Automatic Extension of a Semi-Detailed Synthetic Fuel Reaction Mechanism

Supplementary Materials

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1.1 Approach

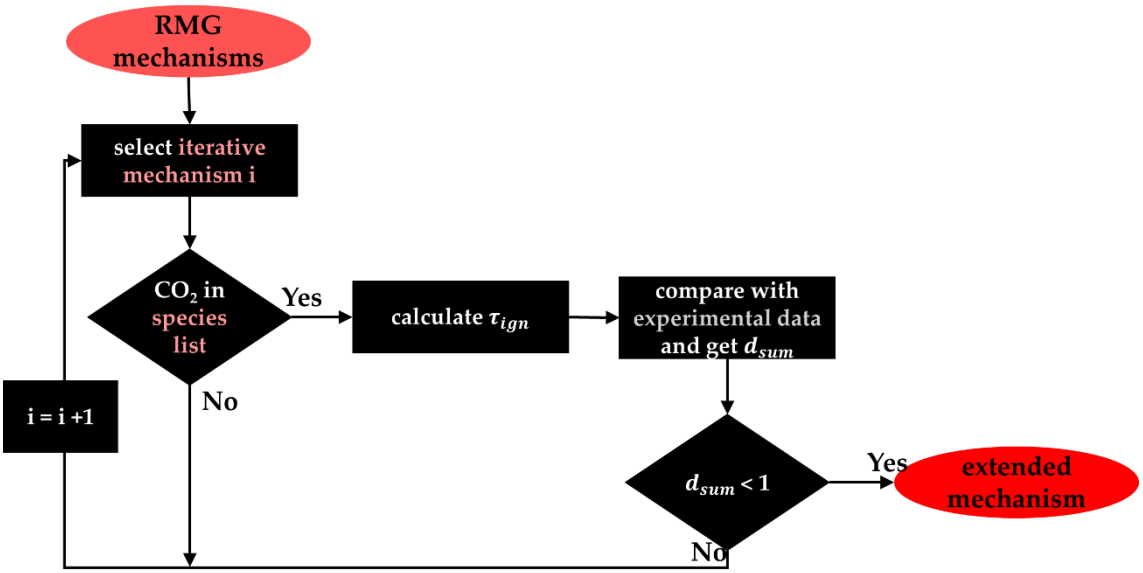

Figure S1. Simulation logic of identifying the extended mechanism.

