

Community analysis of bifurcation maps of diluted hydrogen combustion in WSFRs

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1 Introduction

The introduction of new combustible mixtures obtained from renewable sources, in the need to avoid emissions responsible for global warming, is challenging for traditional approaches, methods, and knowledge in combustion science. Novel approaches are required to obtain a rapid characterization of the behavior of innovative fuels used alongside new combustion regimes. This article focuses on the development of an automatic procedure for the inspection of the very complex kinetic mechanisms required to predict accurately the behavior of new generation fuels. Being the research at an early stage, in order to keep the simplicity required for the theoretical interpretation of the results and their validation, oxygen-hydrogen mixtures are investigated adopting a detailed mechanism for hydrogen. In the past, it was shown [1]-[3] that even these simpler mixtures, in a Jet Stirred Flow Reactor (JSFR), exhibit a complex dynamic behavior showing transitions from low temperature to high temperature regimes interceded by an oscillating regime.

The identification of the species/reactions sensitive to the change of the operating conditions was, already for this simple configuration, a challenging task for a manual inspection of the single reactions. It could reveal prohibitive for kinetic mechanisms of hundreds of species and thousands of reactions. Therefore, it is suggested the employment of automatic procedures for the recognition of groups of species having similar behavior during the evolution of the kinetics coupled with the continuation analysis that allows the mapping of the solutions and thus the identification of the possible regimes while changing the system parameters [4]. It is found that the detection of the species, and thus the reactions, responsible for the change of the regime are detected by different indices, i.e. some “measure” of the species affinity, following the physical mechanism at the base of the regime transition.

2 Methodology

The map of the solutions of the combustion system (equilibrium points), known the mathematical model $x_t = f(x, p)$ that describes the dynamic behavior of its state x ($x = \{Y_1, \dots, Y_N, T\}$, being Y_i the mass

fractions of chemical species and T the temperature of the reactor), as a function of the time t and the parameters p , is obtained by solving the system:

$$F(X) = 0, \quad F: \mathbb{R}^{n+1} \rightarrow \mathbb{R}^n$$

with $n = N + 1$, $X = (x, p)$ and $F(X) = f(x, p)$. Locating the bifurcation points is addressed by studying the eigenvalues λ_i of the Jacobian matrix:

$$J_f = \frac{\partial f(x, p)}{\partial x} \quad (1)$$

The following indexes identify the mains bifurcation points in a computationally efficient manner [5]:

- Limit points (fold bifurcations): $\psi_F(X) = \prod_{i=1}^n \text{sign}(\lambda_i)$.
- Transition to oscillating regime (Hopf bifurcations): $\psi_H(X) = \prod_{1 \leq i \leq j \leq n} \text{sign}(\lambda_i + \lambda_j)$

For the case analyzed in this study, function f describes the contribution of fluxes entering and leaving the reactor and the production (destruction) of species due to chemical reactions:

$$f = \begin{cases} \frac{Y_{i,in} - Y_i}{\tau} + \frac{W_i r_i}{\rho V}, & i = 1, 2, \dots, N \\ \frac{\sum_{i=1}^N Y_{i,in} (h_{i,in} - h_i)}{c_p \tau} - \frac{\sum_{i=1}^N h_i W_i r_i}{c_p \rho V} - \alpha S \frac{T - T_{env}}{c_p \rho V} \end{cases} \quad (2)$$

When a detailed reaction mechanism describes the chemical behavior of the system, special approaches must be adopted to efficiently solve the system (1), as the one proposed in [4].

To capture the global properties of such a complex interactive system, the critical step is to model it as a network whose nodes represent the dynamical units (such as the neurons in the brain) and the links stand for the interactions between the units. The combustion mechanism is first represented as a network, whose nodes are defined as the reactants. If two compounds participate in one reaction, a link is established between the corresponding nodes. In order to facilitate data analysis, a reaction network with N species can be completely represented by the symmetric adjacency (or connectivity) matrix \mathcal{A} , i.e. a $N \times N$ square matrix whose entry w_{ij} ($i, j = 1, \dots, N$) is 1 if the link l_{ij} exists, and zero otherwise. Let's take the following reaction network as an example:

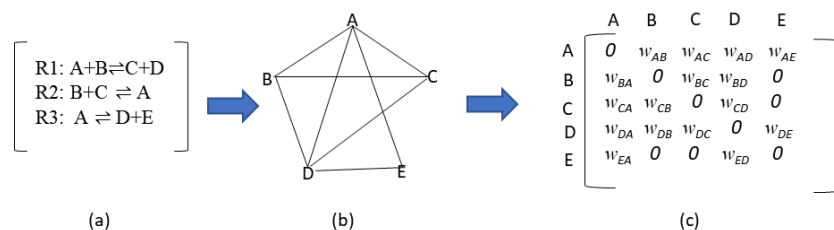


Figure 1: Transformation from reaction mechanism to network for a kinetic mechanism with 3 reactions.

