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Generalized entropy production analysis for mechanism reduction

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The paper introduces a generalized formulation for the computation of the relative contribution of each elementary reaction to the total entropy production, which has been proposed as a measure of the importance of elementary reactions and used for the reduction of detailed chemical reaction mechanisms. The reduction method is extended for the cases where the principle of detailed balance does not hold or apply, namely in the case of irreversible reactions or when the reverse rate constants are not computed via the thermodynamic equilibrium constants. Using a mechanism for *n*-butane consisting exclusively of reversible reactions, the new formulation is compared to the original one, and then applied for the construction of a skeletal mechanism for *n*-dodecane starting from a detailed mechanism which includes predominantly irreversible reactions. The skeletal scheme is found to accurately capture the ignition delay times over an extended range of pressure, initial temperature and equivalence ratio, the steady-state temperature as function of the residence time in a non-isothermal adiabatic perfectly stirred reactor, and the laminar flame speed of atmospheric flames at different unburned mixture temperatures and equivalence ratios.

Keywords: skeletal mechanism; mechanism reduction; entropy production; *n*-dodecane

1. Introduction

Practical fuels like those used for transportation consist of a mixture of several hydrocarbons that vary widely in the number of carbon atoms and concentration [1]. The numerical study of a combustion process involving these fuels requires the adoption of a ‘surrogate’, i.e. a mixture of 2–10 species representing the properties of the real fuel, and of a detailed reaction mechanism involving hundreds or thousands of chemical species participating in roughly five times as many elementary chemical reactions [1,2]. However, it is practically impossible to use these large detailed reaction mechanisms in multidimensional combustion simulations because the computational costs and memory requirements are prohibitive [3]. A significant part of the total computational cost in reactive flow simulations is spent in solving the stiff differential equations for species with negligible concentration and importance [4]. The combustion chemistry should, therefore, be described with the lowest number of species possible when trying to couple a chemical kinetic model with a complex physical model. Indeed, within large mechanisms, the key reactions may be drowned in a sea of marginal steps [5]. Several techniques have been proposed in the literature to reduce

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detailed reaction mechanisms. A brief overview of the reduction methods is presented below while more detailed descriptions can be found in recent books [5,6].

The conceptually simpler approach for reducing the size of a reaction mechanism is to identify species and/or reaction steps which can be removed from the mechanism without losing too much accuracy in the prediction of the key target outputs of the model [5]. The reduced mechanism obtained after elimination of the unimportant reactions and species is the so-called skeletal mechanism. Broadly speaking, algorithms based on the elimination of unimportant reactions and species can be grouped in three main categories: timescale-, graph- and statistical-based approaches. Two well-known timescale-based approaches, the Quasi Steady-State Approximation (QSSA) and the Partial Equilibrium Assumption (PEA) (see e.g. [5]), provide useful information about the chemical kinetics behavior and the dominant species and reactions. More automated methods, including the sensitivity analysis [7] and the Computational Singular Perturbation (CSP) [8], can be used to find the important reactions and species dictating the system behavior, which should be kept in the reduced mechanism. In graph-based approaches, a graph connecting the reactions and/or species through the evolution of the chemical kinetics is constructed. Path Flux Analysis (PFA) (e.g. [9,10]), and methods based on the Directed Relation Graph (DRG) (e.g. [11–13]) belong to the graph-based approaches. A statistical and optimization analysis on the dataset of the detailed reaction models can also reveal the species and reactions determining the system behavior. Among others, the Principal Component Analysis (PCA) [14], and optimization-based methods [15] belong to this category.

Different methods can be developed by considering thermodynamic properties of the system. The role of entropy in the determination of low dimensional manifolds was exploited in other works. The Rate Controlled Constrained Equilibrium (RCCE) method assumes that at any time the system state is the one that maximizes an entropy function subject to a small set of constraints imposed by the slow reactions [16,17]. The Minimal Entropy Production Trajectory (MEPT) method replaces the high dimensional dynamics with a low dimensional approximation using the minimum entropy production principle [18], while Valorani et al. derived expressions that reveal the direct link between timescales and entropy production [19]. However, the aforementioned methods based on entropy have been applied to relatively small detailed reaction mechanisms since they are computationally demanding.

