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RESEARCH ARTICLE

# An a priori thermodynamic data analysis based chemical lumping method for the reduction of large and multi-component chemical kinetic mechanisms

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**Abstract**

A chemical species lumping approach for reduction of large hydrocarbons and oxygenated fuels is presented. The methodology is based on an a priori analysis of the Gibbs free energy of the isomer species which is then used as main criteria for the evaluation of lumped group. Isomers with similar Gibbs free energy are lumped assuming they present equal concentrations when applied to standard reactor conditions. Unlike several lumping approaches found in literature, no calculation results from the primary mechanism have been employed prior to the application of our chemical lumping strategy. An 807 species and 7807 individual reactions detailed mechanism comprising *n*-decane, $\alpha$-methylnaphthalene and methyl decanoate has been used. The thermodynamic data have been analyzed and 74 isomer groups have been identified within the oxidation of *n*-decane and methyl decanoate. The mechanism reduction has led to a mechanism size of 463 species and 7600 reactions. Thereafter the lumped mechanism has been checked under several reactor conditions and over a broad range of temperature, pressure, and equivalence ratio in order to quantify the accuracy of the proposed approach. In all cases, very good agreement between the predictions obtained using the lumped and the detailed mechanism has been observed with an overall absolute error below 12%. Effects of the lumping procedure on sensitivities and on isomer concentrations were considered to further demonstrate the validity of the proposed approach.

**KEYWORDS**

chemical kinetics, chemical lumping, mechanism reduction

## 1 | INTRODUCTION

Increasing oil prizes, the international $CO_2$ emission reduction targets as well as legislation have led the energy and transportation sectors to face an intricate and challenging situation where technological development is sharply constrained by environmental regulations. Combustion of fossil fuels represents nowadays one of the main sources of green-house gases and pollutant emissions and it is therefore subject to more and more stringent emission standards. Although the movement towards the generation of renewable energy has seen a tremendous growth

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in the last years, to supply future human energy demands it is unlikely that fossil fuel combustion will lose the status of major energy source for the decades to come. Because of such scenario extensive research has been carried out toward a deeper understanding of the chemical part of combustion through the usage of advanced measurement strategies and chemical kinetic modeling. Together with experimental investigation, the importance of chemical kinetics in reacting flows has been widely recognized.[1,2] For this matter, the efficient incorporation of complex reaction mechanisms in simulation studies represents one of the main challenges faced by academic and industrial combustion researchers. Typically, mechanisms that are realistic and comprehensive consist of many species and they frequently have vastly different time scales. The combination of these two factors makes their simulation stiff and computationally expensive. Hence there is the need to reduce the size and stiffness of detailed mechanisms that are developed, with minimum loss of chemical fidelity, before they can be adopted for simulations, especially if 3D computational fluid dynamics (CFD) framework is concerned. For many applications in fact, the complete and accurate description of the oxidation system would involve several thousands of transported scalars leading to a prohibitive computational cost and a level of accuracy over-proportioned with respect to the phenomena of interest.

Development of reliable systematic reduction methods that require minimum user input is therefore necessary and great advancements have been made on this topic as broadly discussed by Tomlin et al.[1] and Lu and Law.[2] The most straightforward strategy is to identify and explicitly remove species and reactions from the mechanism that have a negligible contribution to the physical conditions of interest. The resulting skeletal mechanisms, usually of compact sizes, are then suitable for other techniques introducing model assumptions to further reduce the computational time. These techniques are mostly based on time scale analysis, such as Quasi-Steady State Assumption (QSSA),[3] Intrinsic Low-Dimensional Manifolds (ILDM),[4] or Computational Singular Perturbation (CSP).[5] The present work relies on the method called chemical lumping which consists of combining species with similar properties. Since mechanisms of large hydrocarbons typically involve large number of isomers, which present similar thermal and transport properties, they can be grouped into representative species, leading to a noticeable reduction of the mechanism size.

Chemical lumping is usually adopted either as a powerful modeling tool or a convenient reduction technique. In pyrolysis for instance, the large number of molecules in hydrocarbon feedstocks complicates dramatically the development of comprehensive models. Among many approaches, Nigam et al.[6] proposed to lump all molecules depending on the compound classes (i.e., normal, isoparaffins) while the pyrolysis reactions are classified into four families (i.e., H atom abstraction, beta-scission). Rate coefficients for both species and reaction lumping were taken from available experimental data. In most of the applications though, lumping is employed as a tool to reduce the computational time needed to solve detailed chemical models. A significant effort was done to establish a mathematical strategy to lump a system of ordinary differential equations (ODEs).[7] As reported by Lu et al.[2] the main aspects to be considered are firstly, the appropriate choice of the species to lump; secondly accurate evaluation of the quantitative contribution of each isomer species to its lump group. Several approaches that use numerical simplifying assumptions can be found in literature. For methane conversion, Huang et al.[8] proposed to choose the lump groups by introducing numerical criteria based on pre-calculated local concentrations and rates of formation obtained using the detailed mechanism. A similar procedure was outlined by Watson et al.[9] for atmospheric chemistry mechanism reduction where species were selected to maintain the chemical class, prior imposing a chemical classification criterion.

For large hydrocarbon applications instead, where more chemically meaningful assumptions are needed rather than mere numerical consideration, the general trend for the choice of the lump group is to identify species having the same functional group and different distribution of radical or oxygenated sites on the molecule; isomers as such. For the estimation of the relative contribution of the isomers within the lump group several approaches have been published in the past. Such strategies are based either on empirical correlations obtained through pre-calculated reactor experiments[10]; on imposition of the QSSA on the primary mechanism[11]; on statistical information derived from calculation performed using the primary mechanism over a user defined range of conditions[12]; on a general set of conditions imposed to the primary mechanism.[13] With respect to the latter category, several strategies have been focused on an accurate quantification of the isomer contribution, and thus the estimation of the reaction rates, of the lumped pseudo species. Ranzi et al.[10] applied the QSSA and evaluated the rate constants of the lumped mechanism through least-square optimization of the primary product selectivity over a given range of pressures and temperatures. Their method also included lumping of parallel reactions with the same reactants and the stoichiometry of the products was estimated at a given temperature using the detailed mechanism. Pepiot et al.[13] proposed a different procedure based on calculated data using the detailed mechanism over several sample points of a user defined physical space. Statistical data on the isomer contributions were gathered at each sample point and were used to build fitting functions for the lumped

**TABLE 1** Typical commercial European fuels properties

| Property | Method | Diesel | RME |
|---|---|---|---|
| Density at 15°C (kg/m$^3$) | DIN EN 12185 | 839.2 | 883.3 |
| Kinematic viscosity (mm$^2$/s) | DIN EN 3104 | 3.03 | 4.46 |
| Cetane number (–) | DIN EN 15195 | 51.6 | 55.6 |
| Lower heating value (MJ/kg) | DIN EN 590 | 42.55 | 38.23 |

mechanism rates coefficient evaluation. Among other authors, Chang et al.[14] used the so-called decoupling method for the reduction of a multi-component mechanisms for Diesel combustion. This method assumes that, even for large species (i.e., *n*-decane or *iso*-octane), the main combustion characteristics are largely influenced by the small radicals (often included as the $C_0$ – $C_4$ part of the kinetic scheme). Hence, the oxidation of the large molecules is heavily simplified while the small molecule chemistry is described in detail. Wang et al.[15] applied and validated the decoupling method on the modeling of jet-fuel combustion. A small set of lumped reactions was defined and calibrated with the help of experimental data and appended to a detailed base chemistry scheme.

All these procedures showed very good agreement between lumped and detailed mechanism model predictions for the considered set of test cases. However, the mentioned methodologies also rely on either expert knowledge for the formulation of the lumped species/reactions, or on large sets of experimental/statistical data to be computed prior the mechanism reduction process. The method proposed in this work aims to define a set of assumptions for isomers' lumping, which are based exclusively on known properties of the detailed mechanism. In the following sections a short overview of the chemical kinetic scheme adopted will be given together with a detailed explanation of the proposed lumping methodology. The quality of the results obtained using the derived lumped mechanism will be assessed under different reactor configurations.

## 2 | CHEMICAL MODEL

The main surrogate fuel components were chosen to match both European Diesel and Rapeseed Methyl Esther (RME) properties. Cetane number and lower heating value of the commercial fuels listed in Table 1 have been considered, among other properties, as main targets to be matched by the modeled surrogate fuel mixtures. One of the surrogate fuel models typically considered to simulate commercial Diesel is a blend of *n*-decane and $\alpha$-methyl naphthalene respectively in 70% and 30% on a volume base. Such a mixture has been chosen according to average European Diesel composition by means of *n*-alkanes and aromatic contents and it has been presented in several papers.[16–18] To simulate RME behavior instead, a methyl decanoate (MD) reaction mechanism was considered. Many chemical kinetic studies in the last years proposed methyl decanoate as the most suitable surrogate fuel for biodiesel so far.[17,19] In terms of ignition behavior and pollutants formation this component presented similar performance to those of biodiesel fuels such as RME.[17]

The generation of the chemical reaction mechanism was performed using the procedure described in Refs. 20 and 21 In the first step, the detailed mechanisms for *n*-decane and methyl decanoate were generated. The $C_1$ to $C_6$ chemistry was taken from Schenk et al.[20] A wide range of reactor simulations was performed to validate the performance of the single component kinetics and the combined model was validated.[19] The thermodynamic data of the *n*-decane mechanism were taken from Westbrook et al.[16] The thermodynamic data for species within the methyl decanoate mechanism are taken from Ref. 17 The transport data are taken from our in-house data base and literature study.[19] As a final step, the *n*-decane – methyl decanoate mechanism was compiled with a sub-mechanism for $\alpha$-methylnaphthalene (see[19] for details). The detailed reaction mechanism used for the present work is a detailed *n*-decane, $\alpha$-methyl naphthalene and methyl decanoate mechanism with 807 species and 7807 reactions.