Such networks depict the binary relation, that is, the edges between nodes are either present or not, qualitatively describing the transformation connections between the reactant pairs but losing a lot of quantitative dynamical information. Nevertheless, many real networks display a diversity in the interactions, e.g. strong and weak ties between individuals in social networks [6], uneven fluxes in metabolic reaction pathways [7]. These systems can be better described by weighted networks in which the values r_{ij} represent, with not integer values, the strength of the link. How to define properly the edge weight according to elementary reactions, that is, to decouple the relationship between reactants, is the key issue investigated in this study. Edge weights are generally estimated by fluxes/traffic related to transportation in networks such as the metabolic, Internet, railway networks. In a previous work [8], the weighting function was computed starting from the reaction fluxes, following the approach adopted in several existing mechanism reduction methods, e.g. PFA, DRG, CSP [9]:

$$\omega_r = k_{fr} \prod_{i=1}^N \chi_i^{v'_{i,r}} - k_{br} \prod_{i=1}^N \chi_i^{v''_{i,r}} \quad (3)$$

where χ_i is the molar concentration of the i -th specie. k_{fr} and k_{br} are the forward and backward rate constants of reaction r . $v'_{i,r}$ indicates the forward stoichiometric coefficients of species i in reaction r , while $v''_{i,r}$ is the reverse stoichiometric coefficients. The corresponding weighting function is:

$$w_{ij}^f = \frac{\sum_{r=1}^M |v_{i,r} \omega_r \delta_i^r \delta_j^r|}{\sum_{r=1}^M (|v_{i,r} \omega_r \delta_i^r| + |v_{i,r} \omega_r \delta_j^r| - |v_{i,r} \omega_r \delta_i^r \delta_j^r|)} \quad (4)$$

$\delta_i^r = 1$ when species i is involved in the reaction r , and 0 otherwise. In this work, two different weighting functions have been adopted to recognize the community structure of chemical species in the three different regimes identified. The heat release rate (HRR) weighting function is calculated as:

$$w_{ij}^{HRR} = \frac{\sum_{r=1}^M \left| \frac{\dot{Q}_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \delta_j^r \right|}{\sum_{r=1}^M \left(\left| \frac{\dot{Q}_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \right| + \left| \frac{\dot{Q}_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_j^r \right| - \left| \frac{\dot{Q}_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \delta_j^r \right| \right)} \quad (5)$$

where \dot{Q}_r represents the HRR of the r -th reaction. Note that here endothermic and exothermic reactions are normalized separately. The entropy production rate (EPR) weighting function is computed as:

$$w_{ij}^{EPR} = \frac{\sum_{r=1}^M \left| \frac{epr_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \delta_j^r \right|}{\sum_{r=1}^M \left(\left| \frac{epr_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \right| + \left| \frac{epr_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_j^r \right| - \left| \frac{epr_r}{\sum_{r=1}^M \dot{Q}_r \delta_{ij}^r} \delta_i^r \delta_j^r \right| \right)} \quad (6)$$

where $epr_r = \frac{R_c(q_{fr} - q_{rr}) \ln\left(\frac{q_{fr}}{q_{rr}}\right)}{R_c \sum_{r=1}^M (q_{fr} - q_{rr}) \ln\left(\frac{q_{fr}}{q_{rr}}\right)}$, represent the EPR of reaction r , q_{fr} and q_{br} are the forward and reverse rate of reaction r . Based on this weighted network, community detection could easily help us to extract potential functional modules, in which the reactants have similar dynamical roles. The quality of the obtained community structures resulting from these methods is often measured by modularity Q , which evaluates the density of links inside communities as compared to links between communities [7],[10]. Typically, the higher modularity values, the stronger community structures or better network partition quality. Thus, modularity is widely used as an objective optimization function for finding optimum community detection solutions. For weighted networks, Q is defined as Eq. 7 [11]:

$$Q = \frac{1}{2m} \sum_{ij} \left(w_{ij} - \frac{k_i k_j}{2m} \right) \delta(C_i, C_j) \quad (7)$$

where w_{ij} is the element of \mathcal{A} that represents the weight of edge between node i and j . The node strength $k_i = \sum_j w_{ij}$ is sum of the edge weights attached to node i , C_i denotes the community of species i , and $\delta(C_i, C_j)$ is 1 if $C_i \equiv C_j$ and 0 otherwise. $m = \frac{1}{2} \sum_{ij} w_{ij}$ is the total of edge weight.

