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Generation of hybrid chemistry fuel models by optimization methods

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ABSTRACT

The development of the hybrid chemistry (HyChem) methodology for the chemical kinetic modeling of real fuel combustion has introduced new possibilities for the generation of compact, reduced models. The key feature of this methodology is the separation of the chemical kinetic reaction scheme into two main parts. The first part is a global reaction scheme, representative of a real fuel fast pyrolysis step, which models the decomposition of the fuel into the main gas phase products of combustion processes. The second part of the model consists of a detailed gas phase reaction scheme for the oxidation of the aforementioned main gas phase products. The main prerequisite for the generation of a HyChem model is the identification of the branching factors of the main gas phase products from the fast pyrolysis reaction step. The original parameter identification requires an extensive experimental investigation of the fuel pyrolysis and combustion characteristics. We introduce new procedures to create hybrid chemistry models with chemical kinetic parameter optimization based either on experimental or numerically generated targets. With the experimental target approach, indirect chemical kinetic experiments are targeted by the parameter optimization, including ignition delay times and laminar burning velocities as well as species profiles measured in a flow reactor. For the numerical target approach, target data (reactive species profiles) are generated with the chemical kinetic fuel model DLR Concise in combination with a fuel surrogate strategy. HyChem models were generated for two jet fuels. Both the experimental and numerical target approaches are appropriate for generating HyChem models, allowing for highly adaptable model creation with relatively minimal experimental effort.

Novelty and Significance Statement

The novelty of this research is the approach in estimating reaction parameters of the hybrid chemistry (HyChem) global reaction steps by optimization methods based on surrogate modeling and/or significantly diverse experimental targets. The benefit of this method lies in its ability to significantly reduce the amount of work involved in both the experimental and modeling supported determination of these reaction parameters, which originally required extensive experimental studies for the original generation of HyChem models proposed by Wang et al. The new approach not only permits the use of any experimental data for the HyChem model generation, but also facilitates the use of any experimental data that are sensitive to the HyChem parameters. As a result, this greatly broadens the range of experimental setups and conditions that can be considered suitable options.

1. Introduction

The sophisticated development of new combustors necessitates the use of real fuel chemical kinetic combustion models. These models need to be numerically efficient, while mirroring combustion attributes of real fuels, which may consist of hundreds or thousands of fuel components.

A widely used approach for real fuel combustion modeling is through the surrogate fuel strategy [1,2]. With this approach, a fuel composition is designed by a limited number of fuel components to

mimic physical and chemical properties of real fuels. The combustion of surrogate fuel is then modeled by a chemical kinetic model, suitable for the oxidation modeling of the selected fuel components. Recently, Kathrotia et al. [3,4] demonstrated this approach for various conventional and sustainable aviation fuels. In their work, the quantity and type of different hydrocarbon molecule classes present in the fuel was determined by GCxGC/MS measurements [5]. From these results, surrogate fuel compositions were derived. Subsequently, these fuel compositions were modeled with the semi-lumped chemical kinetic

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model DLR Concise [3], validated for ignition delay times, laminar burning velocities, and species profiles measured in plug flow reactors and flames.

Various techniques have been developed to reduce the number of species that are modeled, enabling more numerically efficient chemical kinetic combustion models to be created. These techniques involve lumping together the reaction pathways involved in fuel pyrolysis [6–8]. Westbrook and Dryer [6] combined a global reaction step, for which hydrocarbon species are directly decomposed to CO and H₂, with a detailed syngas submodel. This allowed the numerical modeling with the limited computational resources at the time, while compromising on modeling accuracy. Heberle and Pepiot [7] introduced a method that automatically lumps high-temperature fuel decomposition pathways based on intensive analyses of detailed chemical kinetic models. Wang et al. [8] introduced the strongly generalized hybrid chemistry (HyChem) methodology for the compact and fuel specific chemical kinetic modeling of real fuel combustion. As a key feature, the chemical kinetic reaction scheme is divided into two main parts. The first part is a global reaction scheme, representative of a real fuel fast pyrolysis step that models the decomposition of the fuel into the main gas phase products that result from the combustion process. The second part of the model consists of a detailed gas phase reaction scheme for the oxidation of the aforementioned main gas phase products. The main prerequisite for the generation of a HyChem model is the identification of the branching factors of the main gas phase products from the initial fast pyrolysis reaction step. The identification of these parameters requires an extensive experimental investigation of the fuel pyrolysis and combustion characteristics, *i.e.* in shock tubes and flow reactors. Here, the branching factors were either measured directly [8] or derived from an automated optimization of HyChem parameters on experimental data, as suggested and performed on pyrolysis data and ignition delay times by Tao et al. [9] and Zhang et al. [10]. Furthermore, it was demonstrated that the size of HyChem models can be significantly reduced with further reduction steps to around 30 species, making them highly suitable for the application in CFD simulations [11].

To cut down on the experimental costs for HyChem parameter estimation, Zhang et al. [12] introduced an alternative parameter identification method, based on a functional group approach. With the chemical information on the fuel components, the model parameters are determined from multiple linear regression approaches and rate rule strategies. The HyChem parameter determination strategy by Zhang et al. [12] requires a reduced experimental effort, but is limited to existing databases, *i.e.* the database required for the regression approach for the determination of the HyChem branching ratios.

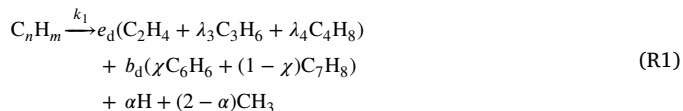
Within this work, two new strategies were developed for the identification of HyChem model parameters including the rate coefficients by chemical kinetic parameter optimization approaches: The first novel approach is numerical, to minimize experimentation. The second approach – as an extension of the approach suggested by Tao et al. [9] and Zhang et al. [10] – is experimental, to increase flexibility in the utilization of chemical kinetic experimental data.

Both methods start with a HyChem model derived from the chemical kinetic model DLR Concise [3] with initial guess values for the HyChem model parameters. Subsequently, the HyChem model parameters are refined by applying the optimization approach of the linear transformation model (linTM) [13]. For the numerical approach, the optimization targets are species profiles, numerically generated by the chemical kinetic model DLR Concise. The surrogate strategy approach by Kathrotia et al. [4] is used for this purpose. For the experimental approach, the optimization targets are any quantity of interest derived from chemical kinetic experiments like ignition delay times, laminar burning velocities or reactive species profiles from reactors or laminar flames.