## 3 | LUMPING STRATEGY

As mentioned in Section 1, chemical lumping is a useful reduction strategy for large hydrocarbons thanks to the presence of many isomers. In general, it is achieved through grouping correlated species such that the number of variables described by differential equations is reduced. Furthermore, since species lumping can result in the same reaction step appearing several times the CHEMKIN duplicate statement was used in the lumped mechanism to include the same reaction step. Hence, the computational cost induced by Jacobian operations and diffusion is reduced.[2] In addition to the reduced system complexity, preservation of the important features of the full scheme, such as main reaction pathways, must be guaranteed. As reported by Lu et al.[2] lumping has indeed a high potential to keep the comprehensiveness of the source mechanism because it is based on the molecular properties of the species which are valid over a broad range of conditions.

In the present article an automatic isomer lumping procedure is proposed, based on an a priori analysis of the thermo data of the detailed scheme. As reported by Tomlin et al.[1] it is quite tough, in principle, to find globally valid a priori assumptions for an automatic lumping procedure due to the highly non-linear nature of chemically reactive systems. With respect to the oxidation of the Diesel and biodiesel surrogate fuels introduced in Section 2, it is explored herein to what extent chemical reaction schemes

can be reduced with thermodynamically driven linear chemical lumping, while keeping an acceptable loss of accuracy. The two main goals are, on the one hand to build an automatic procedure that can be easily implemented in mechanism generators. On the other hand, to build a mechanism reduction procedure that is independent of simulation data to be gathered using the detailed mechanism. A successful attempt in this direction has been recently proposed by Heberle et al.[22] Their procedure allows to automatically identify, and subsequently lump species belonging to the high temperature fuel decomposition pathways. The method in ref. 22 relies on a reference database for the sub-mechanism identification as well as on an optimization driven fitting procedure to determine the reaction rates of the lumped scheme. The present work aims to be applicable to both high and low temperature pathways. The detailed mechanism on which the technique has been applied was compiled using classification of reactions classes as proposed by Curran et al.[23] A concise description of the reaction classes described in ref. 23 are presented in Table 2 for better readability. In this work we only focus on the lumping method and not on the compilation of the detailed mechanism, which was published in ref. 19.

**TABLE 2** Summary of the reaction classes taken used to compile the detailed model[19] as initially proposed in Ref. 23

| Reaction class | Description |
|---|---|
| 1 | Unimolecular fuel decomposition |
| 2 | H-atom abstraction from the fuel |
| 3 | Alkyl radical decomposition |
| 4 | Alkyl radical + $O_2$ to produce olefin + $H\dot{O}_2$directly |
| 5 | Alkyl radical isomerization |
| 6 | Abstraction reactions from olefin by $\dot{O}H$, $\dot{H}$, $\dot{O}$, and $\dot{C}H_3$ |
| 7 | Addition of radical species to olefin |
| 8 | Alkenyl radical decomposition |
| 9 | Olefin decomposition |
| 10 | Addition of alkyl radicals to $O_2$ |
| 11 | $\dot{R} + R'\ \dot{O}_2 = R\dot{O} + R'\dot{O}$ |
| 12 | Alkyl peroxy radical isomerization $R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$ |
| 13 | $R\dot{O}_2 + H\ \dot{O}_2 = RO_2H + O_2$ |
| 14 | $R\dot{O}_2 + H_2\ O_2 = RO_2H + H\dot{O}_2$ |
| 15 | $R\dot{O}_2 + CH_3\ O_2 = R\dot{O} + CH_3 + O_2$ |
| 16 | $R\dot{O}_2 + R'\ \dot{O}_2 = R\dot{O} + R'\dot{O} + O_2$ |
| 17 | $RO_2H = R\dot{O} + \dot{O}H$ |
| 18 | *$R\dot{O}$ decomposition* |
| 19 | $\dot{Q}OOH = QO + \dot{O}H$ cyclic ether formation via cyclization of diradical |
| 20 | $\dot{Q}OOH = olefin + H\dot{O}_2$ (Radical site $\beta$ to OOH group) |
| 21 | $\dot{Q}OOH = olefin + carbonyl + \dot{O}H$ (Radical site $\gamma$ to $OOH$ group) |
| 22 | Addition of $\dot{Q}OOH$ to $O_2$ |
| 23 | Isomerization of $\dot{O}_2QOOH$ and formation of ketohydroperoxide and $\dot{O}H$ |
| 24 | Decomposition of ketohydroperoxide to form oxygenated radical species and $\dot{O}H$ |
| 25 | Cyclic ether reactions with $\dot{O}H$ and $H\dot{O}_2$ |

## 3.1 | Construction of the isomers' lump group

As a first step the Gibbs free energies of all species of each isomer class within methyl decanoate and *n*-decane mechanism were assessed and compared to each other. The minimum relative difference in Gibbs free energy, evaluated across the full temperature range (in most cases: 300–3000 K) of the thermodynamic data, was considered as the main constrain to decide whether to include each isomer in the lumped pseudo-species. In other words, isomers which showed very small differences in Gibbs free energy (less than 1 kJ everywhere over the full temperature range) were selected to be part of the lump group under the assumption that they would present equal concentrations. In the initial phase of the algorithm development a systematic study (using 1 kJ, 5 kJ, 10 kJ, and 20 kJ) was performed to identify the Gibbs free energy $\Delta$ that delivered the most reasonable list of isomer species to be lumped. For values higher than 1 kJ, it was noticed that the algorithm suggested to lump species with significantly different molecular structure and oxidation pathways. The 1 kJ value for the Gibbs free energy $\Delta$ was used also in other publications.[24,25] To verify the validity of this technique, several constant volume reactor calculations were performed, and isomer concentrations were analyzed. A representative outcome of the outlined thermo data analysis and its verification is shown in Figure 1. For both *n*-decane and methyl decanoate, the Gibbs free energy analysis for radical species formed in reaction class 1 (left side chart) and isomers concentration obtained under constant volume reactor conditions at 800 K, 1 bar and stoichiometric conditions (right side chart) are presented. A schematic flow analysis with net carbon fluxes of the isomers for the mentioned reactor conditions is also shown. Considerable differences in Gibbs free energy were noticed between isomers having radical site in a primary position and those in secondary.

Such dependency analysis schematically summarized in Figure 1, was conducted for isomers species formed in

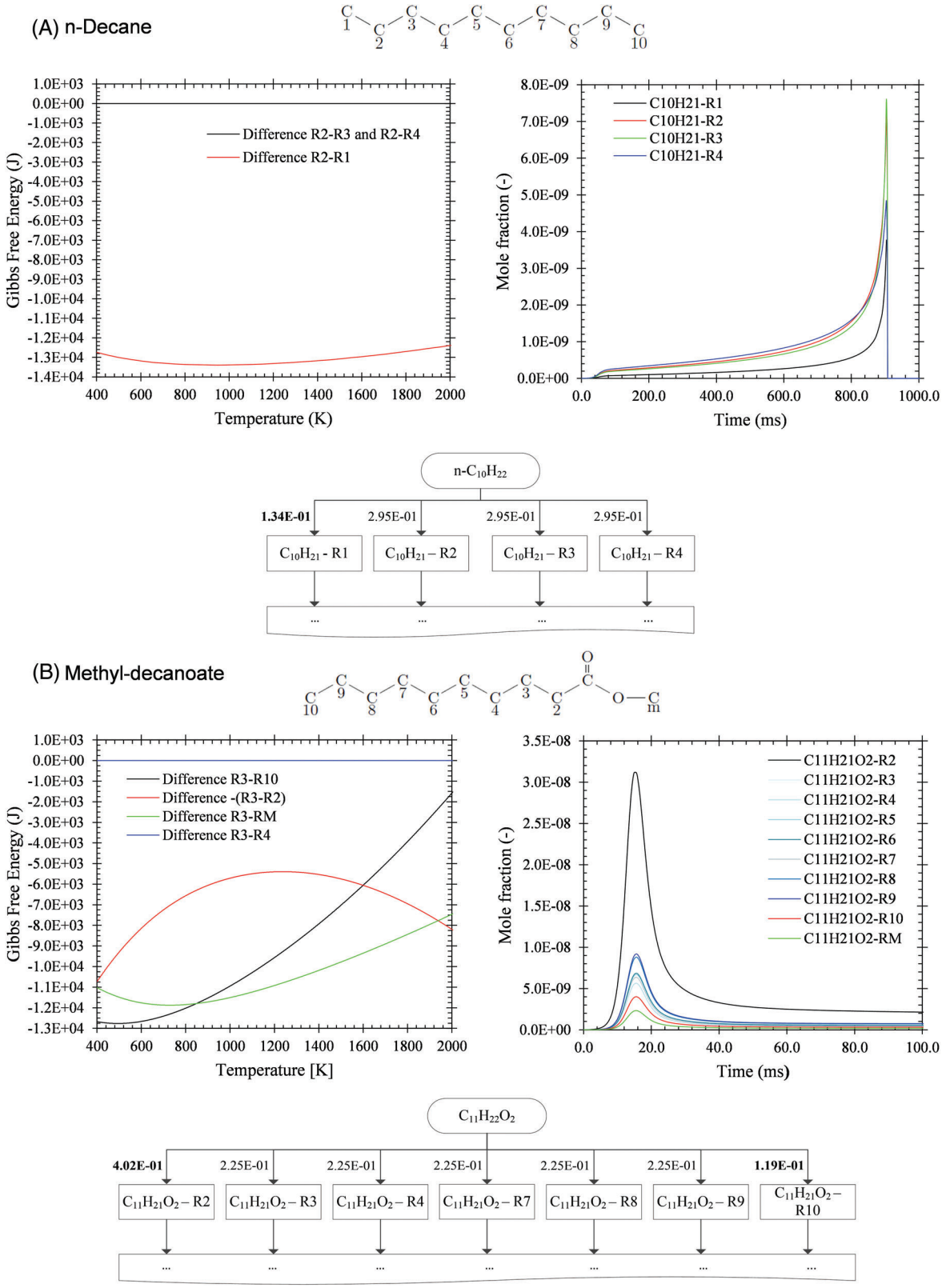


**FIGURE 1** Schematic verification of the strategy adopted to choose the isomers to include in the lumped groups for n-decane (A) and methyl decanoate (B). Left-side charts: relative Gibbs free energy differences between isomers of reaction class 1; right-side charts: class 1 isomers mole fractions profiles; bottom scheme: flow analysis obtained with 0-D reactor at T = 800 K, p = 1 bar, phi = 1.0