The community analysis was executed following the Louvain algorithm [12] based on modularity optimization, which consists of two phases (Fig. 2) that are repeated iteratively. At the start, each node is assigned to a different community. Then, for each node i , the possible gain of modularity, if it is moved into the neighboring community C , is evaluated according to the expression:

$$\Delta Q = \left[\frac{\sum_{in} + 2 k_{i,in}}{2m} - \left(\frac{\sum_{tot} + 2 k_i}{2m} \right)^2 \right] - \left[\frac{\sum_{in}}{2m} - \left(\frac{\sum_{tot}}{2m} \right)^2 - \left(\frac{k_i}{2m} \right)^2 \right] \quad (5)$$

where \sum_{in} is the sum of the weights of the links inside C , \sum_{tot} is the sum of the weights of the links incident to nodes in C , $k_{i,in}$ is the sum of the weights of the links from i to nodes owing to the same community C . Node i is finally moved to the community that produces the maximum modularity gain ΔQ . When all the neighboring community is tried and no more positive gain is achievable, then node i

will stay in its original community. This process is repeated sequentially for all nodes, joining together all the two communities whose amalgamation produces the largest increase in Q , until no further improvement can be achieved, so, the first phase is then completed. The second phase is to construct a new network whose nodes are the communities found during the former phase. The whole procedure repeats iteratively the previous two steps until modularity no longer increases.

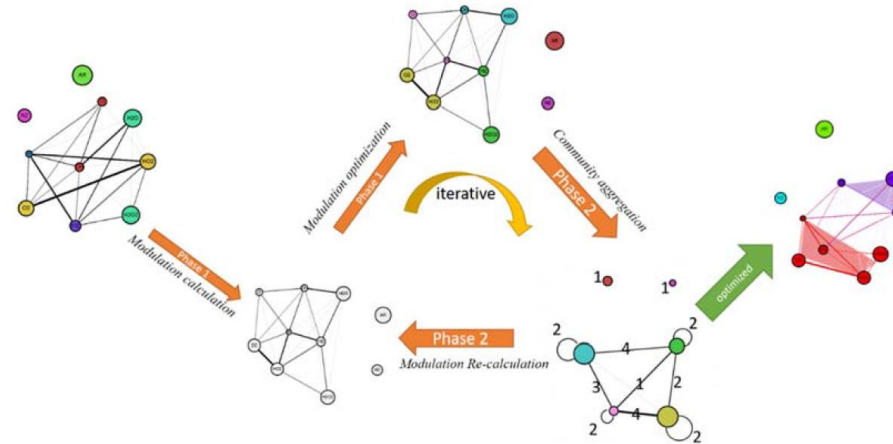


Figure 2: Visualization of the steps of fast-unfolding community detection algorithm.

3 Case study

The premixed burning in a well-stirred flow reactor of a hydrogen/oxygen/nitrogen mixture with hydrogen/oxygen equivalence ratio of 0.5 and a high dilution in nitrogen having 0.94 molar fraction, is studied to investigate the possibility to automatically identify the predominant mechanism leading to the change of regimes. Further details on all parameters' values and experimental results are reported in [3].

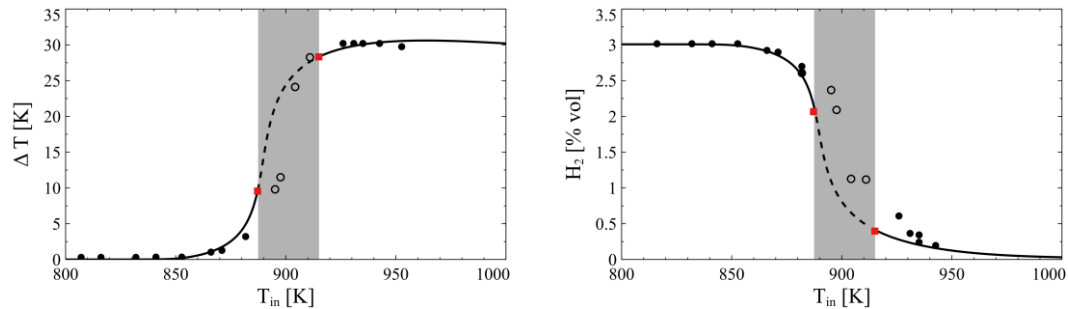
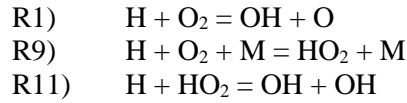


Figure 3: Experimental (dots) and numerical (lines) bifurcation maps of the diluted H_2 - O_2 combustion in JSFR. Filled dots and solid lines for steady equilibrium points, empty dots and dashed lines for oscillating solutions. Red symbols are numerically computed Hopf bifurcation points.

