

# The comprehensive modelling of *n*-heptane / iso-octane oxidation by a skeletal mechanism using the Chemistry Guided Reduction approach

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## Abstract

We apply to the primary reference fuels *n*-heptane and iso-octane the chemistry-guided reduction (CGR) formalism for generating kinetic hydrocarbon oxidation models. The approach is based on chemical lumping and species removal with the necessity analysis method. We demonstrate that the lumping technique can be applied to the branched peroxy radical isomers formed by iso-octane oxidation with minor modifications to the previously studied *n*-heptane. The skeletal model derived by the CGR procedure is validated against different combustion conditions including low and high temperatures, fuel-lean and fuel-rich mixtures, pressures between 1 and 40 bar, and local (species concentration profiles in a jet-stirred reactor) and global parameters (ignition delay times in shock tube experiments and flame speeds).

## Introduction

Combustion of fossil fuels is the major human energy source, a status that will last at least for the near and mid-term future. However, the fossil hydrocarbon supplies will diminish and therefore a movement towards the generation of renewable energy [1-3] is under way to help meet the increased global energy needs. In this respect the second generation of fuels based on biomass is expected to provide both a favourable CO<sub>2</sub> balance sheet and ignitability characteristics that meet future demands of efficiency optimised classical and new internal combustion engines such as the HCCI (Homogeneous Charge Compression Ignition) engine. A large amount of these future fuels will be mixtures of liquid hydrocarbons with respect to transportation, infra-structure and safety. Detailed chemical reaction mechanisms have proven to be powerful tools to model and analyse the chemical process of fuel degradation. Such mechanisms help to deepen the understanding of the chemical part of the combustion process; they provide information about ways to improve fuel qualities and are practical modelling tools in engineering research. However, the direct incorporation of chemical reaction mechanisms within complex reactor models simulations is limited due to their large number of species and elementary steps, especially for liquid reference combustibles such as *n*-heptane and iso-octane that are commonly used to model the combustion of practical fuels. Considering that future model fuels will become multi component mixtures both comprehensive and compact models are needed for the pure components to achieve predictive power for combustion characteristics of mixtures at affordable computational costs.

*n*-heptane and iso-octane are PRF (Primary Reference Fuel) components used for engine knock

rating of spark-ignition engines. They will be standard components also in future model fuel blends that additionally contain aromatic fuels such as toluene [4].

Recently, we presented the chemistry guided reduction (CGR) approach [5], which aims at a mechanism reduction to the skeletal level conserving the predictive power of the detailed starting mechanism. CGR is based on chemical lumping and species removal with the necessity analysis method, a combined reaction flow and sensitivity analysis [6]. A defined sequence of simplification steps, consisting of the compilation of a detailed, but compact chemical model, the application of linear chemical lumping and finally species removal based on species necessity values. This simplification (or process) allows a significantly increased degree of reduction compared to the simple application of the necessity analysis or similar species or reactions removal methods. The lumping approach we used is discussed in detail in [5,7]. For *n*-heptane we derived a skeleton model by CGR, which consists of 110 species, 1174 forward and backward reactions and is validated against the full range of combustion conditions. In the present study we show that the lumping rules derived for *n*-heptane can be applied to the branched peroxy radical isomers formed by iso-octane oxidation with minor modifications. Moreover, a comprehensive skeletal level of reduction can be achieved by applying the necessity analysis analogously [5].

## Chemical model

The *n*-heptane/iso-octane mechanism is based on the baseline chemistry of Hoyermann *et al.* [8], which includes benzene build up and destruction reactions of Wang and Frenklach [9] and detailed oxidation mechanisms for *n*-heptane and iso-octane

from the Lawrence Livermore National Laboratory (LLNL) [10,11].