Recently, a new approach for generating skeletal mechanisms based on entropy production analysis was proposed by Kooshkbaghi et al. [20] and applied on a large detailed mechanism for n-heptane [20,21]. The method exploits the relative contribution of elementary reactions to the total entropy production to identify the most important species to be included in the skeletal mechanisms, i.e. the species participating in the reactions whose relative contribution to the total entropy production is larger than a user-specified threshold. The method is easy to implement, and does not require any prior knowledge about the detailed mechanism (for example, unlike the DRG-based approaches, which require determination of the target species).

In [20], the formulation of the entropy production equation was based on the principle of detailed balance, which states that any elementary process and its reverse occur with equal rates at equilibrium [22,23]. However, it is common to deal with mechanisms containing many reactions that violate the principle of detailed balance. This is, indeed, the case when some reactions are defined as irreversible or when their rate constants depend on user-defined parameters (e.g. defined with the REV keyword in the CHEMKIN input format [24]) instead of being computed through the equilibrium constant.

The aim of this work is to propose a more general formulation of the Kooshkbaghi et al. method [20] that is also valid when the principle of detailed balance is violated. It is shown that an entropy production equation can be derived starting from first principles of chemical reaction thermodynamics without the need to introduce the principle of detailed balance. Thus, a formulation is derived that can be adopted for the reduction of detailed mechanisms containing both reversible and irreversible reactions.

The paper is organized as follows. The theoretical background of the entropy production for chemical kinetics is briefly reviewed. Then, the algorithm for the construction of skeletal mechanisms is illustrated. The implementation is validated by comparison to the approach proposed by Kooshkbaghi et al. [20] in the analysis of a reaction mechanism consisting only of reversible reactions. Finally, the new formulation is adopted in order to generate a skeletal mechanism for *n*-dodecane combustion valid in a wide range of operating conditions starting from a reaction mechanism including predominantly irreversible reactions.

2. Theoretical background: entropy production for chemical kinetics

For the sake of clarity, it is useful to review some thermodynamic concepts. The second principle of thermodynamics postulates the existence of a function of state, called entropy, which has the following characteristics [25]

- it is an extensive property
- its change, dS , can be split into two parts: a contribution due to interactions with the exterior $d_e S$ and a contribution due to changes inside the system $d_i S$

$$dS = d_e S + d_i S \quad (1)$$

Considering the entropy as a function of internal energy U (neglecting any other contribution to the total energy), volume V and the number n_k of moles of each species [26]

$$S = S(U, V, n_1, n_2, \dots, n_{N_s}) \quad (2)$$

the differential form can be written as

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V, n_j} dU + \left(\frac{\partial S}{\partial V} \right)_{U, n_j} dV + \sum_{k=1}^{N_s} \left(\frac{\partial S}{\partial n_k} \right)_{U, V, n_{j \neq k}} dn_k \quad (3)$$

The partial derivatives in the Equation (3) can be expressed by using the definition of absolute temperature, pressure and chemical potentials [27,28]

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, n_j} \quad (4)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S, n_j} = T \left(\frac{\partial S}{\partial V} \right)_{U, n_j} \quad (5)$$

$$\mu_k = \left(\frac{\partial U}{\partial n_k} \right)_{S, V, n_{j \neq k}} = -T \left(\frac{\partial S}{\partial n_k} \right)_{U, V, n_{j \neq k}} \quad (6)$$

Therefore, the entropy differential takes the form

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_{k=1}^{N_s} \mu_k dn_k \quad (7)$$

If chemical reactions occur in the system, the change in the mole number dn_k of the k -th species may be due both to mass exchange with the surrounding and to chemical reaction inside the control volume [26]

$$dn_k = d_e n_k + d_i n_k \quad (8)$$

where $d_e n_k$ and $d_i n_k$ represent the external (due to exchange with the surrounding) and the internal (due to chemical reactions) differential change of the moles of the k -th species, respectively.