classes 1, 11, 12, 13. and 18 for all species with five carbons or more. The overall trend for *n*-decane and methyl decanoate revealed that isomers with either the radical site or the functional group at a primary site show visibly lower concentrations compared to radicals with functions or radical site at the secondary position (see right side charts in Figure 1). Two types of lumped species were therefore introduced to describe the oxidation process. The species are labeled with the prefix LP- for primary and LS- for secondary species with respect to the positions of the radical site or the functional group. With respect to the methyl decanoate analysis only, it is important to underline the following findings: for all isomers' classes assessed, the Gibbs free energy of the species having radical site on position "2" and at the carbonyl group differs overall by 3–4 order of magnitudes compared to isomers having radical site in the primary or secondary position. This agrees with the strong differences in concentrations observed when simulating the mechanism under 0-D constant volume reactor conditions (see right-side chart in Figure 1A). Isomers having radical site in position "2" and "m" were therefore excluded from the lumped pseudo-species.

As an additional a priori assumption, a special exception was introduced for reaction class 12 where QOOH is formed by peroxyl radical isomerization via a 5, 6, 7, or 8 membered rings. As discussed by Ahmed et al.[26] the resulting four species and their subsequent oxidation reactions describe the main low temperature reaction paths and are treated separately. Each path consists of the reactions of the primary and secondary isomers which are described above. If the ring size is not taken into account properly, the linear lumping of all QOOH species results in a complete reorganization of the low temperature reaction pathways. The new lumping order is based on the number of C atoms between the radical position and the OOH group (which is directly correlated to the ring size of the transition state when QOOH is formed) after the first internal H-atom abstraction replacing all $C_xH_yOOH$ isomers in the detailed scheme. Such assumption was found to be necessary since the Gibbs free energy-based assessment showed almost no differences and hence suggesting lumping the whole group. During the validation process however, it was noted that lumping of all the $C_xH_yOOH$ isomers had a strong impact on the mechanism performance in comparison to the detailed scheme. Hence, a lumping strategy based on the ring size was adopted for the hydro-peroxide isomers to improve mechanism accuracy. Such assumption was considered viable after analyzing species sensitivity towards temperature under several constant volume reactor conditions. In LOGEresearch,[27] the sensitivity analysis is a representation of a simultaneous reaction flow and sensitivity analysis. Sensitivities are transported through the mechanism in the sense that a species is rated according to its own importance and its involvement in the production or consumption of important species. The species sensitivity, defined for each species, represents the species' sensitivity towards a chosen parameter, and is the sum of the reaction sensitivities in which the species participates. A detailed explanation on how the sensitivity is calculated can be found in ref. 28.

In Figure 2 sample results from a sensitivity analysis towards temperature for the class 12 species is shown. It can be seen that isomers having the same ring size, show very close sensitivities.

If one compares the sensitivity levels of isomers having different ring sizes, larger differences can be seen (i.e., species in Figure 2A against species in Figure 2B). It was found that also for reaction mechanisms from other groups[29] the ring size-based lumping is necessary (see also discussions in chapter 10.3 in refs. 24 and 25).

The combination of the described methodologies led to the identification of 74 representative isomers. More in detail, 110 species were lumped in the n-decane part of the mechanism and 232 species in the methyl-decanoate part. An additional 76 species were lumped in the base chemistry part of the mechanism. In total 418 species from the detailed mechanism (807 species and 7807 reactions) were lumped into 74 pseudo-species leading to a final size of the lumped mechanism of 463 species and 7600 reactions.

## 3.2 | Calculation of lumped species rate coefficients

Once the isomers to be included in the group were evaluated, a linear lumping approach was applied. All selected isomers lumped to one species were assumed to have equal concentrations. The resulting rate coefficients were weighted by the rates for the lumped isomers and the numbers of reactants and products in the reaction equation. If isomers with different thermodynamic data were lumped, these differences were considered in the formulation of the calculated rate coefficients of the backward reactions. In the lumped scheme the total backward reaction is described as the sum of the duplicate reactions with the different backward rate coefficients of the former isomeric species. Once one lumped species is introduced, the chemical source term $\omega_L$ for the differential equation is transformed from a single species j, via the isomers l to the lumped species as follows:

$$\omega_j = \sum_{k=1}^{N_R} \left( \upsilon_{j,k} \prod_{i=1}^{N_S} \left( c_i^{\upsilon'_{i,k}} \right) k_k \right) \tag{1}$$

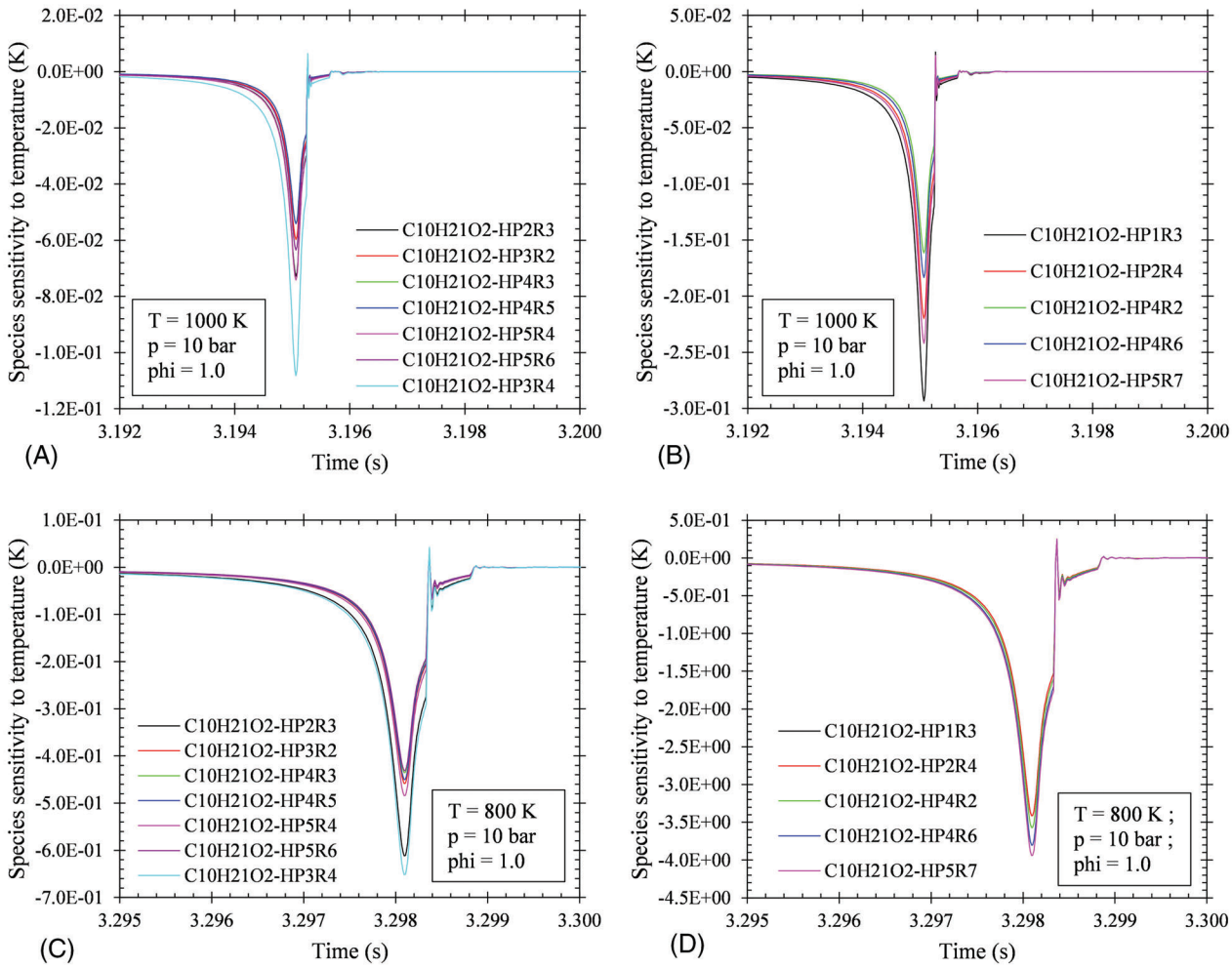


**FIGURE 2** CxHyOOH n-decane isomers (formed in class 12 as per definitions in ref. 23) sensitivity toward temperature changes calculated under constant volume reactor conditions at 10 bar, stoichiometric mixture and: A), B) 1000 K, and C), D) 800 K. The isomers depicted in each plot (grouped assuming the same ring size) have been considered for lumping