In the first step a detailed *n*-heptane/iso-octane oxidation mechanism was compiled using the detailed *n*-heptane mechanism of Ahmed *et al.* [7] and the iso-octane oxidation mechanism of Curran *et al.* [11]. The reactions of branched olefins, iso-butane oxidation and iso-carbonyl compounds were taken from the same source. The LLNL models for *n*-heptane and iso-octane oxidation consist of 25 reaction classes discussed for example in [7,10,11], which are only partly consistent in their kinetic assumptions. However, there is no kinetic reason for differences in collision factors and activation energies that cannot be explained by the branching in the alkyl chain. Therefore we aimed at a consistent description of the main oxidation reactions of both fuel molecules, with the kinetic data for each reaction class only depending on the degree of branching (primary, secondary and tertiary C-atoms). We have almost matched this objective. Only H-atom abstraction by HO<sub>2</sub> (50 % faster for iso-octane) and reaction class 24, the decomposition of ketohydroperoxides (25% slower) show minor deviations in their pre-exponential factors compared to the *n*-heptane model [5,7]. The compiled detailed mechanism consists of 390 species and 3521 irreversible reactions, which is a compact size, compared to the Lawrence Livermore models. According to the CGR method such compact mechanisms (<400 species) are suitable starting points for the next reduction stage.

In the second step chemical lumping was applied to the *n*-heptyl, *n*-heptylperoxy and -oxy radicals as described in [5,7]. The 4 *n*-heptyl radicals and heptyl-peroxy species were lumped to one species in *n*-heptane oxidation sub-mechanism. For iso-octyl we applied a more detailed lumping due to presence of tertiary C-atoms. We introduced three lumped species with primary, secondary or tertiary C-atoms at the radical position. For the isomeric species formed by internal H-atom abstraction we lumped species with a function at the primary site (radical or OOH group) separately from the other isomers. For the iso-octyl-hydroperoxy radical most of its isomers have at least one function on a primary C-atom because 5 of 8 C-atoms carry 3 H atoms. Those isomers were lumped in the same manner as described in [5]. Species with the same number of C atoms between the -OOH function and the radical site are lumped in this case. The remaining 2 isomers with the functionality on the inner C-atoms of the main chain are not lumped and their isomerisation and subsequent decomposition reactions are described in detail. In total a reduction from 14 to 10 parallel oxidation pathways is achieved by linear lumping. The thermodynamic data for the lumped species were taken from the species prior to lumping that had the highest concentration in the simulation of iso-octane ignition experiment at 40 bar and 900 K [12]. The thermodynamic data, the transport data and the

reactions of species introduced with the *n*-heptane oxidation mechanism are provided in [5,7]. The thermodynamic, kinetic and transport data for the species introduced with iso-octane chemistry like iso-butane oxidation and iso-carbonyl oxidation are taken from [13].

In the third stage according to the CGR approach, a skeletal mechanism was generated by the application of the necessity analysis to the lumped mechanism. First the species were removed, which have been identified to be redundant for *n*-heptane oxidation in the preceding study [5]. In this work we derived and discussed criteria for maximum and integrated necessity values that were applied to discriminate the redundant species. Only slightly modified criteria were used in the present study to reduce the lumped iso-octane oxidation model to the skeletal level. A detailed discussion of the procedure is provided in [5].

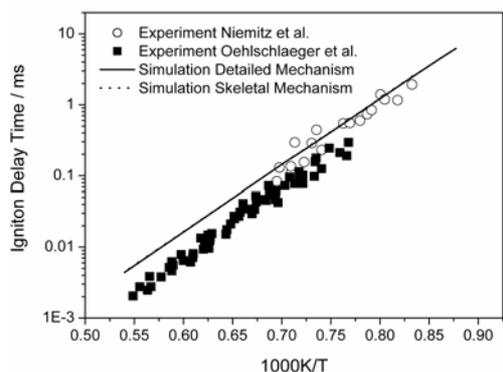
Finally, a skeletal mechanism for *n*-heptane and iso-octane oxidation is derived that consists of 200 species and 1800 irreversible reactions. Thus 90 species and 690 reactions have been introduced with the iso-octane chemistry. Moreover some compounds, especially branched species, which are redundant for *n*-heptane oxidation were necessary for iso-octane oxidation due to different degradation products. Only one lumped iso-octyl-hydroperoxy radical became redundant in the necessity analysis, because a comprehensive description of the low temperature iso-octane oxidation necessitates a rather high level of detail. This is similar to our findings and results of Kazakov *et al.* for *n*-heptane reduction discussed in [5,14]. The application of the CGR approach following the sequence detailed (but still compact) model compilation-chemical lumping-necessity analysis proved efficient to generate a compact and comprehensive skeletal model for *n*-heptane/iso-octane oxidation.