Fig. 3 reports the experimental results by varying the inlet mixture temperature T_{in} . Three main zones can be recognized. At low T_{in} , the exhaust mixture has a temperature very close to the inlet temperature while at high T_{in} the exit temperature increases significantly. These two zones are separated by a region where stable oscillations occur. This global behavior has been reproduced with good agreement adopting the continuation analysis method previously described, which allowed to exactly determine the temperatures at which the regime transitions occur adopting a fixed value for the heat transfer parameter and the detailed kinetic scheme of O'Conaire et al. for hydrogen combustion [13]. The occurrence of the oscillating regime was recognized into the competition between third-body effects in the

recombination of H radicals with O_2 to form HO_2 and the branching reactions that form H and OH radicals:



4 Community Analysis results

Fig. 4 shows the identified communities in the three regimes reported in Fig. 3. When employing flux as edge weight, the community partition is the same in all three regions ($C_1 \equiv \{\text{H}, \text{O}, \text{OH}, \text{H}_2, \text{H}_2\text{O}\}$, $C_2 \equiv \{\text{O}_2, \text{HO}_2, \text{H}_2\text{O}_2\}$). However, when using the two thermal related weighting functions, different partitions were revealed.

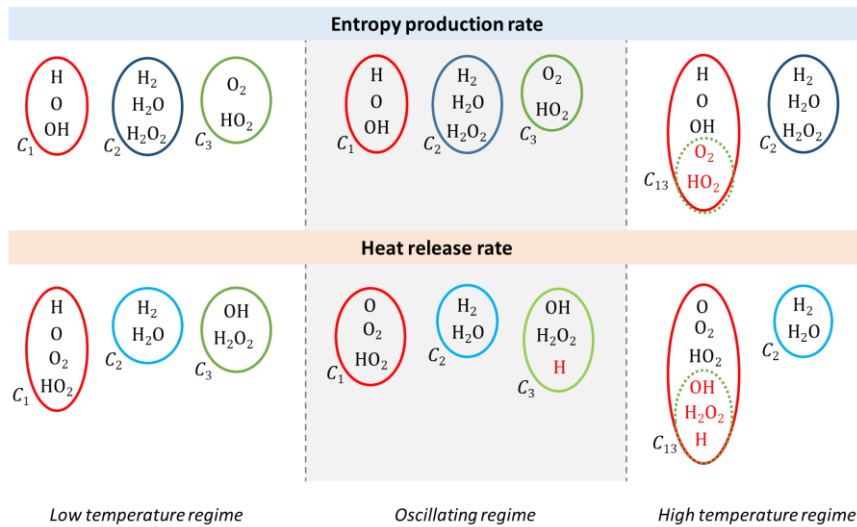


Figure 4: Communities in the three regimes of the well-stirred flow reactor investigated obtained with the EPR index and the HRR index.

A common trait of the analysis conducted with the two new criteria is the detection of three communities at the lower inlet temperatures that reduce to two, by the merging of C_1 and C_3 , at the higher inlet temperatures, revealing a simpler structure of the mechanism behavior at high temperatures. It is also found that is always identified a community of species, C_2 , that is insensitive to regime transitions: H_2 , H_2O for the HRR index, with the addition H_2O_2 for the EPR index. The species that with the transition of the regime shift from one community to another are highlighted in red. It is hypothesized that following these species it is possible to identify the reactions responsible for the change of the regime. However, the results are not the same for the two criteria. The first transition is identified by the HRR index which detects the shift of the hydrogen radical from C_1 to C_3 . This is actually the only species present in all the three reactions R1, R9, and R11 identified in previous studies [1]-[3] as responsible for the occurrence of the oscillating regime. If EPR is the adopted index, the fact that the corresponding community analysis detects different partitions only shifting from the oscillating to the high temperature regimes indicates that different mechanisms govern the low and high inlet temperature transitions.

5 Conclusions

The possibility to extract automatically, from the solution maps of a combustion system, meaningful information for the identification of the key species responsible for the dynamical behavior has been

demonstrated in application to a diluted hydrogen combustion system. This result was obtained by coupling the bifurcation analysis, which identifies the different regimes occurring with a change of the parameters, with algorithms typical of Artificial Intelligence, specifically the Community Analysis, that identify within a large set of individuals (the chemical species) common behavior patterns. An important result is the recognition of effective indexes based on the HRR and the EPR, in contrast with the reaction flux that appears unable to indicate the transition from one regime to another.

This procedure is fully automatic and can be scaled for the analysis of detailed and very complex kinetic mechanisms. To be investigated further, besides the application to more complex systems, is also the possibility to adopt the identified weighting functions, able to catch the dynamic of the system at hand, in the procedures for the mechanisms reduction.

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