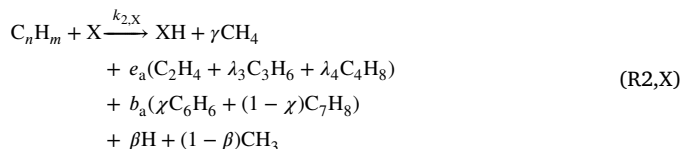
The flexibility and experimental efficiency of both approaches is demonstrated for the HyChem model generation for two jet fuels. The selected fuels are a typical Jet A-1 fuel and a highly branched paraffinic alcohol-to-jet (ATJ) fuel. These fuels have been investigated in prior work and referred to as JS-A1 and JS-B1, respectively [4].

2. Methodology of the HyChem approach

Wang et al. [8] formulated the fast fuel pyrolysis in the HyChem approach with two reaction steps. The C–C fission of the fuel molecule is represented by:



H abstractions are represented by:



with X being H, CH₃, O, OH, O₂, and HO₂. Reaction equations R1 and R2 are defined by the HyChem parameters e_d , b_d , e_a , b_a , α , β , γ , λ_3 , λ_4 , χ , for which α , β , γ , λ_3 , λ_4 , χ are the independent parameters. In a further development, the approach was extended by splitting C₄H₈ into its isomers nC₄H₈ (1-butene) and iC₄H₈ (isobutene), with the corresponding split of λ_4 into $\lambda_{4,1}$ and $\lambda_{4,i}$ [8]. The implementation of both species is beneficial due to their distinct impact on combustion characteristics, but requires specialized experimental setups for which both isomers can be detected. Wang et al. [8] defined the boundary values of all 7 independent parameters, for which only the upper boundary of γ is dependent on the other HyChem parameters. The upper boundary γ_{\max} is defined by:

$$\gamma_{\max} = \frac{-(4 - \chi)m + 0.5(7 - \chi)n + 3\beta}{10 - \chi} \quad (1)$$

With the development of the linTM, it was demonstrated that the decoupling of the optimization parameter boundary is highly beneficial for the optimization process. Therefore, for the practical implementation of γ in the optimization process we normalized it with γ_{\max} to form the normalized parameter γ^* :

$$\gamma^* = \gamma / \gamma_{\max} \quad (2)$$

To complete the chemical kinetic HyChem mechanism a detailed submodel of the C₄ core chemistry as well as a submodel for the oxidation of benzene (C₆H₆) and toluene (C₇H₈) need to be added to the reaction scheme.

3. Determination of HyChem parameters

To create the HyChem models in this work, the detailed chemistry submodels of the C₄ core and the aromatics oxidation were taken from the chemical kinetic model DLR Concise [3]. For the initial HyChem model, reactions R1 and R2 were added with guess values for the independent HyChem parameters as well as for the rate coefficients k_1 and $k_{2,X}$. As the initial guess of the 7 independent parameters of the HyChem approach, the average value between the upper and lower boundaries was chosen, as shown in Table 1. In this work, the impact of selection of the initial parameter set on the final result was investigated. Hereby, six additional fully randomized parameter sets were generated within their parameter boundaries. The optimization was performed for one optimization case and no significant impact on the final optimization result was observed. The iteration progress of the optimization objective function is shown in Fig. S1 in the supplementary material. With the implementation of the HyChem approach the number of species in the chemical kinetic model DLR Concise was significantly reduced from 259 to 124.

The initial HyChem models in this work were created for the two investigated fuels JS-A1 and JS-B1 [4]. Both fuels were analyzed by GCxGC/MS to determine the chemical composition of the fuels by

Table 1
Initial values and optimization boundaries of the HyChem parameters (Par.).

Par.	Initial	Boundary
k	[8]	$\Delta \lg = +/-1.0$
α	1	$+/-1.0$
β	0.5	$+/-0.5$
γ^*	0.5	$+/-0.5$
λ_3	1	$\Delta \lg = +/-2.0$
$\lambda_{4,1}$	1	$\Delta \lg = +/-2.0$
$\lambda_{4,i}$	1	$\Delta \lg = +/-2.0$
χ	0.5	$+/-0.5$

$$\Delta \lg = \log_{10}(\text{par}_{+/-}) - \log_{10}(\text{par}_0).$$

means of chemical classes and number of C atoms [14]. JS-A1 is a typical Jet A-1 representative that contains 20.2% n-alkanes, 30.3% iso-alkanes, 33.0% cyclo-alkanes and 16.5% aromatic compounds. JS-B1 is an ATJ produced by the company Gevo as a synthetic paraffinic kerosene (SPK) and consists fully of iso-alkanes [4]. For both fuels JS-A1 and JS-B1, surrogate fuel compositions were defined by Kathrotia et al. [4]. The surrogates were created using components from the DLR Concise model and validated for various combustion characteristics [3]. The surrogate compositions were utilized to calculate and assign the thermodynamic data of the heat capacity, enthalpy and entropy for the fuels JS-A1 and JS-B1. The detailed surrogate composition can be found in prior work [4].

To determine the final HyChem model parameters, the parameters of the initial model were optimized to match different experimental or simulated chemical kinetic targets. The optimized HyChem model parameters include the stoichiometric coefficients as well as the rate coefficients of R1 and R2. The C₄ core model as well as the aromatics submodel remained unchanged.

For the experimental approach, the optimization targets were experimental values from chemical kinetic investigations. The chosen targets were ignition delay times measured in shock tubes [15], laminar burning velocities [15,16], and species profiles from the oxidation of the real fuels in a flow reactor [14]. The selected experiments added up to 52 target values for JS-B1 and 61 target values for JS-A1. The weighting factors for all numerical targets were set to 1. The only exceptions are the weighting factors of the maximum laminar burning velocity which were increased to 8, due to the low uncertainty and the importance in regard to the general heat release in the combustion process. The full list of optimization targets is given in the supplementary material. The approach has the advantage that any other experimental chemical kinetic target can be used with sensitivity to the HyChem parameters. These targets include e.g. the measurement of ignition delay times in rapid compression machines and species profiles measured in jet-stirred reactors, shock tubes and laminar flames.

For the shock tube studies, the ignition delay time uncertainties were estimated to be approximately 15%, the uncertainty of the temperature estimation is below 15 K [17]. The laminar burning velocities were determined with the cone angle method. The uncertainties were determined to be in a range between 2 cm/s and 5 cm/s with the highest values for fuel-rich mixtures and at elevated pressure. Thus, the relative uncertainties amount to values between 3% and 6% for most of the experimental data with up to 10% for some single points [15,16]. Further influence on the accuracy of the measurement arises from the accuracy of the mass flow controllers. Only stretched burning velocities were determined, the difference between the stretched laminar burning velocity and the unstretched laminar flame speed can be significant at high equivalence ratios and was evaluated to be up to 15% under fuel-rich conditions [18]. For the flow reactor the uncertainties of the mole fractions of calibrated species was estimated to be 20% [14], the absolute uncertainty of the temperature of the flow reactor was assumed to be below 20 K [19].