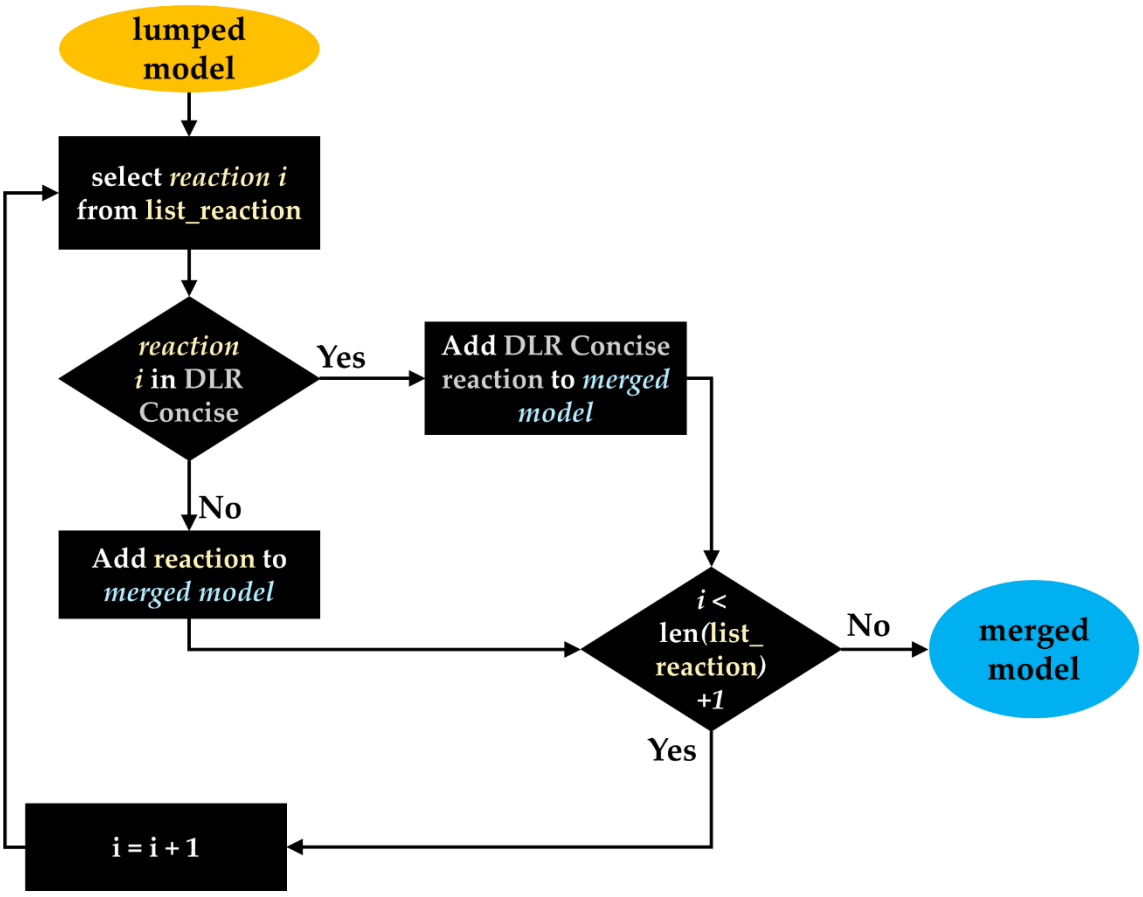

Figure S2. Simulation logic of merging the *lumped model* to the DLR Concise reaction mechanism.

1.2 *n*-heptane

To identify the difference between the *lumped* and *merged* model, a mechanism was constructed, containing the *lumped model* and the DLR Concise reaction rates of the reactions not present in the *lumped model*. A zero-dimensional reactor was simulated at a chosen temperature of 1100 K, due to the deviation of the *merged model* to the experimental data (see Figure 3) and a pressure at 28.4 bar and $\phi = 1$. One after another, the reactions of the constructed model was replaced by the corresponding DLR Concise reactions to identify the sensitive reaction, causing the deviation at HT, see Figure S3(a). Only reactions which have a significant influence were adapted. The highlighted reaction caused the deviation and was replaced in the *adapted merged model* with the corresponding reaction of the *lumped model*, see Table S1. In Figure S3(b) are compared the reactions rates from different mechanism for this reaction. The DLR Concise has the slowest reaction rate compared to the established mechanism from LLNL and the POLIMI.

Table S1. *N*-heptane reactions rates of the DLR Concise and *lumped* model. The first value is the pre-exponential factor, the second is the exponent of the temperature and the last is the activation energy.

DLR Concise	***lumped* model**
	$H_2O_2+C_7H_{15}<=>HO_2+$ *n*-C_7H_{16}
	DUPLICATE
	2.10110e-03 4.133000 542.00
	$H_2O_2+C_7H_{15}<=>HO_2+$ *n*-C_7H_{16}
	DUPLICATE
n-$C_7H_{16}+HO_2<=>C_7H_{15}+H_2O_2$	1.77390e+00 3.328000 1143.00
1.26000e+03 3.400000 13691.63	$H_2O_2+C_7H_{15}<=>HO_2+$ *n*-C_7H_{16}
	DUPLICATE
	2.10110e-03 4.133000 542.00
	$H_2O_2+C_7H_{15}<=>HO_2+$ *n*-C_7H_{16}
	DUPLICATE
	2.10110e-03 4.133000 542.00