For a homogeneous (closed as well as open) system¹, considering Equation (1) and substituting Equation (8) in Equation (7), we obtain

$$d_e S = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_{k=1}^{N_s} \mu_k d_e n_k \quad (9)$$

$$d_i S = -\frac{1}{T} \sum_{k=1}^{N_s} \mu_k d_i n_k \quad (10)$$

where $d_i S$ represents the entropy change due to chemical reactions.

The rate of change of the moles of the k -th species due to chemical reactions can be expressed in terms of production rates [26]

$$\frac{d_i n_k}{dt} = V \sum_{n=1}^{N_r} (v_{kn}^P - v_{kn}^R)(q_n^f - q_n^r) \quad (11)$$

where v_{kn}^P and v_{kn}^R are the stoichiometric coefficients on the product and reactant sides of the n -th reaction and the q_n^f and q_n^r are the forward and reverse rate of progress of the n -th elementary reaction, respectively. Substituting Equation (11) into Equation (10), we obtain the rate of change of entropy due to chemical reactions

$$\frac{d_i S}{dt} = -\frac{V}{T} \sum_{k=1}^{N_s} \sum_{n=1}^{N_r} \mu_k (v_{kn}^P - v_{kn}^R)(q_n^f - q_n^r) \quad (12)$$

Finally, since the quantity

$$a_n = -\sum_{k=1}^{N_s} \mu_k (v_{kn}^P - v_{kn}^R) \quad (13)$$

is the chemical affinity (or De Donder's affinity) of the n -th reaction [26], the rate of change of entropy due to chemical reactions can be written as

$$\frac{d_i S}{dt} = \frac{V}{T} \sum_{n=1}^{N_r} a_n (q_n^f - q_n^r) \quad (14)$$

3. Skeletal reduction using entropy production analysis

The algorithm for reducing a detailed reaction mechanism to obtain a skeletal mechanism follows the same steps as the approach proposed by Kooshkbaghi et al. [20]:

- (1) construct a database of the thermochemical states (temperature, pressure and compositions) for the process of interest (e.g. homogeneous ignition in a constant-pressure or constant-volume reactor),
- (2) identify the most important reactions as the ones contributing to the total entropy production rate more than a user-specified threshold ϵ ,
- (3) select the important species, i.e. the species participating in the elementary reactions which are identified in step (2),
- (4) generate the skeletal mechanism by keeping *all* important species from step (3) and *all* reactions in which these species participate.

The relative contribution of elementary reactions to the total (internal) entropy production is used as a measure of the importance of each reaction in the mechanism, and, consequently, to identify the most important reactions.

When the principle of detailed balance holds, i.e. the chemical affinity can be expressed in terms of production rates [25]

$$a_n = RT \ln \left(\frac{q_{f_n}}{q_{r_n}} \right) \quad (15)$$

the relative contribution of each reaction to the total (internal) entropy production can be written in the form proposed in [20]

$$r_n^K = \frac{d_i S_n / dt}{d_i S / dt} = \frac{\ln \left(\frac{q_{f_n}}{q_{r_n}} \right) (q_{f_n} - q_{r_n})}{\sum_{n=1}^{N_r} \ln \left(\frac{q_{f_n}}{q_{r_n}} \right) (q_{f_n} - q_{r_n})} \quad (16)$$

However, many detailed reaction mechanisms, especially those modeling complex fuels, include irreversible reactions and/or reversible reactions which do not satisfy the principle of microscopic reversibility (e.g. reactions for which the reverse rates are not computed through the equilibrium constant but depend on arbitrary parameters). These mechanisms do not adhere strictly to the principle of detailed balance [22]. In the original formulation of the entropy analysis method, a small positive value (e.g. 10^{-200}) was assigned in place of the reverse reaction rate of an irreversible reaction [20]. Clearly, this choice introduces arbitrariness, calling for a more general form of the relative contribution of each reaction to the total (internal) entropy production.