For the numerical approach, the optimization targets are species profiles in homogeneous isothermal reactors that were simulated with the DLR Concise. Species profiles were simulated for the oxidation of the surrogate fuels in air for different boundary conditions of the initial temperature T , pressure p , and fuel–air equivalence ratio φ . The chosen conditions were representative of typical gas turbine combustion conditions with a temperature range of 1100–2200 K, φ range of 0.5–2.0 and at the pressures of 1 bar and 16 bar. The main products, important radicals and the pyrolysis products were selected as target species: H₂, O₂, CO, CO₂, H₂O, H, O, OH, CH₃, CH₄, C₂H₄, C₃H₆, nC₄H₈, iC₄H₈, C₆H₆ and C₇H₈. The characteristic points for the optimization were selected according to the strategy of prior work [13]. Three characteristic points were defined on the decreasing species profiles of reactants and intermediates (from maximum to end). Three characteristic points were defined on the increasing species profiles of products and intermediates (from start to maximum). Intermediate species were defined in the automatized process for which the start and end mole fractions were below 80% of the maximum. The weighting factors for all numerical targets were set to 1. With the automatized generation of the species profiles 2287 target values were generated for JS-B1 and 2234 target values were generated for JS-A1.

The linTM framework is utilized to conduct the final parameter optimization for the numerical and experimental approach [13].

4. Optimization method

The linear transformation model (linTM) was developed for the highly efficient and effective large-scale optimization of chemical kinetic parameters [13,20]. Specifically, the linTM optimizes all model parameters in chemical kinetic mechanisms, including Arrhenius coefficients, collision efficiencies and Troe parameters. Additionally, this work has expanded the optimization framework with the capability to optimize the independent HyChem parameters α , β , γ^* , λ_3 , $\lambda_{4,1}$, $\lambda_{4,i}$ and χ . The optimization targets or quantities of interest q of the linTM are defined by coordinates of characteristic points on species profiles and profiles of laminar burning velocities. Examples of these characteristic points are maxima of a profile or certain points at which a specific percentage of a maximum on a profile is reached. This approach also includes ignition delay times, as they are commonly defined as characteristic points on e.g. pressure or chemiluminescence emission profiles in experimental approaches. To evaluate the performance of a chemical kinetic model, the distance d_i is formed, which is multiplied by the weighting factor w_i :

$$d_i = w_i \ln \left(\frac{q_{\text{sim},i}}{q_{\text{tar},i}} \right) \quad (3)$$

The optimization objective of the linTM is to minimize the distances. The detailed optimization process of the linTM is described by Methling et al. [13]. All chemical kinetic simulations are conducted using the python package Cantera [21].

5. Results

Three separate optimization strategies were tested for both jet fuels JS-B1 and JS-A1. The first strategy optimizes only on the experimental data and these cases are referred to as *exp*. The second strategy targets numerically generated species profiles through the use of a surrogate model, and is labeled *surr*. Finally, a control case was used to test the experimental and numerical targets simultaneously for the optimization, labeled *both*.

Tables 2 and 3 show how the different cases were optimized by comparing the average distances \bar{d} for each of the target sets. They also compare the differences between the predicted values and actual targets with results obtained from the DLR Concise, as well as the initial HyChem models which used guessed parameter values. With every optimization case, the deviations between the targets and modeling

Table 2

Mean unweighted distances between targeted and simulated values for the JS-B1 cases.

Case	\bar{d}_{exp} $n = 52$	\bar{d}_{surr} $n = 2287$
DLR Concise	0.356	0.000
JS-B1 initial	0.526	0.979
JS-B1 <i>exp</i>	0.189	0.606
JS-B1 <i>surr</i>	0.340	0.284
JS-B1 <i>both</i>	0.301	0.303

Table 3

Mean unweighted distances between targeted and simulated values for the JS-A1 cases.

Case	\bar{d}_{exp} $n = 61$	\bar{d}_{surr} $n = 2234$
DLR Concise	0.322	0.000
JS-A1 initial	0.670	0.738
JS-A1 <i>exp</i>	0.256	0.521
JS-A1 <i>surr</i>	0.370	0.259
JS-A1 <i>both</i>	0.359	0.266

results were significantly reduced compared to the corresponding initial HyChem models.

Neither the models *exp* nor *surr* can consistently reproduce both experimental and the numerical target data sets with the lowest distances simultaneously. As a control case the optimization cases *both* were conducted, confirming that no consistent solution for both the experimental and the numerical target data sets can be achieved. A reason for this limitation is caused by the global reaction steps R1 and R2 of the HyChem approach. Global reactions are significant simplifications of complex reaction pathways. The detailed decomposition pathways including branching of intermediates of fuel species is highly temperature and pressure dependent. Additionally, unimolecular decomposition reactions are usually pressure dependent. Therefore, each set of global reaction parameter is valid for a limited range of temperatures, pressures and gas compositions. As a result, the generated HyChem models are not capable to be fully valid for both boundary condition regimes *i.e.* of the gas turbine combustion conditions and the conditions of the fundamental chemical kinetic experiments. This highlights the need to increase the design flexibility of the HyChem model validity regimes of temperature, pressure and fuel-oxidizer compositions. This can be achieved through the new presented HyChem parameter determination method.

Tables 4 and 5 summarize the estimated HyChem parameters by the optimization on the different target sets. Here the resulting HyChem parameters or branching ratios of the global reaction steps show a strong dependence on the selected strategy *exp* or *surr*. This observation can be related to the validity regimes of temperatures, pressures and compositions needed for the overall reaction steps, as explained in the previous section. Another reason can be found in deviations between the experimental data of the flow reactor and the model predictions of the semi-detailed reaction model DLR Concise, which is discussed later in the results section.

The optimized stoichiometric coefficients of the aromatic species C_6H_6 and C_7H_8 are close to zero for the paraffinic JS-B1 (Table 4). This is to be expected because alkanes produce fewer aromatic species during combustion processes than other fuel components such as cycloalkanes or other aromatic species. In conclusion, the parameter optimization yields chemically consistent results, confirming the robustness of the approach.