$$\omega_l = \sum_{k=1}^{N_R}\left(\upsilon_{l,k}\prod_{j=1}^{N_L}\left(c_j^{\upsilon'_{j,k}}\right)\prod_{i=1}^{N_S-N_L} c_i^{\upsilon'_{i,k}} k_k\right) \tag{2}$$

$$\omega_L = \sum_{l=1}^{N_L}\left(\sum_{k=1}^{N_R}\left(\upsilon_{l,k}\prod_{j=1}^{N_L}\left(\left(\frac{c_l}{N_L}\right)^{\upsilon'_{j,k}}\right)\prod_{i=1}^{N_S-N_L} c_i^{\upsilon'_{i,k}} k_k\right)\right) \tag{3}$$

$$\omega_L = \sum_{k=1}^{N_R}\left(\sum_{l=1}^{N_L}\left(\left(\upsilon_{l,k}\right) c_L^{\sum_{f=1}^{N_L}\upsilon'_{f,k}}\right)\prod_{i=1}^{N_S-N_L} c_i^{\upsilon'_{i,k}} k_k \prod_{j=1}^{N_L}\left(\frac{1}{N_L}\right)^{\upsilon'_{j,k}}\right) \tag{4}$$

with $N_R$ denoting the number of reactions, $N_S$ the total number of species, $N_L$ the number of species lumped to $L$, $c_x$ the concentration of species $l$, $\upsilon_{l,k} = \upsilon''_{l,k} - \upsilon'_{l,k}$ is the net stoichiometric coefficient of species $l$ in reaction $k$ where $\upsilon'$ indicates the reactants and the $\upsilon''$ products, $k_k$ the rate coefficient of reaction $k$. After lumping the new number of species is calculated together with the new rate coefficients and new stoichiometric coefficients of the lumped group:

$$N_S^* = N_S - N_L + 1 \tag{5}$$

$$k_k^* = k_k \prod_{j=1}^{N_L}\left(\frac{1}{N_L}\right)^{\upsilon'_{j,k}} \tag{6}$$

$$\upsilon_{L,k}^* = \sum_{i=1}^{N_L}\upsilon_{l,k} \tag{7}$$

$$\upsilon'_{L,k^*} = \sum_{i=1}^{N_L}\upsilon'_{l,k} \tag{8}$$

Equation (4) therefore reads as:

$$\omega_L = \sum_{k=1}^{N_R} \left( \upsilon'^{*}_{L,k} \prod_{i=1}^{N_S^*} (c_i^{\upsilon'_{i,k}}) k_k^* \right) \tag{9}$$

where $\upsilon'_{i,k} = \upsilon'_{L,k}$ for $i = L$. Further lumping of species transforms the source term sequentially in this manner.

With respect to the thermodynamic properties, the lumped pseudo-species are given as polynomials based on the average of those of the species involved in the lumping group. Specifically, each of the NASA polynomial coefficients, for both high and low temperature, was linearly averaged over the chosen lumped isomers. No additional refitting procedure was performed for the lumped species. Such averaging strategy for the NASA polynomials provides reasonable results primarily because the thermodynamic data for the isomers were compiled from the same source using the same approach (i.e., Benson rules) and the same way to calculate the NASA coefficients (i.e., LU-decomposition). However, to further improve the applicability of the method, a more advanced strategy could be implemented in future studies, where the average thermodynamic properties (i.e., enthalpy, heat capacity) are computed first and then a new set of polynomial coefficients is refitted for the pseudo-species.

An exemplary calculation of the rate coefficient is presented for a lumping step where all the secondary fuel radicals ($C_{10}H_{21}$-R2, $C_{10}H_{21}$-R3, $C_{10}H_{21}$-R4, and $C_{10}H_{21}$-R5) are represented by the pseudo-species LS-$C_{10}H_{21}$. For a reaction where the secondary fuel radical is on the right-hand side the rate coefficients in the detailed mechanism in standard format (A n Ea) is given as:

$$\begin{aligned} &\text{n}-C_{10}H_{22} + H \\ &\quad = C_{10}\,H_{21}R2 + H_2 \quad 9.80E7 \quad 2.00 \quad 5.002E3 \end{aligned} \tag{10}$$

Since $C_{10}H_{21}$R2 is a product, the concentration of the pseudo-species will have no impact on the resulting forward rate. For the reverse reaction however ($C_{10}H_{21}$R2 + $H_2$ = n-$C_{10}H_{22}$ + H), the reaction rate depends on the concentration of $C_{10}H_{21}$R2. Since we represented four isomer species via LS-$C_{10}H_{21}$, the concentration is assumed to be four times as high, therefore the reverse rate needs to be given explicitly while the A factor must be divided by the number of species in the lumped group (four in this case). This single reaction is not in equilibrium anymore. Hence this reaction in the lumped mechanism in standard format reads as:

$$\begin{aligned} &\text{n}-C_{10}H_{22} + H \\ &\quad = LS - C_{10}\,H_{21} + H_2 \quad 9.80E7 \quad 2.00 \quad 5002.00 \\ &\quad \text{REV/ 1.727879E2 2.97 9831.29 /DUPLICATE} \end{aligned} \tag{11}$$

The reverse rate of the detailed mechanism can be calculated from the thermodynamic properties and the forward rate. The DUPLICATE statement is necessary since in the detailed mechanism also the products $C_{10}H_{21}$-R3, $C_{10}H_{21}$-R4, and $C_{10}H_{21}$-R5 exist. This results in the same elementary reactions as stated in Equation (11) four times in total. These reactions can have different rate coefficients, though. Should the species to be lumped be on the left-hand side, the reverse rate is not affected, while the forward rate needs to be divided by the number of isomers in the lumped group instead. The procedure described above, is executed as a series of lumping steps where the rate coefficients for a newly introduced pseudo-species are calculated one after the other. The order in which each pseudo-species is introduced does not impact the final mechanism.

## 4 | RESULTS AND DISCUSSION

To illustrate the effect of lumping on the reaction flow the simulation results of several combustion systems using both the detailed (803 species 7807 reactions) and the lumped mechanism (463 species 7600 reactions) are compared. Both reactions schemes and a list of identified isomers with its representative lumped species can be found in the supplementary material. All presented simulations have been performed using LOGEresearch 1.10.[27] In the following paragraphs the results are discussed and sorted by reactor setups.

### 4.1 | Constant volume reactor

Modeling of auto ignition was carried out assuming constant-volume and homogeneous adiabatic conditions. The predicted ignition delay was determined by the evaluation of the maximum temperature gradient. To comprehensively verify the effect of the lumping procedure on the mechanism performance, single fuel calculations were performed separately and a mixture including all three components was tested as well. The motivation behind the choice of the mixture, comprising 0.71 *n*-decane – 0.23 $\alpha$-methylnaphthalene – 0.06 methyl decanoate in mole fraction, was on the one hand side done based on the current legislation for European Diesel by means of aromatic/biodiesel content allowed. On the other hand, the authors wanted to monitor potential influences of the lumping on the fuel-fuel interactions and therefore a blend, which is labeled as "European Diesel model" in the following sections, was widely studied. In Figure 3 comparisons between ignition delay times predictions obtained using detailed and lumped mechanisms are presented for all sets of gas compositions considered. Very