Considering instead the definition of the rate of change of entropy due to chemical reactions, Equation (14), and that, for modern thermodynamics, when two processes/reactions take place simultaneously in the same system, the following relations hold [29]

$$d_i S_1 < 0, \quad d_i S_2 > 0 \quad \text{and} \quad d_i S = d_i S_1 + d_i S_2 \geq 0, \quad (17)$$

the relative contribution of each reaction to the total (internal) entropy production can be defined as

$$r_n = \frac{|a_n(q_{f_n} - q_{r_n})|}{\sum_{n=1}^{N_r} |a_n(q_{f_n} - q_{r_n})|} \quad (18)$$

The absolute values are needed because the most important reactions must be identified regardless of the sign of their contribution to the total (internal) entropy production. The

absolute values are unnecessary in Equation (16) because when the principle of detailed balance holds (the product $\ln(q_{f_n}/q_{r_n})(q_{f_n} - q_{r_n})$ is always positive), or reactions follow the law of mass action (see [30] for further details), the entropy production of a reaction cannot be negative (i.e. thermodynamic coupling is not possible [31]).

Equation (18) highlights the importance of the role played by the chemical affinity and consequently by the chemical potentials of chemical species (see Equation (13)). For a species in a mixture of ideal gases, the chemical potentials can be expressed as [27]:

$$\mu_k(T, P) = \mu_k^{\text{pure}}(T, P) + RT \ln(X_k) \quad (19)$$

where μ_k^{pure} is the chemical potential of the pure species.

In the simple case of a single-component system, the chemical potential is equal to the specific Gibbs free energy [27]

$$\mu_k^{\text{pure}}(T, P) = g_k^{\text{pure}}(T, P) = g_k(T, P^0) + RT \ln\left(\frac{P}{P^0}\right) \quad (20)$$

where P^0 is the standard state pressure (usually 1 bar) and $g_k(T, P^0)$ is the standard state specific Gibbs free energy that is evaluated from standard state enthalpies and entropies:

$$g_k(T, P^0) = \frac{g_k^0}{RT} = \left(\frac{h_k^0}{RT} - \frac{s_k^0}{R} \right) \quad (21)$$

The latter can be computed from thermodynamic data by adopting the NASA polynomials [32].

Since the computation of the contributions defined by Equation (18) is straightforward and computationally inexpensive, it can be easily applied to a large number of states in the database. For example, the whole set of states that describes the trajectory obtained by integrating the governing equations from the initial state to complete ignition in a homogeneous reactor at the condition of interest can be adopted.

After determining the relative contribution of each reaction to the total entropy production, the important species are identified by retaining all elementary reactions for which $r_n > \varepsilon$ and the skeletal mechanism is generated. The important species are defined as the species participating in at least one important reaction. Obviously, the list of important species can be extended to include any additional species of interest, e.g. unimportant species that are needed for comparison with experimental measurements. The size of the skeletal mechanism will slightly increase because of the inclusion of the requested species and the reactions where the requested species participate with the selected important species. The skeletal mechanism is constructed by keeping only the important reactions and the species they contain. Elimination of the unimportant species from the detailed mechanism is done using a Python tool written using subroutines from PyMARS [33,34] in order to generate directly the skeletal mechanism in the Cantera [35] format.

The current formulation, which will be referred to as the generalized entropy production analysis (GEPA) approach, is compared with the original approach of [20] that will be referred to as EPA. Firstly, the equivalence between the two approaches is established for a reaction mechanism including only reversible reactions. The San Diego mechanism (version 2016-08-15) [36–38] satisfies this requirement, and is adopted to find the entropy production contributions of elementary reactions during the isobaric and

isenthalpic autoignition of an *n*-butane/air mixture. The equivalence is established by comparing the relative contribution of each reaction to the total (internal) entropy production computed respectively with Equation (16) and Equation (18).