The original HyChem parameter estimation approach faced a major challenge in distinguishing between the isomers nC_4H_8 and iC_4H_8 or the parameters $\lambda_{4,1}$ and $\lambda_{4,i}$, respectively. This method specifically requires experimental techniques that resolve these isomers to determine $\lambda_{4,1}$ and $\lambda_{4,i}$ directly [8,11]. Here, both presented strategies *exp* and

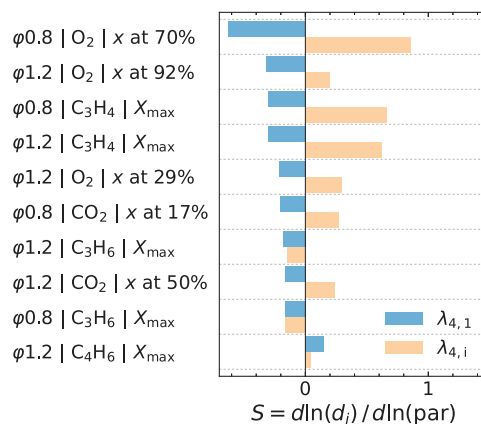


Fig. 1. Sensitivity analysis of HyChem parameters $\lambda_{4,1}$ and $\lambda_{4,i}$ on targets from JS-A1 flow reactor experiments from Oßwald et al. [14].

surr allow the estimation of $\lambda_{4,1}$ and $\lambda_{4,i}$ without these specialized experiments. When optimizing HyChem parameters on numerical data (*surr*), the formation and decomposition of nC_4H_8 and iC_4H_8 can be modeled by the detailed mechanism and targeted—in case both isomers are given in the chemical kinetic model. Even when numerical (*surr*) or experimental data (*exp*) cannot resolve the C_4H_8 isomers, various different quantities of interest q can be sensitive to the parameters $\lambda_{4,1}$ and $\lambda_{4,i}$. As an example, the sensitivity analysis of these parameters on several q defined on species profiles measured for the JS-A1 oxidation in the flow reactor [14] is given in Fig. 1. It should be noted that each measurement point at a certain oven temperature of this flow reactor requires a homogeneous reactor simulation with a constraint temperature profile [14]. Therefore, the targeted quantities of interest of the reactants and products – shown in Fig. 1 – are coordinates of the distance in the reactor [13]. The patterns of the sensitivity values for $\lambda_{4,1}$ and $\lambda_{4,i}$ in Fig. 1 are not similar to each other, meaning they can be mathematically distinguished. Therefore, the parameters can be determined independently, proving the high flexibility of the presented approach for the determination of HyChem parameters.

Xu and Wang [22] discussed the relation between speciation data and HyChem parameters. With their numerical investigation of near stoichiometric fuel oxidation in a homogeneous reactor, the authors showed a stronger sensitivity on speciation data of the parameter β compared to α . With the experimental set in our investigation we were able to identify target quantities with high sensitivity coefficients for α in comparison to β , as shown for the decomposition of O_2 in the flow reactor in Fig. 2. Additionally, Fig. 2 also reveals strong sensitivities of β on ignition delay times.

Figs. 3 and 4 demonstrate that all optimized HyChem models are capable to reproduce the targeted global combustion characteristics of ignition delay times and laminar burning velocities. Under fuel-rich conditions, deviations appear between experimental laminar burning velocities and numerical laminar flame speeds. These deviations are most likely caused by the unavailable stretch correction for the cone angle method as reported by Kick et al. [18]. The overall good results for the global combustion characteristics further confirm the validity of the use of HyChem models to accurately simulate heat release in flames and the ignition behavior of complex real fuels. The Sensitivity analysis of the HyChem parameters on the laminar flame speed in Fig. 5 demonstrate the significant impact of these parameters on this quantity of interest, underlining the usefulness of these data points for HyChem parameter estimation.

Fig. 6 shows the comparison between modeled major species and experimental data obtained from fuel oxidation process in a flow reactor [14]. Both – detailed and HyChem models – have similar results to the experimental data, confirming the reproducibility of the general

Table 4
Fast pyrolysis reaction steps of the HyChem approach for the JS-B1 cases.

Case	Reaction equations
JS-B1 <i>exp</i>	$C_{13}H_{28} \xrightarrow{k_1} 0.651C_2H_4 + 0.496C_3H_6 + 0.008nC_4H_8 + 2.045iC_4H_8 + 0.000C_6H_6 + 0.000C_7H_8 + 0.003H + 1.997CH_3$
	$C_{13}H_{28} + X \xrightarrow{k_{2,X}} 0.516CH_4 + 0.654C_2H_4 + 0.499C_3H_6 + 0.008nC_4H_8 + 2.056iC_4H_8 + 0.141C_6H_6 + 0.031C_7H_8 + 0.641H + 0.359CH_3 + XH$
JS-B1 <i>surr</i>	$C_{13}H_{28} \xrightarrow{k_1} 0.357C_2H_4 + 1.211C_3H_6 + 0.079nC_4H_8 + 1.736iC_4H_8 + 0.000C_6H_6 + 0.000C_7H_8 + 0.606H + 1.394CH_3$
	$C_{13}H_{28} + X \xrightarrow{k_{2,X}} 0.054CH_4 + 0.371C_2H_4 + 1.258C_3H_6 + 0.082nC_4H_8 + 1.803iC_4H_8 + 0.017C_6H_6 + 0.001C_7H_8 + 0.218H + 0.782CH_3 + XH$

Table 5
Fast pyrolysis reaction steps of the HyChem approach for the JS-A1 cases.

Case	Reaction equations
JS-A1 <i>exp</i>	$C_9H_{19} \xrightarrow{k_1} 1.008C_2H_4 + 0.391C_3H_6 + 0.152nC_4H_8 + 0.748iC_4H_8 + 0.451C_6H_6 + 0.049C_7H_8 + 1.839H + 0.161CH_3$
	$C_9H_{19} + X \xrightarrow{k_{2,X}} 0.003CH_4 + 0.886C_2H_4 + 0.343C_3H_6 + 0.134nC_4H_8 + 0.658iC_4H_8 + 0.451C_6H_6 + 0.050C_7H_8 + 0.026H + 0.974CH_3 + XH$
JS-A1 <i>surr</i>	$C_9H_{19} \xrightarrow{k_1} 1.361C_2H_4 + 0.629C_3H_6 + 0.121nC_4H_8 + 0.122iC_4H_8 + 0.448C_6H_6 + 0.052C_7H_8 + 0.633H + 1.367CH_3$
	$C_9H_{19} + X \xrightarrow{k_{2,X}} 0.001CH_4 + 1.475C_2H_4 + 0.681C_3H_6 + 0.131nC_4H_8 + 0.133iC_4H_8 + 0.448C_6H_6 + 0.052C_7H_8 + 0.101H + 0.899CH_3 + XH$