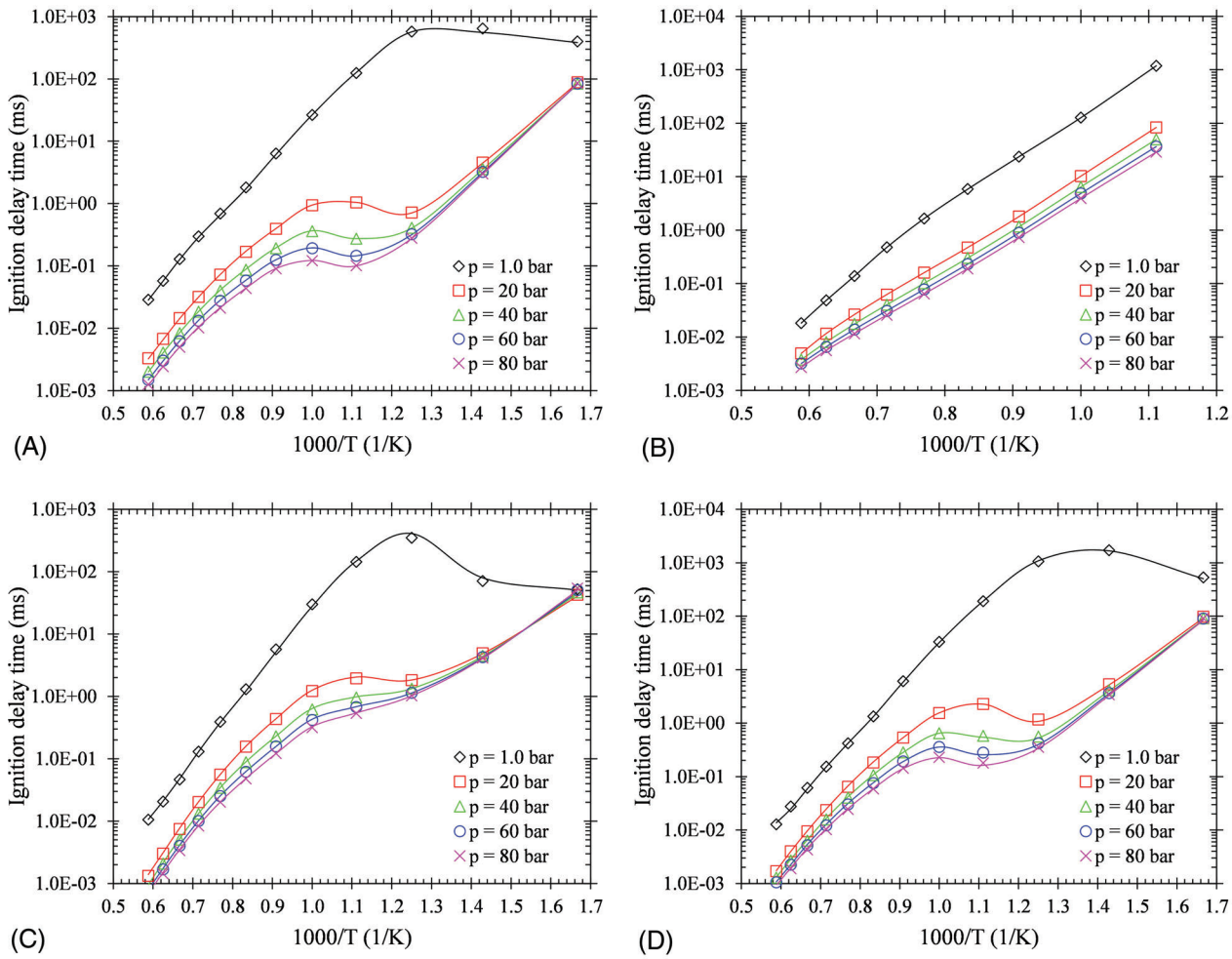


**FIGURE 3** Simulated ignition delay times at $\varphi = 1.0$ for detailed mechanism (symbols) and lumped mechanism (solid line). A) Pure n-decane; B) pure $\alpha$-methylnaphthalene; C) pure methyl decanoate; D) European Diesel model: 0.71 n-decane – 0.23 $\alpha$-methylnaphthalene – 0.06 methyl decanoate

good agreement was found between detailed and lumped mechanism predictions at stoichiometric conditions.

However, as logarithmic plots are misleading in estimating error levels, Figure 4 shows the relative ignition delay time prediction differences in percentage between detailed and lumped mechanism on a linear scale for various pressure and equivalence ratios. Each chart row in Figure 4 is obtained for a different fuel labeled as A), B) and C), or fuel mixture D). To cover most of the typical light-duty Diesel engine's combustion regimes, errors were assessed for a pressure varying between 1 and 120 bar, equivalence ratio between 0.5 and 3.0. It is noteworthy to mention that in Figure 4 negative error means under prediction of the ignition delay, with reference to the detailed mechanism simulation results, and vice versa.

Good agreement is found for all conditions with an overall average error within ± 10%. To the authors' opinion, the results in in Figure 4A may suggest that the proposed methodology to treat the lumped species rate coefficients (outlined in Section 3.2) can be successfully applied to straight chain hydrocarbons, with an acceptable loss in accuracy. Especially in the NTC region the lumped mechanism showed negligible deviations from the predictions with the detailed mechanism. The current results, and those in reference,[26] are in contradiction with those obtained by Pepiot et al.[13] where a comparison between different methodologies to evaluate the reaction rates of the lumped species is presented. In ref. 13 it is shown that when assuming equal repartition of the reaction rates for *n*-heptane isomers, considerable errors (over 200%) in ignition delay prediction were obtained. This finding underlines the fact that the correct choice of the isomers to include in the lumped group is essential and should be carefully selected.

With reference to Figure 4B, no errors were noticed when pure $\alpha$-methylnaphthalene is used. Such results

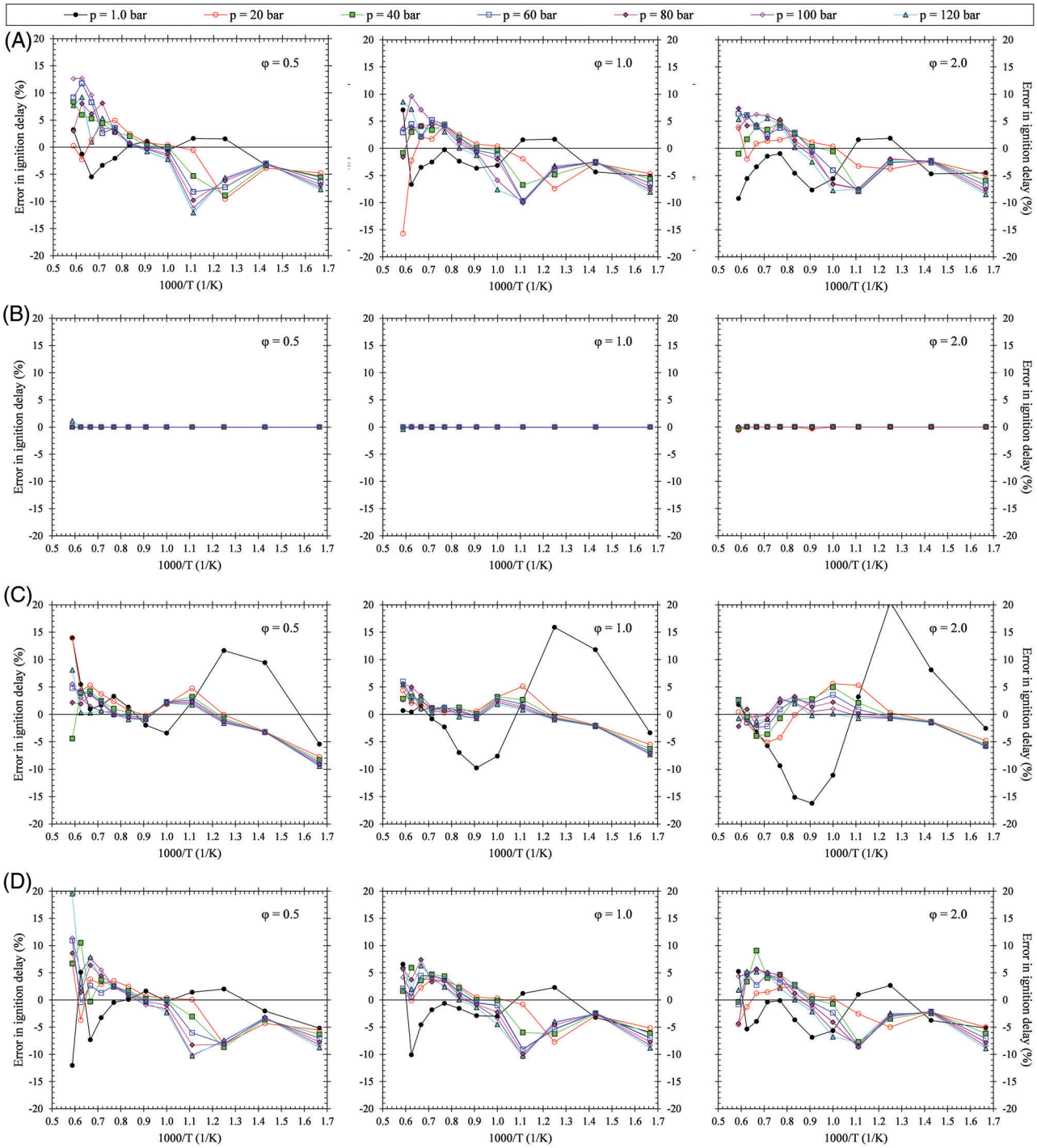


**FIGURE 4** Relative ignition delay time predictions' differences in percentage between detailed and lumped mechanism on linear scale for pressure = 1.0–120 bar and For Peer Review $\varphi$ = 0.5–2.0. Pure n-decane A); Pure $\alpha$methylnaphthalene B); Pure methyl decanoate C); European Diesel model: 0.71 n-decane – 0.23 $\alpha$methylnaphthalene – 0.06 methyl decanoate D)

were expected as the lumping procedure did not involve any species belonging to the aromatic oxidation pathways. As previously mentioned, such test was of high importance to verify whether the lumping of a multi-component mixture influenced the other fuels or not. As for the methyl decanoate part instead (Figure 4C) higher deviations (absolute maximum = 21% at T = 800 K, and $\varphi$ = 2.0) were found just at 1 bar. For this matter, a deeper investigation was carried out, to explore the validity of the assumptions made on the calculation of the lumped species rate-coefficients. As compactly shown in Figure 5, several 0-D constant volume reactor calculations were performed between 1 and 4 bar at rich conditions ($\varphi$ = 2.0) in order to compare isomers' concentration