Then, a skeletal mechanism for *n*-dodecane is derived from the comprehensive mechanism developed by the CRECK Modeling Group in Politecnico di Milano (thereafter indicated as the POLIMI mechanism) [39,40], which mainly consists of irreversible reactions, to assess the capability of the newly proposed approach.

4. Entropy production analysis of *n*-butane–air mixture: the San Diego mechanism

The San Diego mechanism (version 2016-08-15) describes C_1 – C_4 oxidation and is designed to model a range of conditions that encompass both low and high temperature and

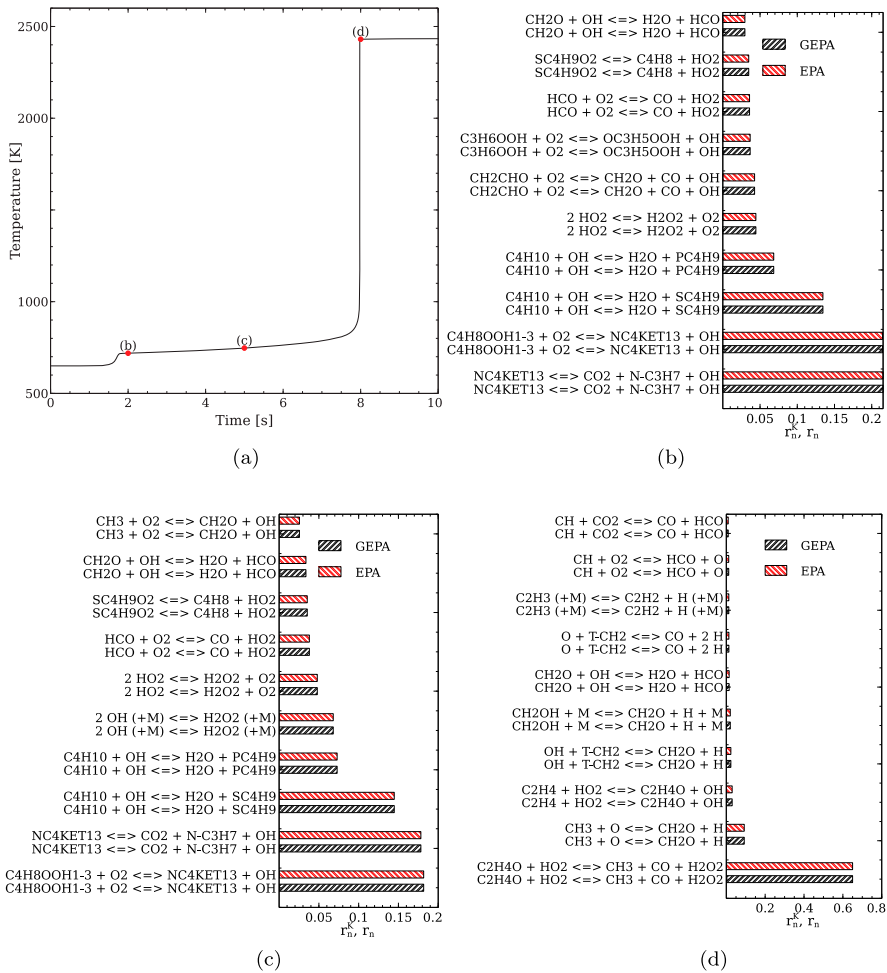


Figure 1. Comparisons of the entropy production contributions of the 10 most contributing elementary reactions obtained using the EPA (forward slanted lines) and the GEPA approach (backward slanted lines) ($\phi = 1$; $P = 1$ atm, $T_0 = 650$ K for *n*-butane–air ignition.) (a) Temporal evolution of temperature, (b) Entropy production contributions at 2 s, (c) Entropy production contributions at 5 s, and (d) Entropy production contributions at 8 s.

pressure chemistry [36–38]. It involves 269 reversible elementary reactions and 57 chemical species. The philosophy underlying this mechanism is to include only a relatively small number of elementary steps that are of crucial importance in order to reproduce the target combustion phenomena. It is adopted here because it includes only reversible reactions and therefore it is suitable to demonstrate that the two formulations given by Equations (16) and (18) are equivalent for this class of mechanisms. Among C_1 – C_4 hydrocarbons, *n*-butane was selected because it exhibits behaviors similar to that of more complex hydrocarbons [38].