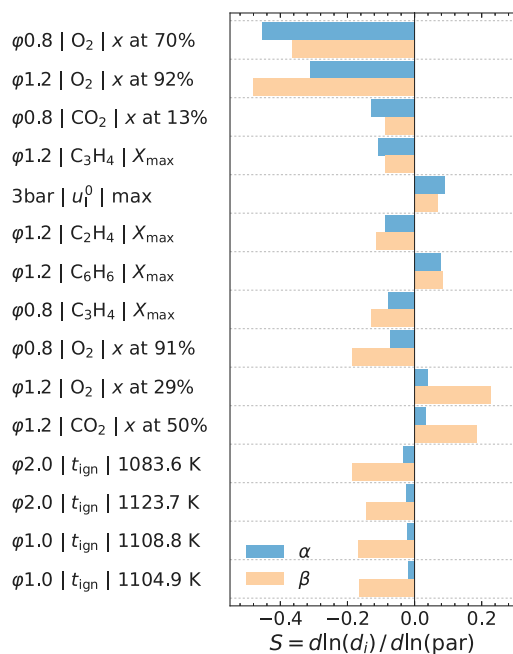


Fig. 2. Sensitivity analysis of HyChem parameters α and β on targets from JS-A1 experiments.

heat release as indicated by the major species. Differences in the model predictions of the models *exp* and *surr* can be observed, caused by differences of the targeted experimental flow reactor and numerical data from DLR Concise. As discussed before, the decomposition and formation of major species is highly sensitive to the HyChem parameters (Figs. 1 and 2). Consequently, these minor inconsistencies between the experimental and numerical data are a main reason for the varying results of HyChem parameters in Tables 4 and 5. Major deviations between experimental and modeling results can be seen for slope of the CO_2 formation under the fuel-rich conditions. These deviations have been observed before with this experimental setup. There seems to be a transition equivalence ratio at which the slope of the CO_2 formation

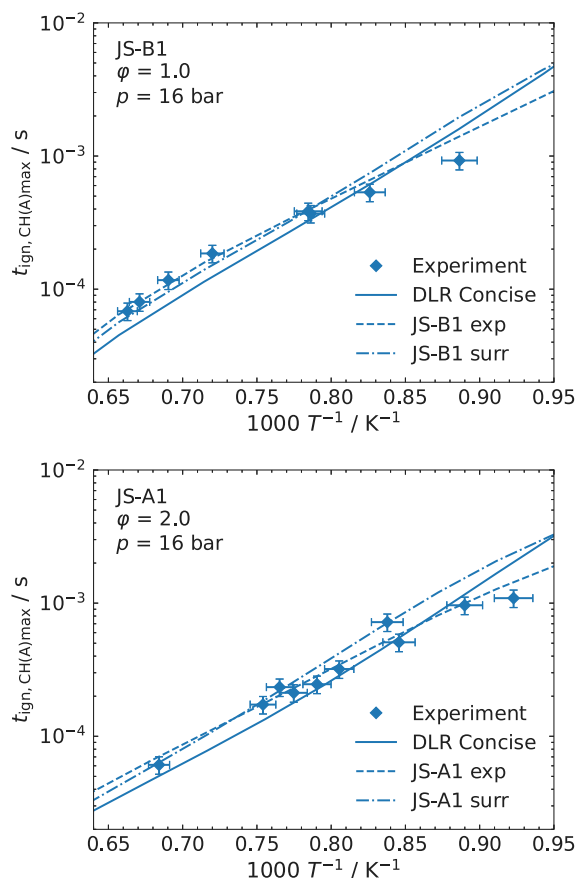


Fig. 3. Modeling results of JS-B1 (top) and JS-A1 (bottom) ignition delay times compared to experimental data from Richter et al. [15].

changes from an abrupt increase to a continuous rise, e. g. shown by Kathrotia et al. [23]. This mismatch between the experimental and simulated transition point was observed to be consistent with various chemical kinetic models, examples are given in Fig. S2 in the

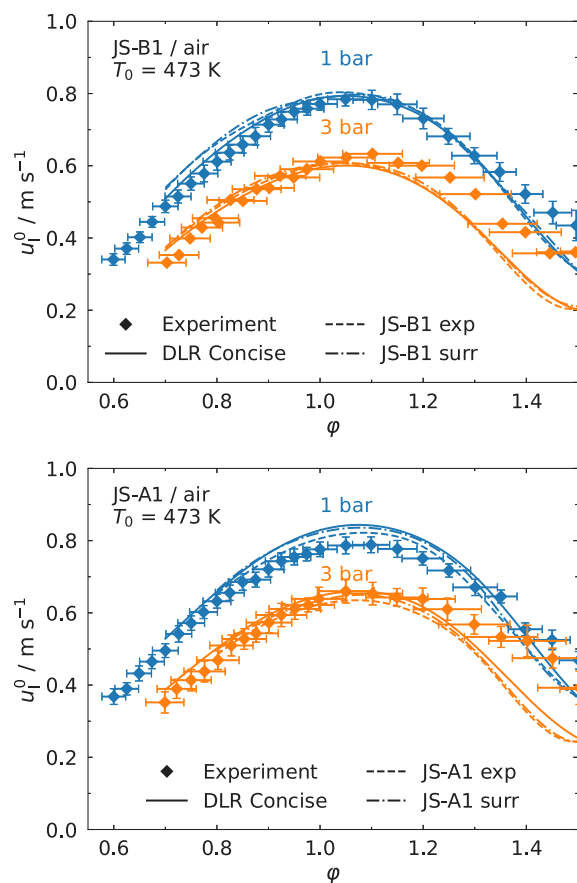


Fig. 4. Modeling results of JS-B1 (top) and JS-A1 (bottom) laminar burning velocities compared to experimental data from Richter et al. [15,16].

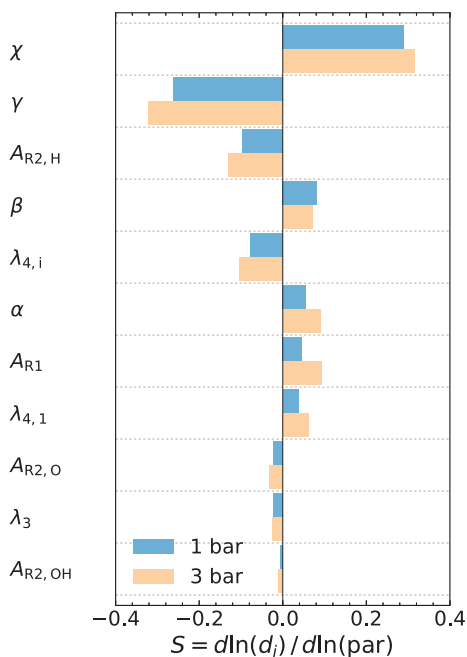


Fig. 5. Sensitivity analysis of the HyChem parameter on the maximum laminar burning velocity of JS-A1.

supplementary material. The cause of the deviations could therefore be systematic errors in the base chemistry of current chemical kinetic models. Nevertheless, the modeling performance of the generated HyChem models in this work is similar to current state of the art chemical kinetic fuel models as demonstrated in Fig. S2. Another possibility could be inhomogeneous two-dimensional or three-dimensional effects in the flow reactor, which can have a significant impact on modeling results under certain conditions [24]. Thus, these deviations are not fully understood by now and require further investigations.