### Mechanism validation

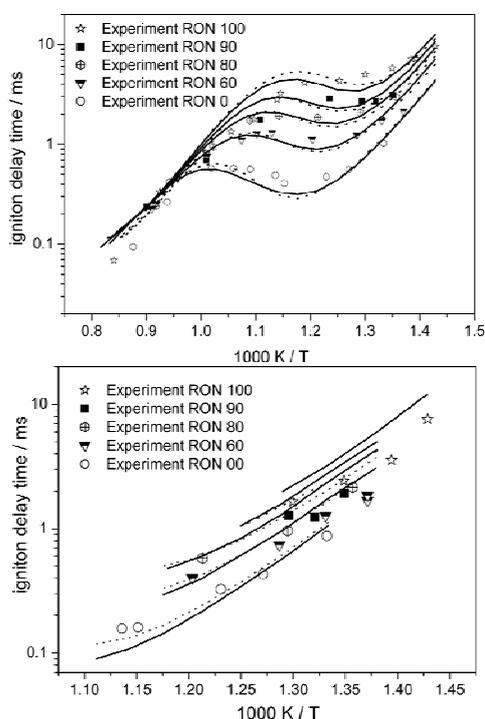
The skeletal *n*-heptane/iso-octane oxidation mechanism is validated against high, intermediate and low temperature shock tube experiments for different pressures and mixture strengths. Moreover experiments providing species concentration profiles in jet stirred reactor and laminar flame speeds data were taken into account.

### Shock Tubes

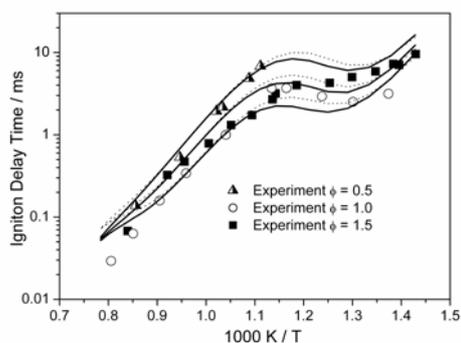
The autoignition of iso-octane and *n*-heptane/iso-octane mixtures has been studied in the literature for high and intermediate temperatures and different pressures in shock tube experiments. We have used the *n*-heptane/iso-octane mechanism assuming constant-volume and homogeneous adiabatic conditions behind the reflected shock wave to simulate high temperature shock tube experiments from the High Temperature Stanford Gasdynamics Laboratory [15] and experiments at intermediate temperatures



**Fig. 1** Experimental (symbols) and predicted (black line detailed, dotted line skeletal mechanism) ignition delays. All data normalized to 1 atm,  $\phi = 1$ , and 21%  $O_2$ . Circles: Niemitz *et al.* [16]; Squares Oehlschlaeger *et al.* [15].



**Fig. 2** Experimental (symbols) and predicted (black line detailed, dotted line skeletal mechanism) ignition delays for different *n*-heptane/*iso*-octane mixtures. All experiments are performed for  $\phi = 1$  at 40 bar [12]. Upper panel: Main ignition; lower panel: first ignition (cool flame).



**Fig. 3** Experimental (symbols) and predicted (black line detailed, dotted line skeletal mechanism) ignition delays for different *iso*-octane. All experiments are performed at 40 bar for  $\phi=0.5$  (triangle,  $\phi=1.0$  (circles) and,  $\phi=1.5$  (squares) [12].

