r \, k_r \delta_j^r$$

in which when in reaction r, i is the product and j is the reactant, $\delta_{i,j}^r$ =1; and when j is the product, δ_j^r =1. Otherwies, they are 0. Zero or small ω_{ij} represents no or weak functional interaction, while large or unit ω_{ij} denote strong or dominate influence. The contribution of reaction r in $i \rightarrow j$ pathway can be qualitatively determined by:

$$\Psi_r^{ij} = \frac{1}{T} \int_0^T \frac{k_r}{\sum_{r=1}^{R} k_r} \times \frac{\omega_{ij}}{\omega_{jI}} dt$$

By setting a thresholds for ω_{ij}, a skeleton mechanism can be constructed by the species in pathes whose ω_{ij} is greater than the thresholds and reactions within some or all of these species.

Periodic oscillation usually occurs when positive and negative feedback both present and separated by a certain time-lag [2]. In reaction networks, the accumulation of some species in a sequence of reaction steps may affects or regulates the pathways and/or rates of earlier processes through the loop-formed structure, i.e., giving rise to effective chemical feedback. From network structure aspect, it means feedback in chemical reaction networks is also realized through species interaction loops. Finding the important loop ingredient in the network may help to understand the thermokinetic driving forces for the oscillation. To find the crucial loops, ternary loop structures are identified in the obtained skeleton mechanism, since they are the motif loop structure. According to the short plate theory, the path with the minimum ω_{ij} value in the loop is taken as the quantitative parameter to sort the loops. The top ranking ones will be the *Crucial Loops*.

3 Results and discussion

The proposed method is applied to analysis the oscillation mechanism in the MILD combustion reaction system of methane [3] and propane [4]. Kinetic simulation were performed by chemkin II software package in PSR reactor with POLIMI (C1C3LT_1412) model. Fig. 2 shows how the ratio of retained

reactions changes with the threshold of functional weight coefficient. It is obvious that the distribution of edge weights is highly heterogeneous, which can effectively help us to identify important reactions.

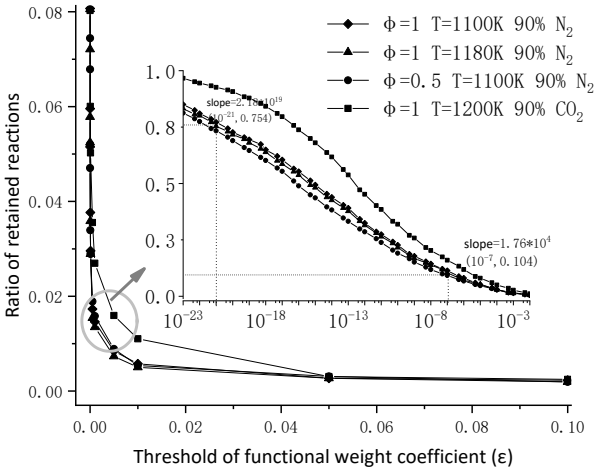

Figure 2: Panorama of ratio of retained reactions distribution with threshold of functional weight coefficient (ε) in methane MILD combustion system. Inlet is the local enlarged diagram in logarithmic coordinate system.

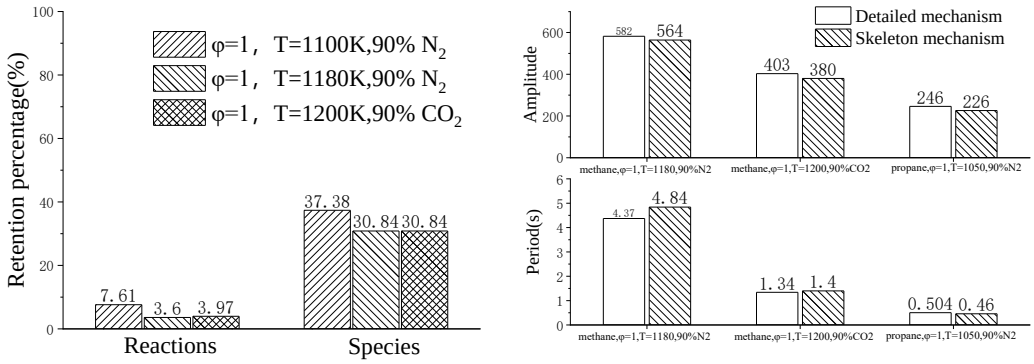

Figure 3. Left: retention percentage of species and reaction number in skeleton mechanism of methane MILD combustion. Right: Oscillation amplitude and period predicted by the detailed and skeleton mechanisms of methane and propane fueled MILD combustion system

Taking the oscillatory working condition of φ = 1, T=1100K, bath gas 90%N_2 as an example, we discuss the obtained skeleton mechanism, important reactions and *crucial loop*s. Since the influence of functional weight is directly reflected by reactions, it is obvious from Fig. 3 that the skeleton mechanism obtained get better ability in reducing reactions. It can be seen that the skeleton mechanisms with simplified efficiency higher than 90% measured by reaction number can be obtained based on functional weight analysis method, and these mechanisms can still highly retain oscillation characteristics such as amplitude and period in detailed mechanisms.