Figure 1(b–d) shows a comparison of the entropy production analyses using the EPA (forward slanted lines) and GEPA (backward slanted lines) at the three time instants ($t = 2, 5$ and 8 s) marked in the temporal evolution of temperature during the ignition of a stoichiometric mixture ($\phi = 1$) at atmospheric pressure ($P = 1$ atm) and initial temperature $T_0 = 650$ K (Figure 1(a)). Clearly, the entropy production contributions obtained with the two approaches are identical for the ten most important reactions shown. The same was observed at all time instants and for all reactions of the mechanism.

5. Skeletal reduction for CRECK modeling group mechanism: *n*-dodecane oxidation

The POLIMI mechanism is a lumped mechanism for modeling pyrolysis, partial oxidation and combustion of hydrocarbon and oxygenated fuels [40]. Version 1412 of December 2014, consisting of 451 species and 17,848 reactions, is selected because the vast majority (about 95%) of the reactions are irreversible. This reaction mechanism can be used to study oxidation of hydrocarbons from C_1 to C_{20} .

The *n*-dodecane is considered here for reduction because it is a primary reference component in several transportation fuel surrogates, especially for jet fuels (e.g. [41–43]). The reduction is performed using a database consisting of reaction states sampled from autoignition simulations over a wide parameter range: pressure of 1, 5, 10, 20 atm, initial temperatures ranging from 650 to 1400 K resolved with a step of 50 K in the range from 650 to 1000 K and a step of 100 K in the range from 1100 to 1400, and equivalence ratios of 0.5, 0.8, 1.0, 1.2, 1.5. In total, 46,273 states were included in the database, which was constructed by sampling the trajectories every 10^{-4} s from the initial state till shortly after ignition. For this fuel, a skeletal mechanism consisting of 120 species, including argon, and 2164 reactions was obtained using GEPA by keeping all reactions for which $r_n > \epsilon = 4.2 \times 10^{-3}$. The threshold was chosen to obtain a skeletal mechanism of size comparable to that of the mechanism proposed in [44]. Specifically, this mechanism was obtained, starting from the same detailed mechanism here adopted, by using initially a Reaction Flux Analysis approach [44], and then by DRG-based approaches [45]. This mechanism, thereafter referred as R-POLIMI, consists of 130 species and 2323 reactions.

The comparisons between the skeletal and the detailed mechanisms are performed for autoignition in a constant-pressure reactor, the dependence of the steady-state temperature on residence time in a perfectly stirred reactor (PSR), and the laminar flame speed. Figure 2 reporting the ignition delay times as a function of the initial temperature at pressures of 1 and 20 atm, and equivalence ratios of 0.5, 1, and 1.5 for skeletal and detailed mechanisms, shows a very good agreement between the GEPA-reduced and the detailed mechanism. The relative deviation between the detailed and the skeletal mechanism is, on average, lower than 10%, with larger differences (with a maximum less than 23%) arising only at low