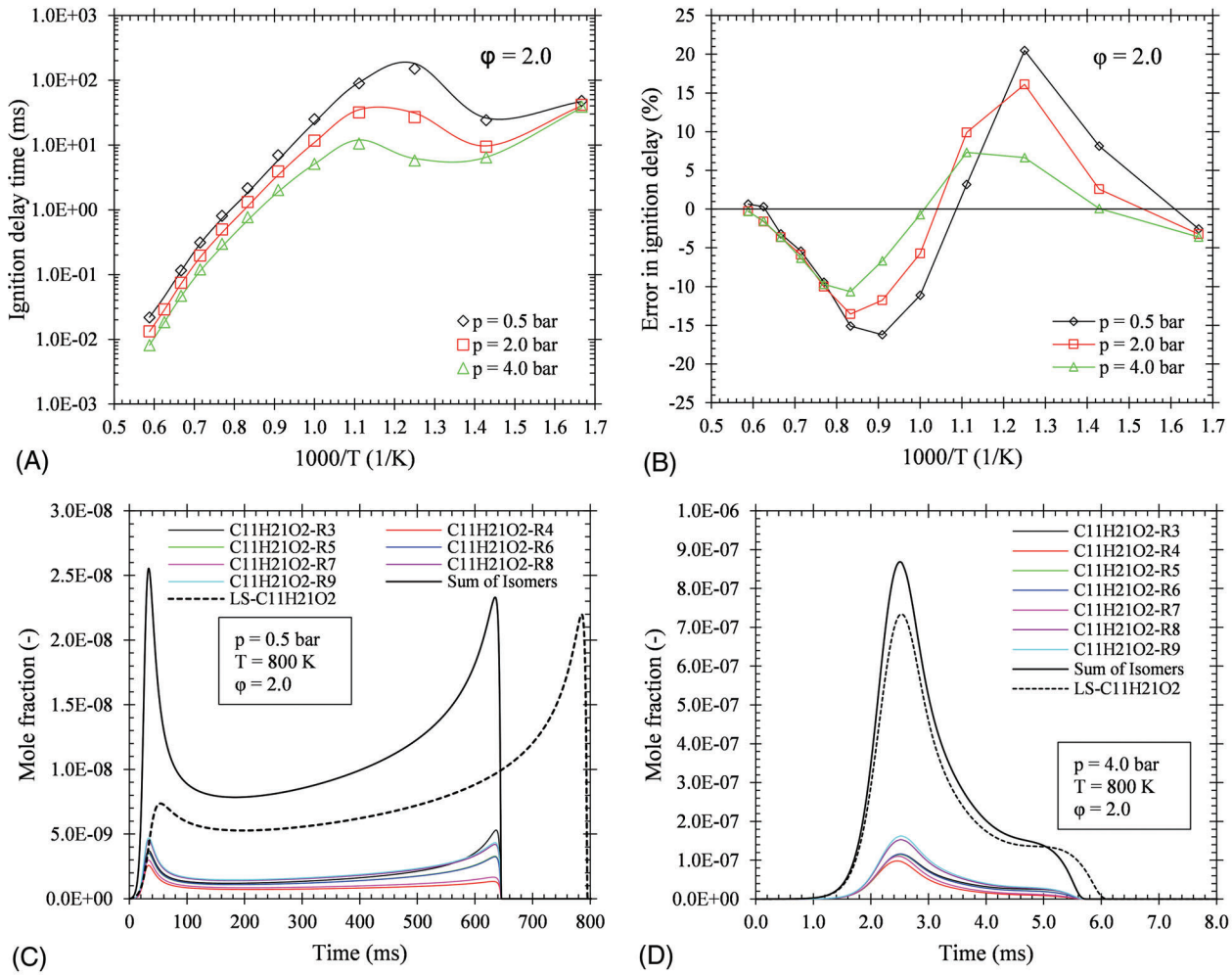


**FIGURE 5** Investigation on lumped methyl decanoate mechanism pressure dependency. Ignition delay times of pure methyl decanoate/air at $\varphi = 2.0$ for detailed mechanism (symbols) and lumped mechanism (solid line) A); Relative ignition delay time predictions' differences in percentage between detailed and lumped mechanism for $\varphi = 2.0$ and p = 1, 2, and 4 bar B); Comparison of predicted concentrations with detailed and lumped mechanism at T = 800K, $\varphi = 2.0$. Pressure is 0.5 bar in (C) and 4 bar in (D)

profiles between lumped and detailed mechanism. Isomer's species profiles were compared at 800 K since it was the condition where the lumped mechanism showed the lowest accuracy. Figure 5C and D show that concentration profiles of the single isomers differs much more than those at pressures of 4 bar. Since the proposed methodology relies on the assumption of equal concentration of the lumped species and therefore on equal distributed rates, higher deviations are expected compared to the detailed mechanism. In addition, the non-symmetry of the methyl decanoate molecule might also play a significant role and explain why such behavior was not noticed for *n*-decane.

To check also whether the lumping strategy influenced anyhow the fuel-fuel interactions, the previously mentioned European Diesel model was tested (see Figure 4D). Overall, the lumping approach did not show to affect the mechanism performance over the full range of operating conditions assessed for the three component blend.

A sensitivity analysis at 750 and 950 K, in a similar manner as applied to the *n*-heptane mechanism from Curran et al.,[23] for both the detailed and the lumped mechanism was performed. The main focus was on low-medium temperature kinetics of the European Diesel model. Hence, reactions belonging to classes 1–25 of *n*-decane and methyl decanoate part were assumed to be of major importance for the reactivity at low and medium temperature. The forward rate coefficients of these reactions were multiplied by a factor of two and the relative change in the ignition delay times was compared. Thus, negative sensitivity coefficient means that the overall rate of fuel oxidation is enhanced by the examined reaction. The sensitivity coefficients were calculated at two different mixture conditions ($\varphi = 1.0$ and 2.0) and two different pressures between the

detailed and lumped mechanism ($p = 13$ and 50 bar). All the investigated sensitivities at the mentioned conditions are displayed in Figure 6.

Overall, very similar levels of sensitivities were found. The comparison of the sensitivities of reaction classes for the detailed and lumped mechanisms is a direct test on how the reactivity of the kinetic scheme is affected by the reorganization of the reaction mechanism. Only negligible deviations were found for main sensitive reaction classes demonstrating that not only the overall reactivity but also the class reactivities are maintained after the reduction process. The conclusion of these findings is that the structure of the reorganized mechanism is not influenced by the kinetic assumptions for reaction rates proposed in this paper. In terms of CPU time a speed-up factor of 1.75 was noted on a single core (Intel i7-7600U from the year 2017) when comparing detailed and lumped mechanisms computational performances.

## 4.2 | Perfectly stirred reactor

Another common reactor condition suitable to analyze fuel oxidation is the perfectly stirred reactor. A stirred reactor with a constant in and out stream can be operated under steady state conditions which are characterized by a constant mean residence time of the reactants and a constant composition of the out-stream mixture. This reactor type is determined by many different boundary conditions compared to constant volume reactors. Therefore, an additional test of lumped mechanism predictions against those from the detailed mechanism is very useful to validate the reduction methodology and assess the comprehensiveness of the lumped mechanism. Reference conditions to set up the calculations were chosen based on the experiments performed by Dagaut et al.[30] for pure *n*-decane. In Figure 7 the comparisons between detailed and lumped mechanisms in terms of absolute predicted species concentration (left side charts) and relative percentage error between the two simulations (right side charts) are shown using the European Diesel mixture. In accordance with the convention adopted for the ignition delay error maps (see Figure 4), also in Figure 7 negative error percentage means an under prediction, with reference to the detailed mechanism simulation result, and vice versa. The reactor conditions refer to an *n*-decane-air mixture at 10 atmospheres with temperatures varying from 550 to 1050 K. Only the major species concentration profiles are included in Figure 7. Overall, the lumped mechanism shows negligible deviations from the detailed one. As seen for the auto ignition simulation, higher deviations are visible at low temperature where termination reactions are dominant. It is noteworthy to mention that the largest deviations are found where species concentrations are very low (below mole fractions 1e-6) and therefore the error levels on a linear scale become more visible. However, the absolute error between lumped and detailed mechanism predictions was found to be below 20% over the full range of tested conditions.

## 4.3 | Stochastic reactor engine model

The detailed and the lumped mechanism were further tested within a direct injected Diesel engine simulation framework. For these calculations, a 0-D Direct Injection Stochastic Reactor Model (DI-SRM) was applied. The 0D DI-SRM is a probability density function (PDF) based method for modeling physical and chemical processes occurring in an engine cylinder. It is capable to model effects of inhomogeneities in the gas phase in the combustion chamber due to fuel injection, air-fuel mixing, and heat transfer. The DI-SRM also allows the usage of detailed chemical models to simulate fuel oxidation and emissions formation. A more detailed description of the engine modeling framework and several successful model applications can be found in literature.[31–33]

The simulation setup was prepared based on the experiments found in ref. 32 where combustion of commercial Diesel fuel was examined on a direct injected research engine at one operating condition: 1500 rpm and 7.4 bar Indicated Mean Effective Pressure (IMEP). Simulations were carried out for the closed part of the engine cycle: between -133 Crank Angle Degree (CAD) and 133 CAD after top dead center. The previously mentioned European Diesel model was used for both detailed and lumped mechanisms simulations. To isolate the effects of the chemical schemes the entire set of DI-SRM model parameters was kept the same as in ref. 32 Figure 8 shows the comparison between detailed and lumped mechanisms predictions in terms of in-cylinder pressure and Rate of Heat Release (ROHR) histories. Relative errors between detailed and lumped mechanisms predictions are also presented over crank angle degree to better quantify the accuracy of the lumping methodology. In agreement with the trends seen when simulating fundamental chemical reactor systems, negligible performance differences were noticed between detailed and lumped mechanisms. The location, on a crank angle basis, and the maximum value of pressure is almost perfectly captured by the lumped mechanism. With reference to the percentage errors over the engine cycle, fluctuations have been noticed with respect to the detailed and lumped mechanisms predictions. Although the error remains in an acceptable range (± 5% from the detailed solution), it is important to remind that due to the stochastic nature of the DI-SRM it is expectable to notice a small