The top 10 important inter-species pathways and the related dominant reactions are listed in Tab. 1. It turns out that most of the reactions found had been reported to play an important role in other related

works. Lavadera et al. [5] revealed that the oscillatory behavior in methane-fueled low-temperature combustion originate from the competition between two pairs of processes, one is methyl oxidation (R725) and recombination (R23) pathways, the other is the low- (R3)and high-temperature (R1) branching reactions of the H_2/O_2 sub-system. Joannon [6,7] et al. also reported that methyl recombination pathways is crucial for oscillatory combustion in methane MILD combustion. Sabia et al.'s [8] analysis in CO_2 diluted CH_4/O_2 system also get several important reactions in Tab. 1, like R1, R3, R7, R18, R23, R402 and R725. These similar results demonstrate that our functional weight analysis can effectively help to get the important reactions contribute to oscillation.

Table 1: Top 10 important pathways and dominant reactions in methane MILD combustion system

Rank	Path	ω	Dominate Reaction		ψ
			Reaction #	Reaction Equation	
1	OH-H	0.852	R18	CO+OH<=>CO_2+H	0.696
2	CO-H	0.562	R18	CO+OH<=>CO_2+H	0.715
3	H-OH	0.471	R1	H+O_2<=>OH+O	0.459
4	H-O	0.283	R1	H+O_2<=>OH+O	0.999
5	H-HO_2	0.139	R3	H+O_2(+M)<=>HO_2(+M)	0.989
6	H-H_2	0.135	R402	H+H_2O<=>H_2+OH	0.665
7	O-OH	0.099	R7	OH+OH<=>O+H_2O	0.77
8	OH-CH_3	0.099	R725	OH+CH_4=>H_2O+CH_3	0.942
9	CH_3-C_2H_6	0.035	R23	CH_3+CH_3(+M)<=>C_2H_6(+M)	0.999
10	O-H	0.031	R2	O+H_2<=>OH+H	0.961

Table 2 shows the five most important *Crucial Loops* and their dominant reactions in methane MILD combustion system. It can be seen that the vast majority pathways in the *Crucial Loops* are within the TOP 10 paths listed in Table 1. All the paths in loop 1 and 3 ranks the TOP 10. Many newly selected dominate reactions in other loops were also proved to be important for oscillating combustion in previous reports. For example, in the investigation of both Lavadera et al.[9] and Wada et al.[10], R271: $CH_3 + HO_2 = CH_3O + OH$ in loop 4 is proved to be an important path for methyl oxidation under low-temperature MILD conditions, and it is among the key reactions that induce the oscillations.

Table 2: Top 5 *Crucial Loops* and dominant reactions in methane MILD combustion system

Rank	Crucial Loop	ω	Path	Dominate Reaction		ψ
				Reaction #	Reaction Equation	
1	O-OH-H	0.099	O-OH	R7	OH+OH<=>O+H_2O	0.770
		0.852	OH-H	R18	CO+OH<=>CO_2+H	0.696
		0.283	H-O	R1	H+O_2<=>OH+O	0.999
2	H-HO_2-OH	0.139	H-HO_2	R3	H+O_2(+M)<=>HO_2(+M)	0.989
		0.029	HO_2-OH	R5	H+HO_2<=>OH+OH	0.955
		0.852	OH-H	R18	CO+OH<=>CO_2+H	0.696
3	H_2-OH-H	0.013	H_2-OH	R2	O+H_2<=>OH+H	0.999
		0.852	OH-H	R18	CO+OH<=>CO_2+H	0.696
		0.135	H-H_2	R402	H+H_2O<=>H_2+OH	0.665

4	H-CH_3-OH	0.012	H-CH_3	R405	H+CH_4<=>H_2+CH_3	0.636
		0.026	CH_3-OH	R271	HO_2+CH_3<=>CH_3O+OH	0.550
		0.852	OH-H	R18	CO+OH<=>CO_2+H	0.696
5	CO-H-HCO	0.562	CO-H	R18	CO+OH<=>CO_2+H	0.715
		0.014	H-HCO	R394	H+CH_2O<=>H_2+HCO	0.832
		0.011	HCO-CO	R174	HCO+M<=>CO+H+M	0.569

Since R1: H+O_2=OH+O is a strong endothermic reaction, loop 1 provides not only a strong chemical positive feedback with the chain branching involved self-promoting loop form, there is also a significant thermal negative feedback within the loop, which is the driving force of the self-sustained unsteady heat release [11]. Figure 6 is the loop diagram of the Top 5 *Crucial Loops*, with red arrows indicate the dominate reaction is endothermic, and the black ones exothermic. It is interesting to find that in most of these loops, there are both exothermic and endothermic reactions that give rise to effective thermal feedback. This again confirms the crucial role of these loops in the oscillatory combustion mechanism.

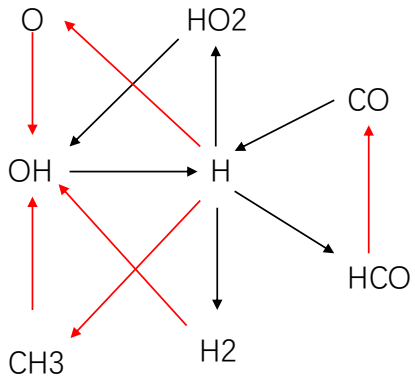

Fig. 6. Loop diagram of the top 5 Crucial Loops in methane MILD combustion system.

4 Conclusions

An efficient oscillatory combustion mechanism analysis and reduction method is proposed and demonstrated based on the appropriate defined the inter-species functional weight coefficient. Application in oscillatory MILD combustion systems reveal that the distribution of functional weight is highly heterogeneous, which enables us to construct skeleton mechanisms for oscillatory combustion and identify the crucial loops that provide thermokinetic feedback. The reduction and prediction ability for oscillatory combustion is validated, and the reactions found to be important are in good agreement with previous related reports, which further confirms the effectiveness of the method.

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