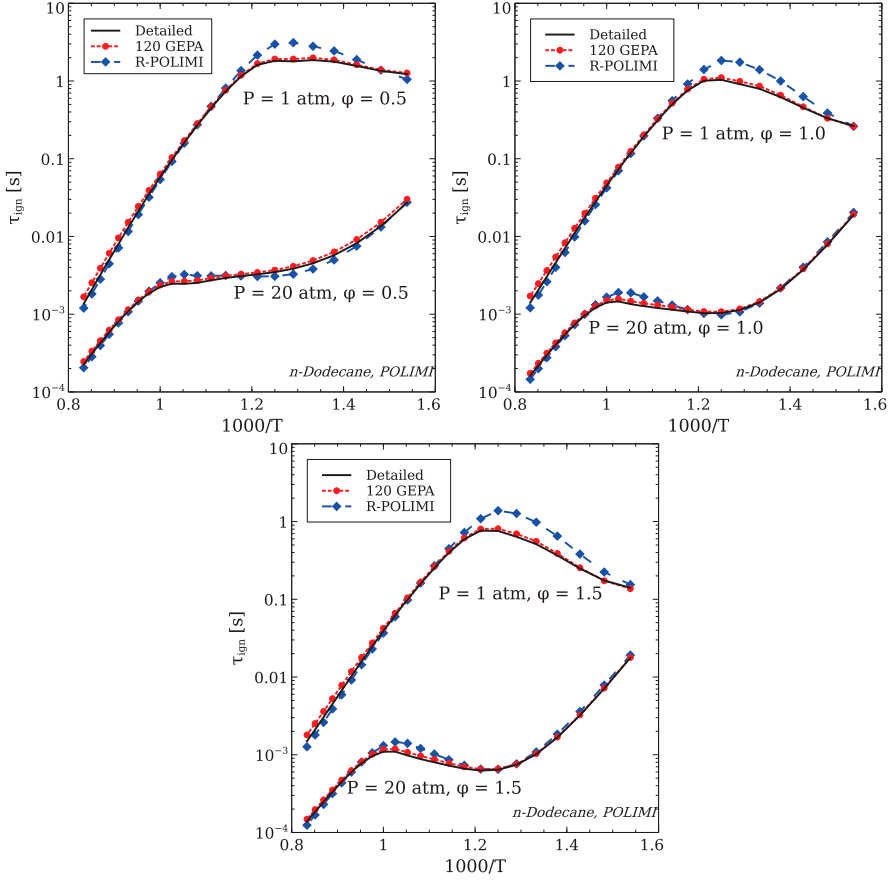


Figure 2. Dependence of the *n*-dodecane ignition delay time on initial temperature under various pressures and equivalence ratios calculated with the detailed and skeletal mechanisms.

pressures for temperature greater than 1000 K. It is worth pointing out that in the authors' experience, accuracy can be improved when a narrower range of conditions is considered for reduction. The comparison with the results obtained with the R-POLIMI mechanism illustrates that all features of the autoignition profiles are accurately reproduced by the skeletal mechanism constructed with the new approach, especially in the NTC region, without the need for any further tuning.

The skeletal mechanism is further validated against the detailed mechanism by computing the steady-state temperature as function of the residence time in a non-isothermal adiabatic PSR. A stoichiometric mixture of *n*-dodecane with air at inlet temperature of 650 K and pressures of 1 atm and 20 atm is considered. The results reported in Figure 3 were obtained using the parametric continuation tool introduced in [46,47], and a very good agreement with those of the detailed and R-POLIMI mechanisms can be seen. Appreciable differences arise around the low- and high-temperature extinction points (the second and the fourth turning points) counting from below in the high-pressure case.

Finally, the accuracy of the skeletal mechanism to predict the laminar flame speed with respect to the equivalence ratio was examined under atmospheric pressure and unburned mixture temperatures (u) of 400, 470 and 650 K. The laminar flame speed was computed

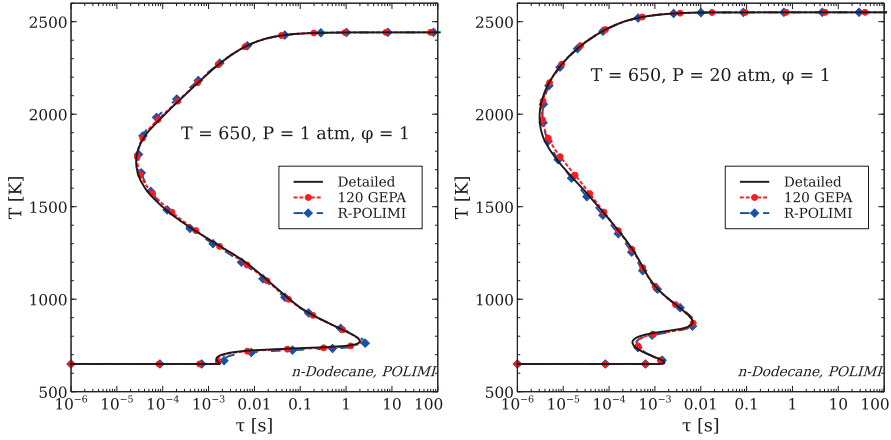


Figure 3. Temperature as a function of residence time in an adiabatic PSR fed with a stoichiometric mixture with *n*-dodecane and air. Left $P = 1$, right $P = 20$ atm.