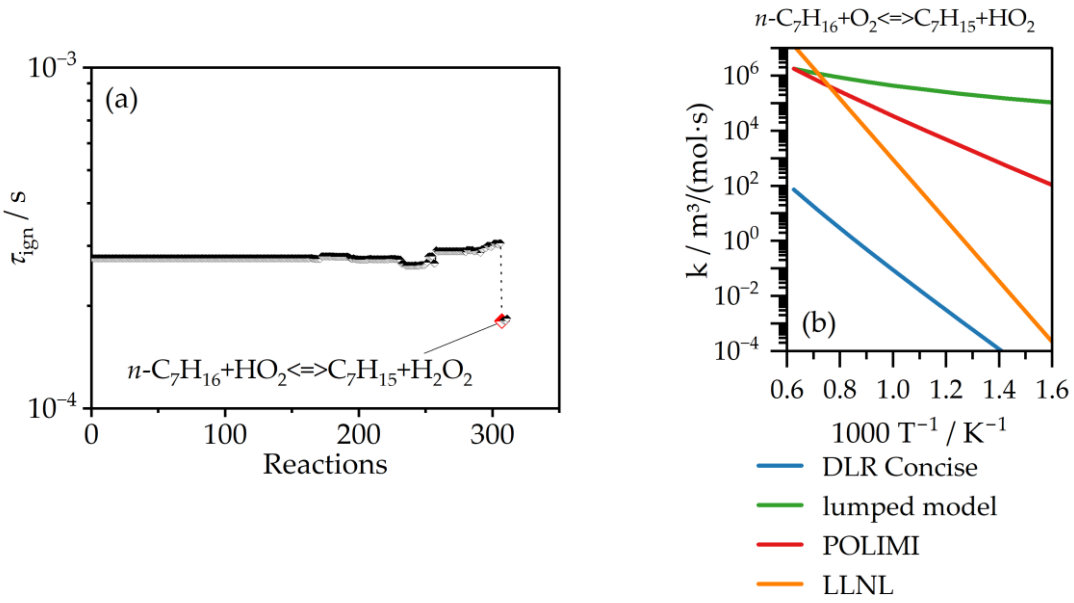

Figure S3. (a) Cumulative replacement of the reactions data and investigation. Simulation of the chemical ignition delay time τ_{ign} of *n*-heptane in air at 1100 K with ϕ = 1 at 28.4 bar. (b) Reaction rate of identified reaction of (a) the *adapted lumped* model compared to the DLR Concise, LLNL and Polimi reaction mechanism

Table S2. *n*-heptane reactions rates of the *merged* and *optimized* model. The first value is the pre-exponential factor, the second is the exponent of the temperature and the last is the activation energy.

Reaction	*Merged* model	*Optimized* model
$C_2H_6O_2$(73)+C_7H_{15}<=> $C_2H_5O_2$(53)+*n*-C_7H_{16}	2.51000e-11 6.770000 -8600.00 DUPLICATE 2.51000e-11 6.770000 -8600.00 DUPLICATE 2.51000e-11 6.770000 -8600.00 DUPLICATE 2.51000e-11 6.770000 -8600.00 DUPLICATE	4.15474e-12 6.973419 -9230.53 DUPLICATE 7.40347e-22 10.097113 -11293.22 DUPLICATE 9.29810e-22 9.797537 -12601.81 DUPLICATE 2.51000e-11 6.770000 -8600.00 DUPLICATE
$C_7H_{15}O_4$(454)<=> $C_7H_{15}O_4$(669)	1.75000e+02 3.10 17500.00	1.40937e+11 0.403992 21193.19

1.3 Isooctane

First, the thermochemistry of each species was analyzed by replacing the DLR Concise thermochemistry with the corresponding data from the *lumped model*. A zero-dimensional reactor was simulated at a chosen temperature of 833 K, due to the deviation of the *merged model* to the experimental data (see Figure 6) and at a pressure of 55.7 bar and $\phi = 1$. As shown in Figure S4(a) the thermochemistry of the species iC_7H_{13} and iC_7H_{14} species has an influence on the ignition delay time. Compared to other reaction mechanisms, the estimated data from the RMG software are in the same magnitude, see Figure S5. By adapting these two thermochemical data an improvement in the prediction of chemical ignition delay was performed, see Figure 6. A mechanism was constructed, containing the *lumped model* and the DLR Concise reaction rates of the reactions not present in the *lumped model*. One after another, the reactions of the constructed model was replaced by the corresponding reactions DLR Concise to identify the sensitive reaction, causing the deviation at LT, see Figure S4(b). The highlighted reaction caused the deviation and was replaced in the *adapted merged model* with the corresponding reaction of the *lumped model*, see Table S3. Figure S5 compares the reaction rates of different mechanism for this reaction. The LLNL and the POLIMI mechanisms have slower reaction rates compared to the DLR Concise.