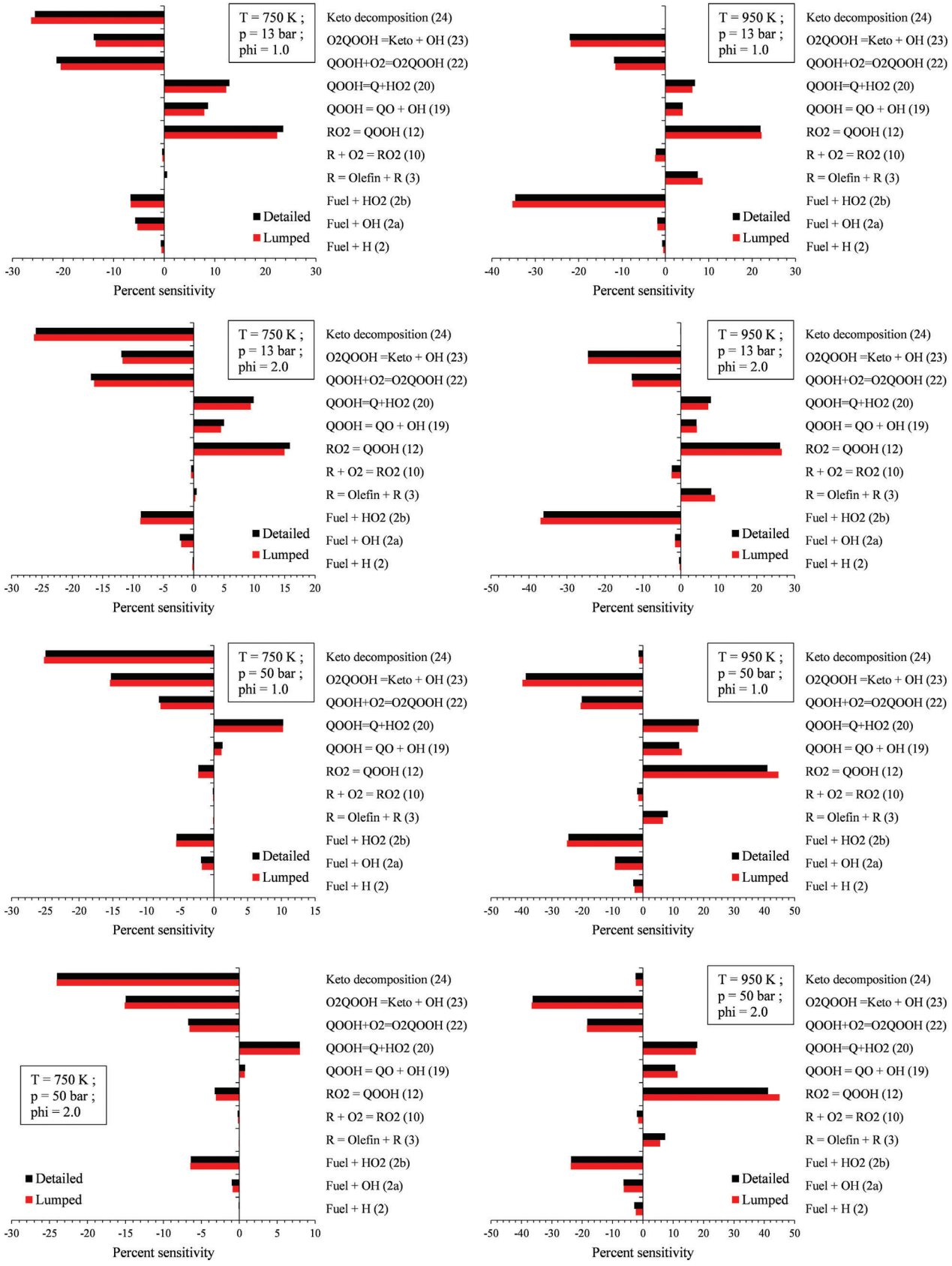


**FIGURE 6** Sensitivity coefficients for ignition delays, mixture of 0.71 n-decane – 0.23 For Peer Review$\alpha$-methylnaphthalene – 0.06 methyl decanoate at T = 750, 950 K and $\varphi = 1.0, 2.0$

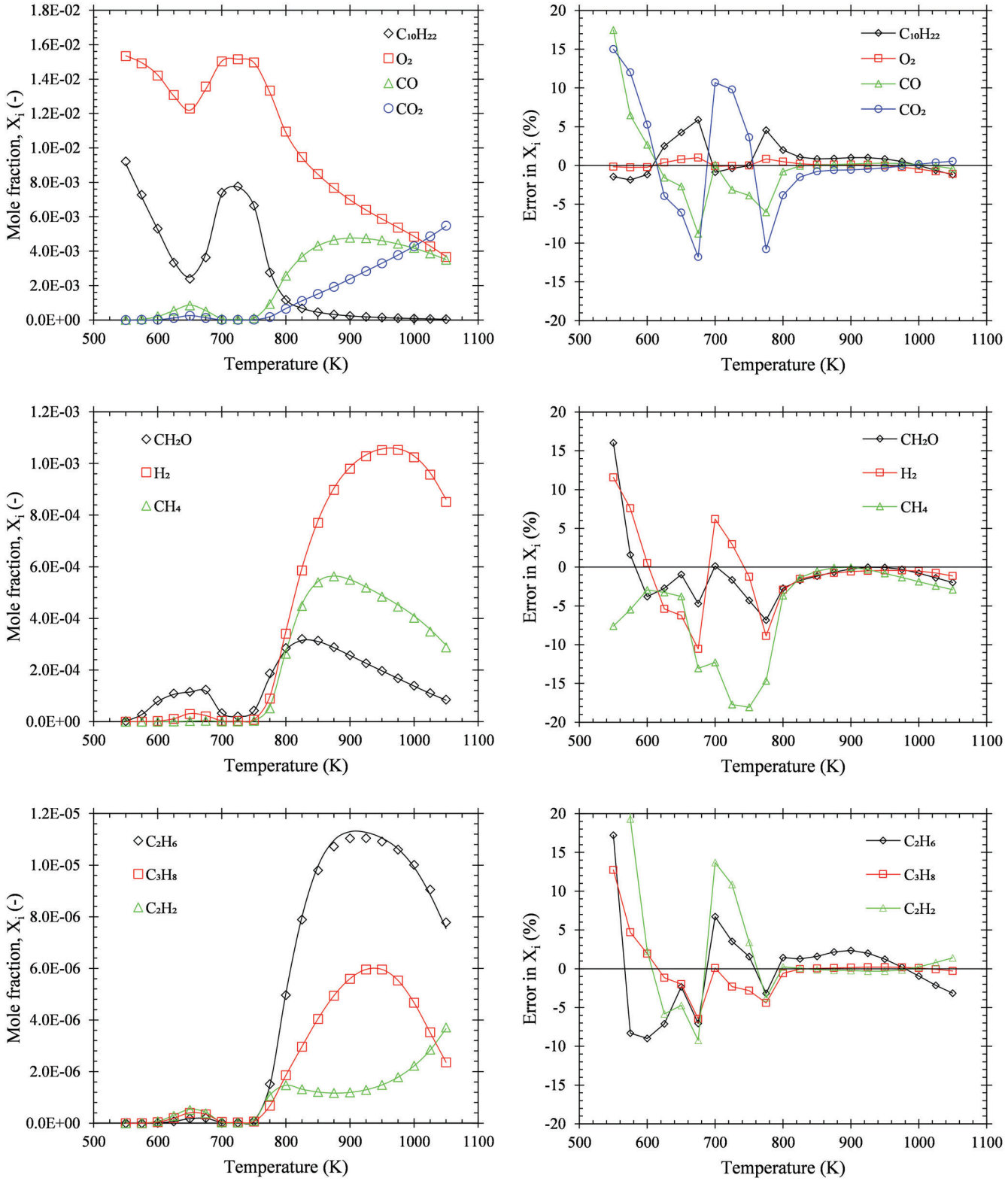


**FIGURE 7** Oxidation of n-C10H22 = 0.1%; O2 = 1.55%; N2 = 98.35%, $\tau = 1$ s at 10 atm in a perfectly stirred reactor for detailed (symbols) and lumped mechanism (solid line) on the left side. Relative predicted species concentration differences in percentage between detailed and lumped mechanism on the right side

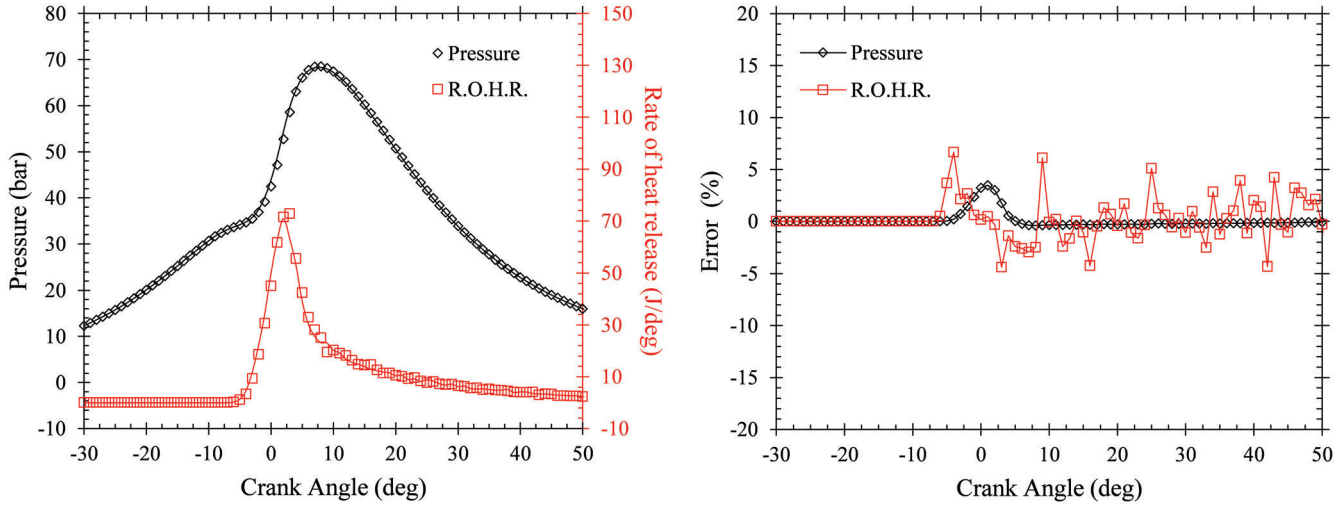


**FIGURE 8** Comparison of the in-cylinder pressure and the rate of heat release (ROHR) histories between detailed (symbols) and lumped (solid line) mechanism on the left side. Relative predicted pressure and For Peer Review ROHR differences in percentage between detailed and lumped mechanism on the right side. Engine data:Bore 90 mm, stroke 74 mm, volume 470 $cm^3$, rod length 121 mm, compression ratio 16.5, speed 1500 rpm, load 7.4 bar IMEP

variation in the final results. The reported predictions represent the average over 50 consecutive simulated engine cycles.