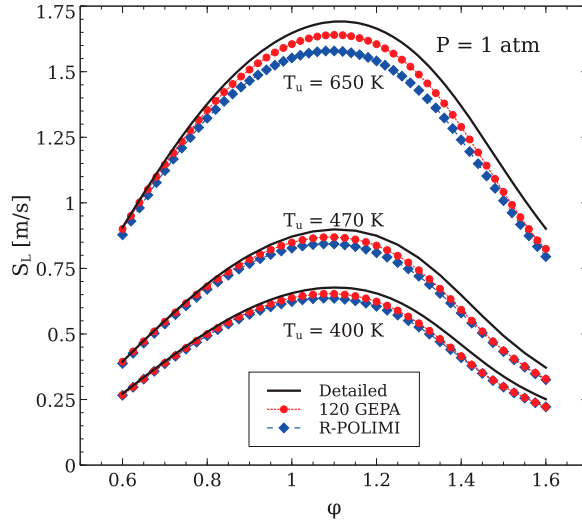


Figure 4. Laminar flame speed vs equivalence ratio at $P = 1$ atm, $T_u = 400, 470, 650$ K.

using Cantera [35] and the results are reported in Figure 4. The GEPA skeletal mechanism correctly predicts the dependence upon temperature and equivalence ratio, but the accuracy of the results progressively deteriorates with increasing equivalence ratio. The GEPA skeletal mechanism exhibits an average error of 5.2% at 400 K, of 4.9% at 470 K, and of 4.1% at 650 K, with maximum errors of 11.6%, of 11.8%, and of 8.5%, respectively. It should, however, be pointed out that the flame speed depends on both kinetic and transport parameters. Indeed, the total entropy production rate in premixed laminar flame is the sum of four contributions: viscous dissipation (that can usually be neglected), heat conduction, mass diffusion, and chemical reaction [48]. Therefore, a reduction based on a database consisting only of reaction states sampled from autoignition simulations, where convection and diffusion processes are absent, cannot ensure the generation of a skeletal mechanisms that is accurate for laminar flame speed calculations over such an extended range of equivalence ratio [49]. Although the major process for the entropy production in

premixed flames is chemical reaction, the effect of heat conduction and mass diffusion may not be negligible (see e.g. [48]). The contribution of these processes in entropy production will be investigated in future work.

6. Conclusions

A generalized formulation of the entropy production analysis method for mechanism reduction was presented that can accurately account for reactions that do not satisfy the principle of detailed balance. The new formulation was verified to be consistent with the original one in the case of a reaction mechanism consisting purely of reversible elementary reactions. Then, it was used for generating a skeletal mechanism for *n*-dodecane starting from a lumped detailed scheme consisting mainly of irreversible reactions. The 120-species skeletal mechanism, provided as supplementary material, corresponds to a reduction ratio of the 73% of the number of species in comparison to the detailed mechanism, at the price of a low reduction of accuracy, demonstrates the effectiveness of the generalized entropy production approach.

Future work will investigate the stiffness of the skeletal mechanisms constructed with the help of entropy production analysis and the possibility for further reduction using lumping and timescale analysis. The contribution of the convective and diffusive processes present in spatially varying combustion phenomena will also be investigated.

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Disclosure statement

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Supplemental data

Supplemental data for this article can be accessed at <https://doi.org/10.1080/13647830.2018.1504990>.

Note

1. Having neglected all other contributions to the total energy, changes of internal energy cannot arise in the homogeneous system.

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