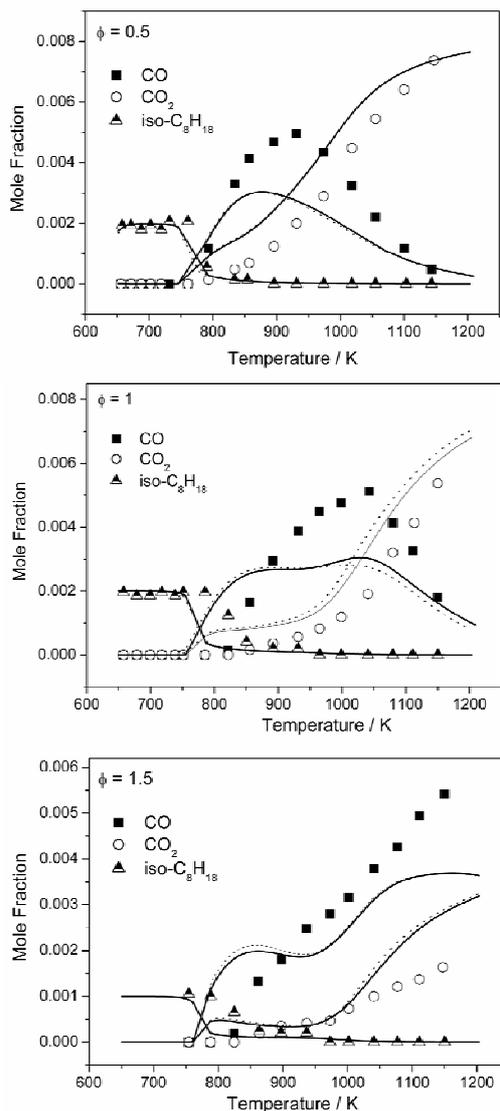
by Fieweger *et al.* [12]. The predicted ignition delay time was determined from the CH-profile for [15] and from the pressure profiles for [12]. For the high temperature experiments we found an excellent agreement of predicted ignition delays with the experimental values of Niemitz *et al.* [16] (Fig.1). The results from the Stanford group are slightly faster than our predictions. The differences between the detailed and the skeletal model are almost indistinguishable. For *n*-heptane we found a minor deviation, which is caused by the lumping of all 4  $C_7H_{15}$  isomers to one lumped species. For *iso*-octane the three lumped species give a much more detailed representation of the *iso*- $C_8H_{17}$  isomers and their decomposition products leading to identical predictions of the detailed and the lumped mechanisms.

The low and medium temperature autoignition of *n*-heptane and *iso*-octane mixtures was studied in shock tube experiments by Fieweger *et al.* [12]. The measurements were performed in the temperature range of 600–1300 K for different mixture strengths ( $\phi = 0.5$ –2) and pressures around 40 bar. They determined the main ignition delay times and also, characterized by a peak in peroxy radical ( $C_xH_yO_2$ ) concentrations, the times between the shock and the first ignition. We simulated these experiments using the detailed and skeleton mechanisms under the assumption of constant volume. In Fig. 2 the results are shown for  $\phi = 1$  and different *n*-heptane/*iso*-octane mixtures with the Research Octane Number (RON) varying from 0 to 100. Fig. 3 shows results for pure *iso*-octane for  $\phi = 0.5, 1.0, 2.0$ . Good agreement is found for all conditions and all applied mechanisms. The increase in reactivity with both rising *n*-heptane and fuel mole fractions is nicely captured by the kinetic models. We can state that only minor deviations are found between the skeletal and the detailed models.

### Jet Stirred Reactor

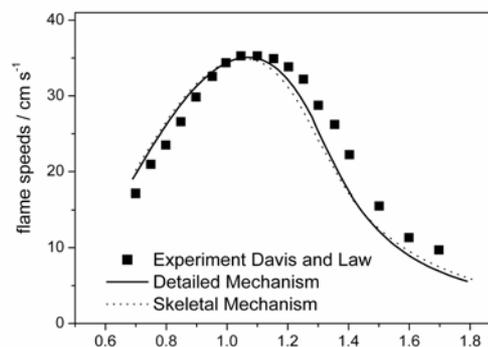
Another reactor type suitable to study fuel oxidation is the jet-stirred reactor (JSR). A stirred reactor with a constant in and out stream can be operated under steady state conditions which are characterized by a constant mean residence time of the educts and a constant composition of the out stream mixture. This reactor type is determined by much different boundary conditions compared to shock tubes and therefore provides a partly complementary test for the low and intermediate temperature oxidation chemistry of mechanism used.

Dagaut *et al.* studied the oxidation of *iso*-octane in a well characterized jet stirred reactor [17]. Concentration profiles of reactants, final and intermediate products are obtained applying gas chromatography and gas chromatography/mass spectrometry analysis tools. The experiments cover the temperature range from 550 K to 1150 K and were performed at a pressure of 10 bar for fuel lean, stoichiometric as well as fuel rich conditions



**Fig. 4** Oxidation of 0.1% *iso*-octane in  $O_2/N_2$  in a jet stirred reactor at  $p = 10$  bar, for  $\phi = 0.5$  (upper panel),  $\phi = 1$  (middle panel), and  $\phi = 1.5$  (lower panel). Experimental results (Ref. 17, symbols) versus model predictions (black lines detailed, dotted skeletal mechanism).