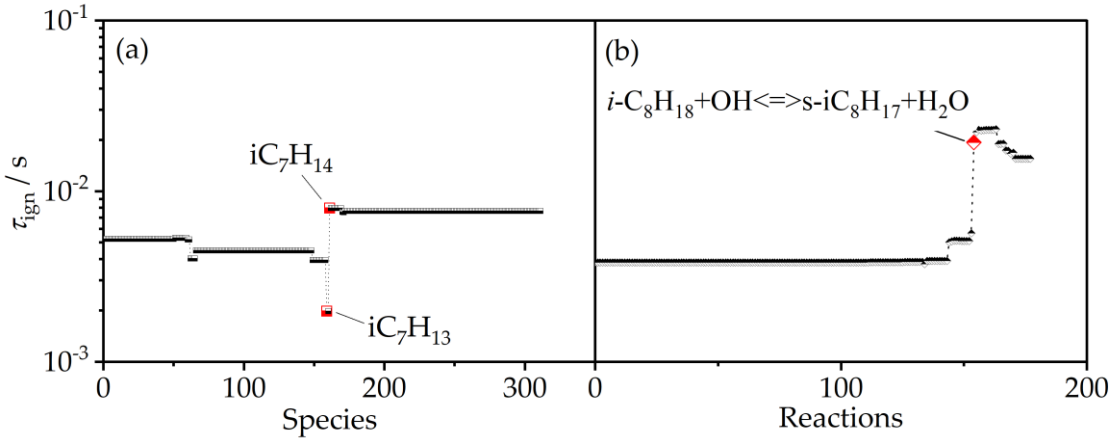

Figure S4. Simulation of the chemical ignition delay time τ_{ign} of isooctane in air at 833 K with $\phi = 1$ at 55.7 bar. (a) Comparison of the influence of the thermochemistry of each species. (b) Cumulative replacement of the reactions data and investigation.

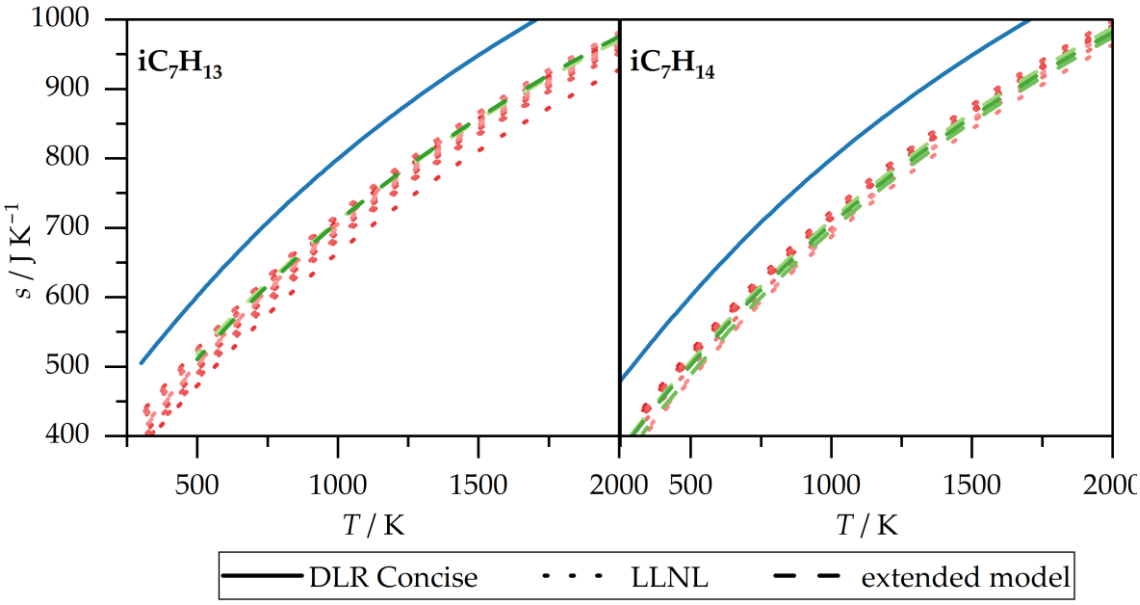

Figure S5. Entropy of the species iC_7H_{13} and iC_7H_{14} from the DLR Concise compared to the entropy properties of the isomers of iC_7H_{13} and iC_7H_{14} of the *extended* model and the LLNL.

Table S3. Isooctane reactions rates of the DLR Concise and the *adapted lumped* model. The first value is the pre-exponential factor, the second is the exponent of the temperature and the last is the activation energy.

DLR Concise	***lumped* model**
i-C_8H_{18}+OH<=>s-iC_8H_{17}+H2O	OH+ *i*-C_8H_{18}<=>H_2O+s-iC_8H_{17}
3.61400e+01 3.500000 -2329.89	2.30651e+11 -0.000000 12858.00
DUPLICATE	DUPLICATE
i-C_8H_{18}+OH<=>s-iC_8H_{17}+H2O	OH+ *i*-C_8H_{18}<=>H_2O+s-iC_8H_{17}
2.40900e+09 1.000000 -9.93	1.40011e+07 1.600000 471.00
DUPLICATE	DUPLICATE

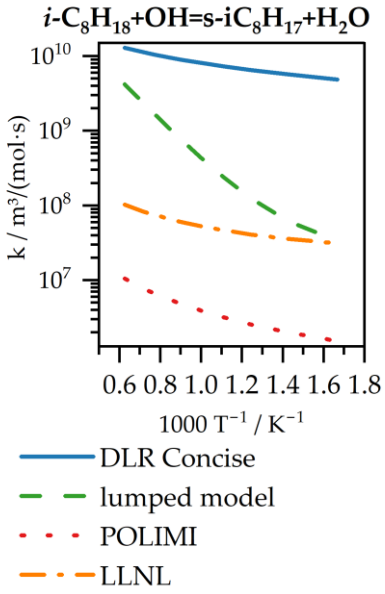

Figure S6. Reaction rate of the *lumped* model compared to the DLR Concise, LLNL and POLIMI reaction mechanism.