Figs. 7 and 8 exemplary demonstrate the capability of the models to reproduce the peak values of important intermediate species, measured in the flow reactor. The shifts between the modeled and experimental data in the direction of the temperature axis are consistent with the shift of the major species, as discussed in the previous paragraph. In this work, only the peak mole fractions and not the positions of the intermediate profiles along the temperature axis were targeted by the optimization in this work. Figs. 7 and 8 also show that the peak mole fraction is reached before the formation of CO_2 begins in Fig. 6. It can be verified that the detailed chemical kinetic model DLR Concise is capable to reproduce the targeted peak concentrations of the key species. This proves the suitability of the surrogate strategy with the DLR Concise model as suggested by Kathrotia et al. [4] and verifies the utilization of this strategy with the new numerical approach of the HyChem parameter determination. Additionally, the accurate reproduction of the peak values from all models shown in Fig. 4 confirms the applicability to model intermediate species, which are typically crucial to investigate detailed pollutant formations in combustion processes.

Figs. 9–11 show the comparison between modeled species profiles and the targeted numerical data from the surrogate model. Here, the generated HyChem model *surr* is in excellent agreement with the targeted data. Even though the pyrolysis pathways are fully modeled by global reactions steps with the HyChem model, the outcome of the modeling results is identical to the semi-detailed base mechanism DLR Concise. The HyChem models are capable to model the equivalence ratio, temperature and pressure dependencies with the same accuracy as DLR Concise, demonstrating the validity of the HyChem models for a broad range of boundary conditions. To check the validity of the HyChem models for any other boundary condition, the model can always be compared to the results of the semi-detailed DLR Concise at the corresponding boundary conditions. The excellent agreement between the semi-detailed model and the HyChem models also demonstrates the significance of the HyChem approach in generating efficient, reduced, fuel specific chemical kinetic models from detailed models. The new approach presented in this work is thereby an essential step in the overall reduction process, which can be further continued by conventional reduction methods to produce highly reduced models for, e.g. for CFD applications, as demonstrated by Xu et al. [11].

By examining the formation of aromatic compounds in Figs. 12 and 13, limitations in the current HyChem approach can be revealed. The detailed model DLR Concise can predict experimental flow reactor peak values of benzene (C_6H_6) and toluene (C_7H_8) with the applied surrogate strategy (Fig. 12). In contrast, although all HyChem models can reproduce the peak values of C_7H_8 , they all systematically overpredict the peak values of C_6H_6 for both experimental (Fig. 12) and numerical (Fig. 13) optimization targets. A reason for this overprediction could be the formulation of the global reaction steps R1 and R2, which leads to an enforced production of the two aromatics. Aromatics formation is a crucial step in the formation of polycyclic aromatic hydrocarbons (PAH), and subsequently soot. The HyChem approach has the potential for further improvement in order to allow the investigation of soot formation in combustion processes. Further production channels of key intermediate species could be investigated and additional corresponding product species could be added to the reaction steps R1 and R2. Examples are different aromatic species, longer alkenes or even alkyl radicals as suggested by Heberle and Pepiot [7]. Also experimental results from the flow reactor and modeling results from DLR Concise