( $\phi = 0.5, 1.0$  and  $1.5$ ). The detailed and the skeletal mechanisms were used to calculate the concentration profiles of the fuel and the major species CO,  $CO_2$  for these experiments. The results are presented in Fig. 4. In general simulations are for all mixtures in reasonable agreement with the experiments. Furthermore the skeleton mechanism shows only negligible deviations from the detailed one. For all mixtures we found that both models overestimate *iso*-octane reactivity at lower temperatures. This is seen from the onset of CO formation which shifted around 30 K to lower temperatures in comparison with the experiments. While for  $\phi=0.5$  the reactivity is only slightly increased, we see that for  $\phi=1.5$  the higher reactivity carries through to higher temperatures as indicated by the enhanced  $CO_2$  formation from CO above 1050 K. We believe that the imported chemistry of intermediate species such as *iso*-butyl



**Fig. 5** Numerically and experimentally determined laminar flame speeds,  $S_u^0$ , for *iso*-octane/air mixtures.  $p = 1$  bar,  $T_u = 298$  K. Lines: Calculations performed with the detailed (black) and skeletal (dotted) mechanisms. Experiments (squares) are performed by Davis and Law [18].

and its oxidation products [13] is responsible for these deviations. We have not incorporated any changes to the *n*-heptane/*iso*-octane oxidation mechanism to better capture JSR combustion. In future the sub-mechanisms containing the reactions of branched hydrocarbons and their interplay with our baseline chemistry [8] will be extensively evaluated and separately validated. We expect an improved performance of the model predictions for *iso*-octane oxidation. However, the agreement, which we found at the present stage, is very reasonable, especially with respect to the skeletal model.

### Flame

The prediction of flame speeds of liquid hydrocarbons was difficult in earlier studies [18 and references therein]. Recently we demonstrated that based on the Hoyermann *et al.* C1-C4 mechanism [8] and the *n*-heptane oxidation mechanism of Curran *et al.* [10] a model can be derived [7] that is capable to predict flame speeds of a large number of C1-C4 fuels and *n*-heptane in excellent agreement with state of the art flame speed measurements [7 and references therein]. In the present study the same base chemistry is combined with the modified *iso*-octane oxidation model of Curran *et al.*. The results of the model predictions using the detailed and the skeletal mechanisms are shown together with the experimental results in Fig. 5. We see that simulated flame speeds show nice agreement with the experimental data over the whole fuel/air-mixture range. Under fuel-lean conditions the model very slightly overestimates flame speeds while for fuel-rich conditions the modelled flame speeds are slightly too slow. However, with respect to experimental difficulties in extrapolating flame speeds to zero stretch and the dependence of the flame speed measurements on mixture strength (compare the experimental studies on *n*-butane flame speeds under fuel rich conditions in Fig. 22 of [7]) the model predictions are well within the experimental uncertainty.

## Conclusions

In the present study we present a compact detailed *n*-heptane/iso-octane oxidation model and a skeletal version of it that has been compiled according to the CGR approach [5]. A reduction from 390 to 200 species and 3521 to 1800 irreversible reactions has been achieved. For the target experiments of the present study (shock tube ignitions, jet stirred reactor oxidation and flame speeds) only negligible deviations between the detailed and the skeletal model are found. The compilation of the detailed mechanism has been done straight forward by simply adding kinetic sub-models of the LLNL database to our *n*-heptane mechanism. In future an improved model performance for iso-octane can be achieved when the simply added chemistry of branched species like the reactions involved in iso-butane oxidation is evaluated and validated on the same extensive level as for the linear fuels [8]. The main conclusion of the present study is that CGR reduction shows the same efficiency we found for *n*-heptane [5] also for the branched fuel iso-octane. This underlines the high reduction potential that can be achieved when chemical lumping [7] and necessity analysis [5,6] are effectively combined. Future applications on oxygenated or aromatic fuels are promising.

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