Table S4. Isooctane reactions rates of the merged and optimized model. The first value is the pre-exponential factor, the second is the exponent of the temperature and the last is the activation energy.

Reaction	*Merged* model	*Optimized* model
O_2+$C_8H_{17}O_2$(617)<=> $C_8H_{17}O_4$(1272)	2.96276e+12 -0.119000 -0.00	2.11508e+11 -0.078502 -2434.76
$C_8H_{17}O_2$(544)<=> $C_8H_{17}O_2$(618)	1.48000e+06 1.220000 13840.00	3.73452e-12 6.549189 8270.67

1.4 AutoSM

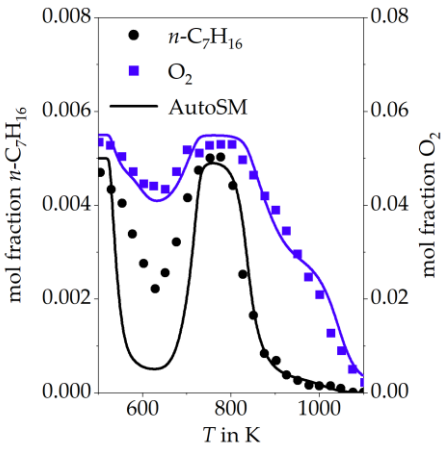

Figure S7. Simulation a jet-stirred reactor of n-heptane at 1.06 bar, a residence time of 2s and ϕ = 0.9 diluted in helium [43].

As an example of using the AutoSM for predicting technical key parameters, the approach from Schmidt et al. [8] was used to predict the DCN. The ignition delay times of n-heptane, isooctane and PRF10-95 were simulated with the model AutoSM and used in equation (S1)-(S3). The results are in a ±5 range, see Figure S8. Using the AutoSM with the focus on ignition delay times reproduction shows leads to an accurate prediction of DCN.

$$DCN_{\text{calc}} = 10.48 + \frac{1}{ID_{\text{phy}} + ID_{\text{chem}}} \tag{S1}$$

$$ID_{\text{phy}} = 0.01 \cdot \left(\frac{\rho}{\rho_{\text{PRF50}}}\right)^{9.59} \cdot \left(\frac{\eta}{\eta_{\text{PRF50}}}\right)^{-2.9} \cdot \left(\frac{\sigma}{\sigma_{\text{PRF50}}}\right)^{-4.31} \cdot \left(\frac{\lambda}{\lambda_{\text{PRF50}}}\right)^{0.032} \cdot \left(\frac{D_{iff}}{D_{iff_{\text{PRF50}}}}\right)^{e-19.77} \cdot \left(\frac{c_p}{c_{p_{\text{PRF50}}}}\right)^{-10.42} \cdot \left(\frac{\Delta h^{LV}}{\Delta h^{LV}{}_{\text{PRF50}}}\right)^{6.204} \tag{S2}$$

$$ID_{\text{chem}} = 0.007 \cdot \frac{\tau_{\text{ign}}}{\tau_{\text{ign}_{\text{PRF50}}}} \tag{S3}$$

With ID_{phy} as dimensionless physical ignition delay time, ID_{chem} as dimensionless chemical ignition delay time, density ρ, viscosity η, surface tension σ, heat conductivity λ, diffusion coefficient D_{iff}, heat capacity c_p, enthalpy of evaporation Δh^{LV} and with PRF50 as index of the reference fuel PRF50 (volumetric mixture of 50 vol. % *n*-heptane and 50 vol. % isooctane).

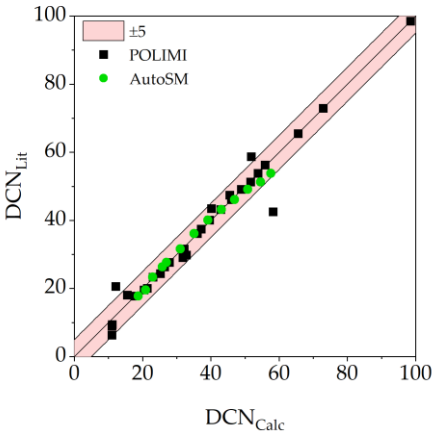

Figure S8. Using the approach from Schmidt et al. [8] and demonstrating the potential of the AutoSM for predicting technical key parameters like the DCN.