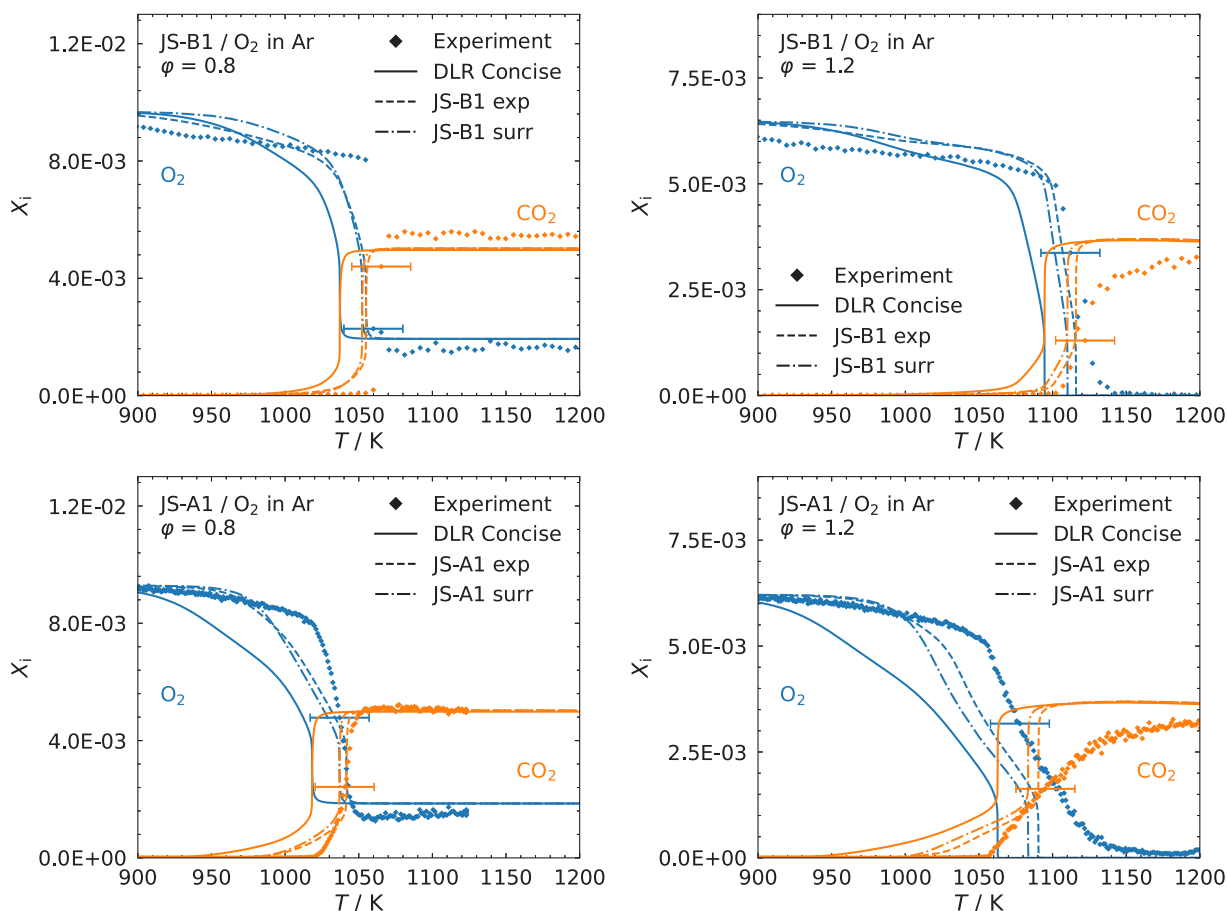


Fig. 6. Modeling results of JS-B1 (top) and JS-A1 (bottom) major species at $\phi = 0.8$ (left) and $\phi = 1.2$ (right) compared to experimental flow reactor data from Oßwald et al. [14].

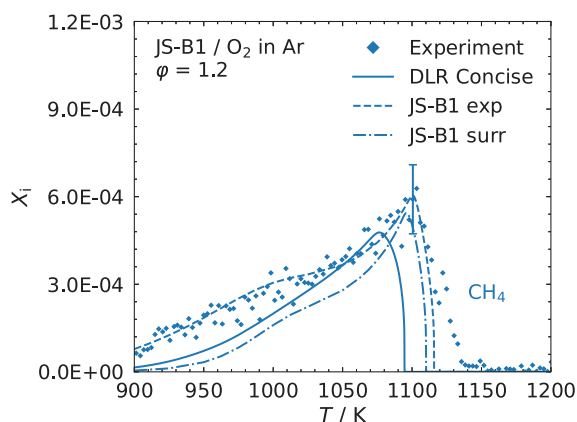


Fig. 7. Modeling results of JS-B1 major intermediate species compared to experimental flow reactor data from Oßwald et al. [14].

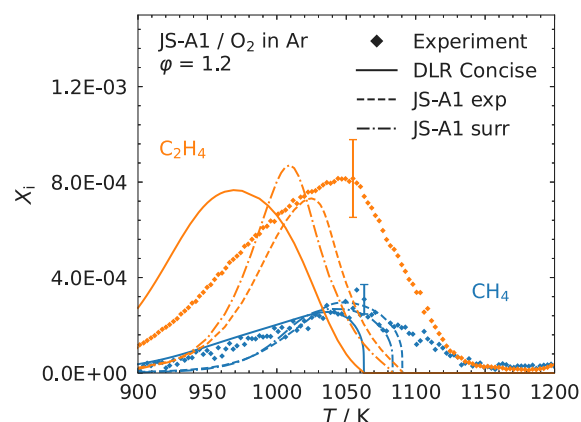


Fig. 8. Modeling results of JS-A1 major intermediate species compared to experimental flow reactor data from Oßwald et al. [14].

show a significant formation of larger aromatics in a similar order of magnitude compared to benzene and toluene. Therefore, another reason of the overprediction of C_6H_6 could be a compensation of the C balance due to the missing formation channels of larger aromatics.

6. Conclusions

Two new approaches were developed to create HyChem models for the chemical kinetic combustion modeling of two real jet fuels. Numerical optimization techniques from linTM were employed to identify the crucial model parameters of the HyChem model.

In the case of the availability of a detailed chemical kinetic mechanism for real fuel surrogates, a HyChem model can be created, solely based on the fuel composition obtained using a GCxGC/MS analysis and a surrogate fuel strategy. This presented numerical approach allows the efficient generation of HyChem models with a minimum experimental effort. Additionally, this approach represents as a crucial intermediate step for the generation of reduced, fuel specific models, directly derived from detailed or semi-detailed chemical kinetic models.

When a chemical kinetic surrogate model is not available for a fuel mixture, the new experimental approach is applicable for the generation of HyChem models. Compared to the conventional experimental