However, the overall lumped model performances proved to be of high accuracy with reference to the detailed mechanism even under more engineering related test cases using a multi-component mixture.

## 4.4 | Freely propagating flame

The simulation of laminar flame speed was also considered as a critical test case for both the detailed and the lumped mechanism. The motivation was to check the validity of the reduction approach for a different combustion process at much higher temperatures and for a diffusion driven problem. In this last subsection a comparison between detailed and lumped mechanism laminar flame speed predictions are presented. Typical conditions used for laminar flame speed measurements, such as those adopted by Egolfopoulos et al.,[34] were taken as reference to setup the simulations. In the cited references, *n*-decane – air mixtures at 1 atmosphere were measured at several cold side temperatures. In the presented simulation results though, gas composition was assumed to be European Diesel model, whereas initial conditions have been fixed according to the mentioned experimental setups. Since assessment of the error related to the reduction strategy was the main concern of the present work, the gas composition was chosen to consider all the main fuel components included in the detailed mechanism adopted. In Figure 9 comparisons are given between predicted laminar flame speeds using detailed and lumped mechanisms at several conditions. At the right side of Figure 9 the relative error in percentage between the two considered chemical schemes is also shown. Almost no differences were noticed between the two mechanism performances. Such results were expected considering the very good trends noticed already for auto ignition results at high temperatures.

To explore also in the 1-D setup under consideration how much the reduction strategy discriminates the mechanism reactivity, a sensitivity analysis has been performed for the flame speeds at p = 1 bar, stoichiometric and fuel rich conditions ($\varphi = 1.0, 1.3$). Results are presented in Figure 10.

## 5 | CONCLUSIONS

A chemical lumping method based on a priori thermodynamic data analysis has been proposed. It was applied to the reduction of a large three component reaction mechanism where each isomer group was replaced with one single representative lumped pseudo species. The choice of isomers was based on their Gibbs free energy values and the rate coefficients of the resulting lump group were assigned assuming equal repartition. With respect to isomers belonging to class 12, an additional assumption, based on the ring structure has been imposed to improve mechanism accuracy under low temperature combustion regimes.

The lumped reaction mechanism was extensively tested and compared to the detailed mechanism for a variety of 0-D and 1-D combustion systems and found to be in acceptable agreement with the detailed mechanism solutions.

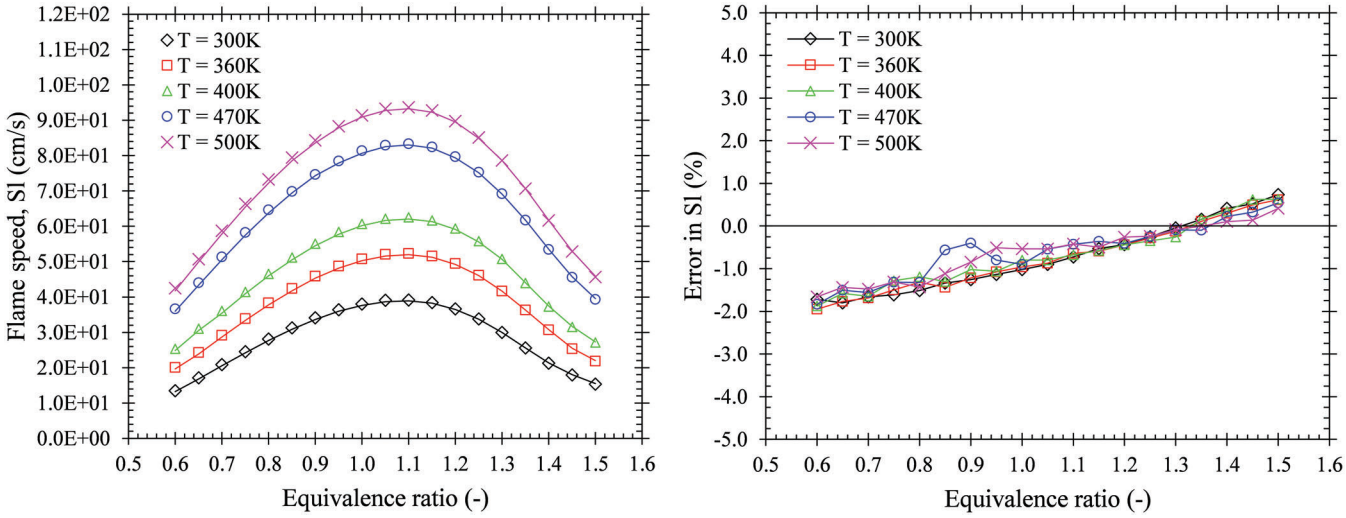


**FIGURE 9** Left side chart: Comparison of predicted laminar flame speeds at p = 1 atm between detailed For Peer Review(symbols) and lumped mechanism (solid line). Right side chart: Relative laminar flame speed differences in percentage between detailed and lumped mechanism

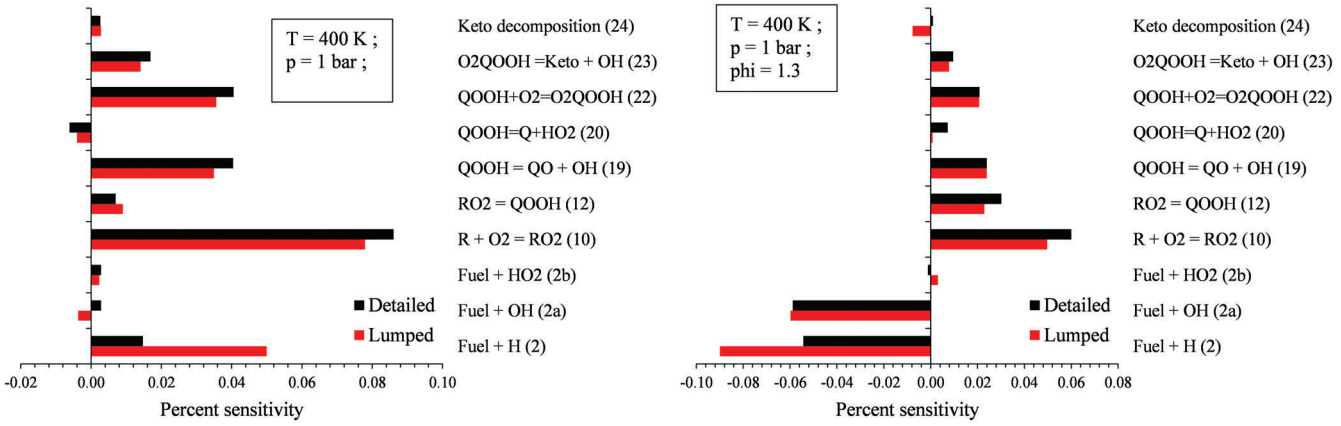


**FIGURE 10** Results of sensitivity analysis for the flame speed of a freely propagating laminar 0.71 n-decane – 0.23 $\alpha$-methylnaphthalene – 0.06 methyl decanoate/air flame at p = 1 bar under stoichiometric ($\varphi = 1.0$) and fuel rich ($\varphi = 1.3$) conditions

Even in the very sensitive NTC region, typical of low temperature ignition of large alkane and oxygenated fuel molecules, the lumped mechanism showed to be overall never beyond 12% of the accuracy of detailed mechanism predictions. Regarding the applicability of the methodology in general purpose mechanism reduction tools, both the Gibbs free energy assessment and the ring size-based lumping assumption, can be easily implemented in reduction codes if the molecule structure is known. However, in many published mechanisms it is not straight forward to derive molecule structure and functional group just based on the species naming. Given the current Chemkin format, there is no dedicated section, or parameter that allows the user to get the position of the functional groups in each isomer. On the other hand, it must be noted that the quality of the thermodynamic data used for each isomer plays a crucial role. Potentially, a more accurate set of thermodynamic data may make the additional ring-size based assumption not necessary and hence remove the dependency of the method on the molecule structure information.

Nevertheless, considering that the present methodology aimed to be implemented as a sequential step to be done right after the detailed mechanism generation step, where information on the molecule structures is implicitly known, it was considered acceptable. Furthermore, the resulting mechanism gives an advantageous starting point for additional model reduction by species removal techniques. Since the main oxidation pathways are largely condensed, an easier distinction of "important" from "unimportant" species is allowed.

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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