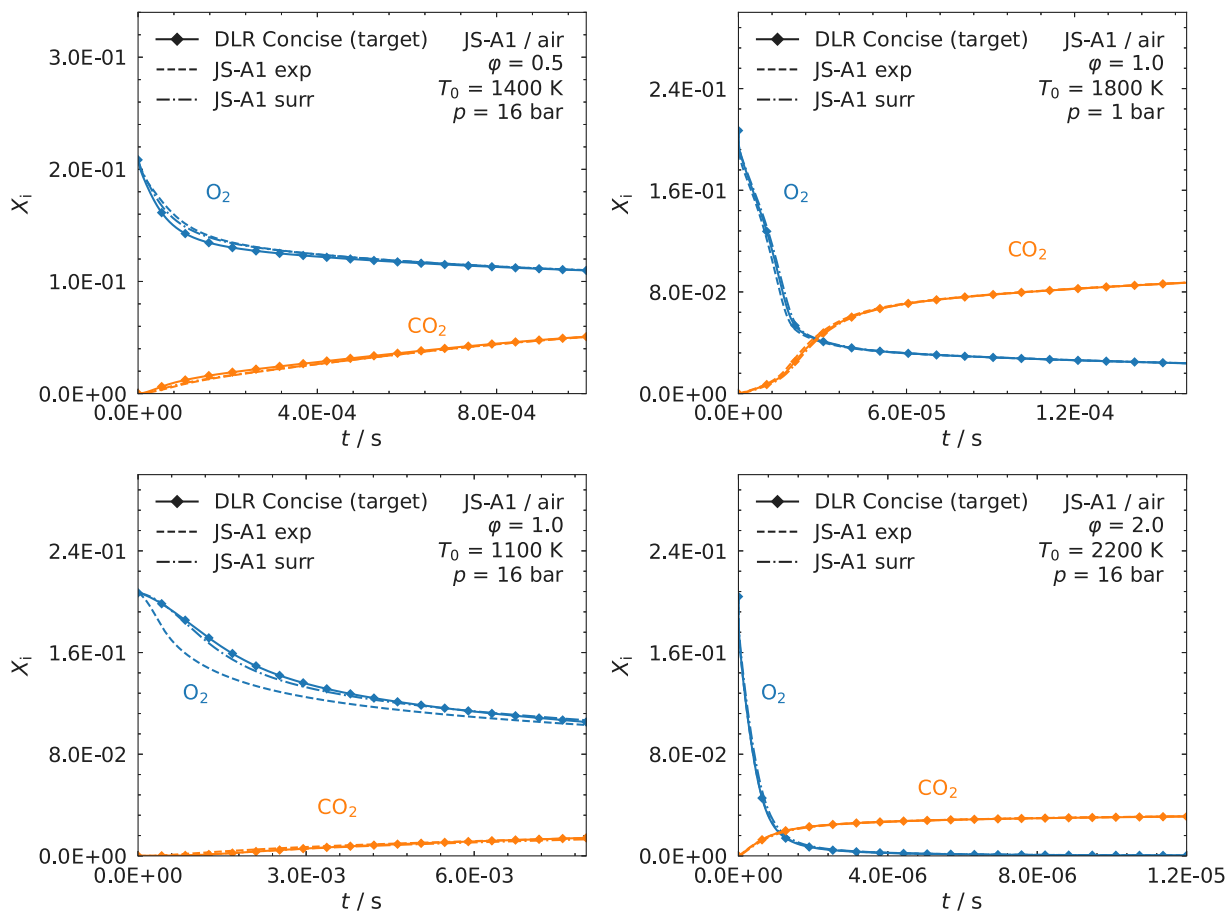


Fig. 9. Modeling results of JS-A1 major species at various conditions compared to targeted numerical data from the surrogate model.

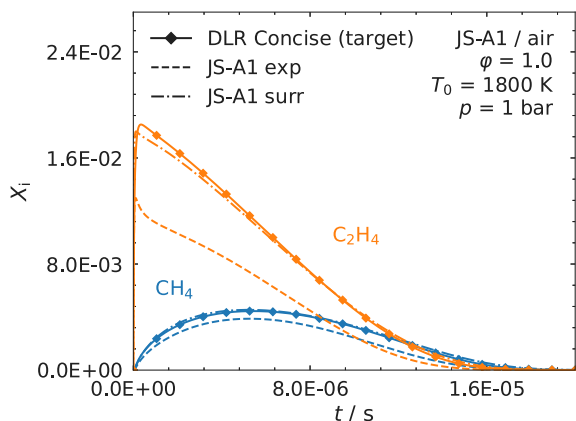


Fig. 10. Modeling results of JS-A1 major intermediate species CH_4 and C_2H_4 compared to targeted numerical data from the surrogate model.

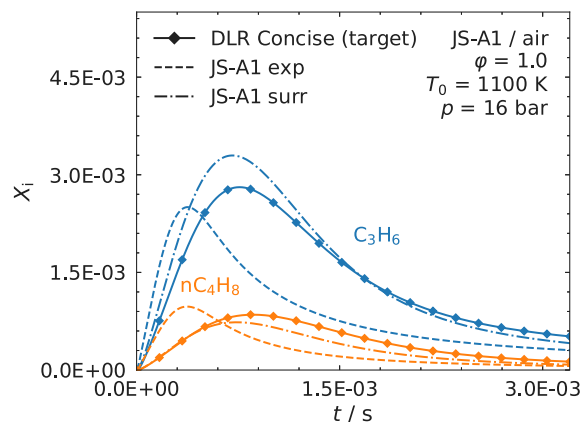


Fig. 11. Modeling results of JS-A1 major intermediate species C_3H_6 and nC_4H_8 compared to targeted numerical data from the surrogate model.

approach, the selection of chemical kinetic experiments and experimental boundary conditions to estimate the HyChem parameters is highly flexible. While the conventional optimization approach is highly reliant on fuel pyrolysis experiments and the detection of the HyChem products and ignition delay time measurements, the new presented approach demonstrates the direct utilization of indirect, sensitive targets like laminar burning velocities and reactive species profiles.

Both presented approaches allow a highly flexible design of the validity regimes of temperature, pressure and fuel-oxidizer compositions, for the semi-global HyChem modeling approach. The fitting of the HyChem parameters is not limited to experimental conditions

and can rather be performed for conditions representative for applied combustion processes.

Overall, the generated HyChem models demonstrate great conformity with the targeted experimental and numerically derived values for fuel-specific ignition delay times and laminar burning velocities along with species concentration profiles. The validation of the generated HyChem models also revealed the potential for improvement of the modeling of aromatics formations, as benzene formations were systematically overpredicted.

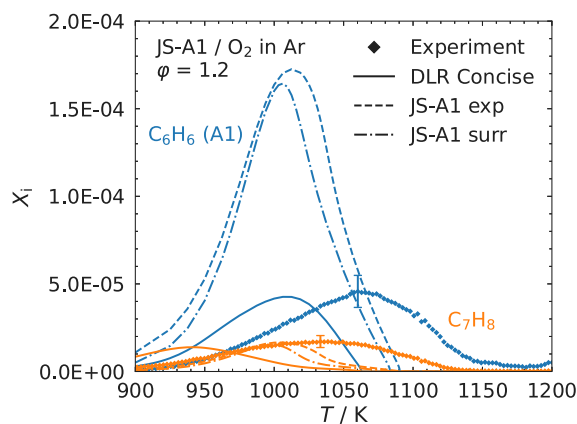


Fig. 12. Modeling results of JS-A1 major intermediate aromatic species compared to experimental flow reactor data from Oßwald et al. [14].

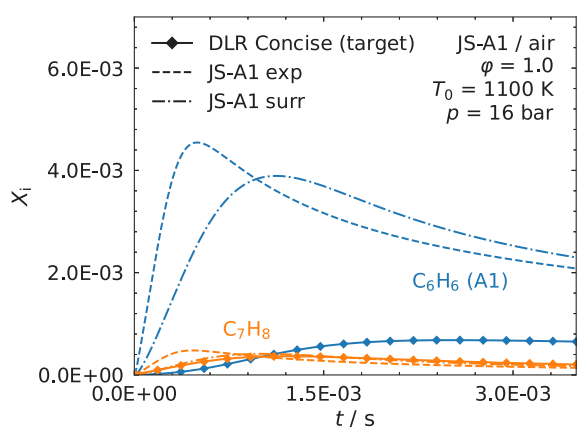


Fig. 13. Modeling results of JS-A1 intermediate aromatic species compared to targeted numerical data from the surrogate model.

Employing further model reduction techniques could further boost the model's efficiency for CFD simulations, aimed at designing modern combustion applications.

CRedit authorship contribution statement

Torsten Methling: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Trupti Kathrotia:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Conceptualization. **Julia Zinsmeister:** Writing – review & editing, Writing – original draft, Validation, Investigation, Data curation. **Sandra Richter:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Jens Melder:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Clemens Naumann:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Patrick Oßwald:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Markus Köhler:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version. Attached files include details on the optimization and the chemical kinetic models *surr* of JS-A1 and JS-B1 in the Chemkin format.

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.combustflame.2024.113646>.

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