Computer Aided Detailed Mechanism Generation for Large Hydrocarbons: n-Decane

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1 Introduction

Common engine fuels consist of a mixture of hundreds of hydrocarbons which differ in chain length and structure. For engine simulations real fuels are modeled by surrogate fuels. The most known surrogate fuel for gasoline is a mixture of n-heptane and iso-octane, and for diesel a mixture of n-decane and α-methylnaphthalene. For predicting pollutant formation more comprehensive fuel models are needed. Automatic mechanism generators can be applied to limit the amount of work in developing mechanisms for complex surrogate fuel blends.

Our group developed in the past detailed kinetic mechanisms for n-heptane [1] and iso-octane [2]. For this we followed the mechanism generation rules provided by Curran et al. [3] [4], with rate constants optimized such that the base chemistry from Hoyermann et al. [5] can be applied. We kept the reaction mechanism compact by applying the generation rules for low temperature oxidation to the fuel molecules only, and by introducing a linear lumping algorithm. In this work we demonstrate that rate coefficients, resulting from the mechanism optimization for n-heptane, can be used to generate a reaction mechanism for higher hydrocarbons i.e. n-decane. The thermodynamic data for the larger species are derived by Benson rules based on the thermodynamic data for n-heptane.

The final mechanism is validated by shock tube [6–9] and jet stirred reactor experiments [10]. The mechanism is analyzed by reaction flow and sensitivity analyses. Ignition delay times and species concentration profiles agree well with the experimental data. Our prior work [11] was limited to the prediction of ignition delay times. Recently detailed mechanisms for n-decane have been generated by Ranzi et al [12], Battin Leclerc et al. [13] and Curran et al. [14].

2 Mechanism Generator

To provide a tool which assists in the generation process, a semi-automatic mechanism generator was developed. The generator follows the ideas of prior work [11, 15], but applies the modern object oriented database system CouchDB [16]. All species and reaction related data such as thermo data, molecule structures, names and reaction coefficients are part of the database. In addition a Haskell [17] based

software is stored, which is used to perform graph rewriting representing the classes of reactions proposed by Curran et al. [3]. The system is not limited to those classes or coefficients, and can be easily extended.

The generation of a mechanism is a semi-automatic procedure. It starts with specifying the fuel species. CouchDB applies all reaction classes on this seed molecule. Every reaction class analyses the structure of the given molecule and decides whether the class can operate on it. It returns either nothing or a list of reactions which includes the reaction coefficients as well as lists of product and reactant species structures. Those lists are then presented by the web interface and the user can select which reactions to include in the mechanism adjust their coefficients and additionally name newly created species structures. Reactions and species are placed into the database after passing an isomorphism check, which filters out structures already present in the mechanism. Finally all reaction classes are applied to the newly created structures. This generation process stops when the reaction classes only produce species given in the base mechanism. A functionality to share names of newly created species within a working group is built into the web-frontend. Furthermore it allows different users to work on the same mechanism and keep consistency in species names when generating different mechanisms. It can also export a mechanism from CouchDB to a Chemkin compatible format. Post-processing can be applied to a mechanism to assist the user, e.g. by automatically doubling the coefficients of specific reaction classes for a reaction class sensitivity analysis, as provided in this paper. CouchDB can also couple a reaction mechanism with external simulation software achieved through HTTP and JSON [18]. Future work is the specification of reaction classes not through raw Haskell code, but with a so called Graph Grammar [19].

2   n-Decane Oxidation Mechanism

The n-decane mechanism consists of two sub-mechanisms. 1) The base mechanism for smaller hydrocarbons is described in an extended version (addition of alcoholic species) of the hand compiled mechanism by Hoyermann et al. [5]. 2) The generated mechanism for n-decane. All 25 reaction classes (except class 4) developed by Curran et al. have been applied. The rate coefficients of the n-decane mechanism follow the previous n-heptane study by Ahmed et al. [1]. The final mechanism consists of 340 species and 1500 reactions.

Different experiments available in the literature were chosen for the validation of the mechanism. The species concentrations at low temperatures between 550K and 1050K were validated by the help of Jet Stirred Reactor (JSR) experiments (Fig. 1) performed by Dagaut et al. [10]. Good agreement between simulation and experiment is found for the fuel, O_2, CO and CO_2. For the given residence time O_2 is in general higher predicted by the model when compared to the experiments. This is consistent with a lower prediction of CO. At temperatures higher than 950 K the model predicts too high CO_2 concentrations.

Figures 2, 3, 4 show predicted ignition delay times for fuel-air equivalence ratios ϕ between 0.5 and 2.0, pressures p between 11 bar and 80 bar and Temperatures T between 650 K and 1400 K. Ignition delay times are in general well predicted. For low temperatures the ignition delay is overpredicted for all cases. The most probable reason is the decomposition of ketohydroperoxide (class 24), as can be seen from the sensitivity analysis shown in figure 6. While reaction class 23 is most sensitive at temperatures around 950 K, class 24 is only sensitive at temperatures lower than 800 K. The shift in sensitivity for some reactions between 950 K and 1100 K clearly marks the transition from the negative temperature regime to the high temperature regime.

Figures 2, 3, 4 also show that the pressure and ϕ dependencies of the ignition delays are well understood. The sensitivity analysis shown in 5 demonstrates that the dependence on the fuel-air equivalence ratio

of the sensitivity coefficients of the most sensitive reaction classes is weak. Hence the good prediction of the ϕ and pressure dependence of the model is explained by the base chemistry.
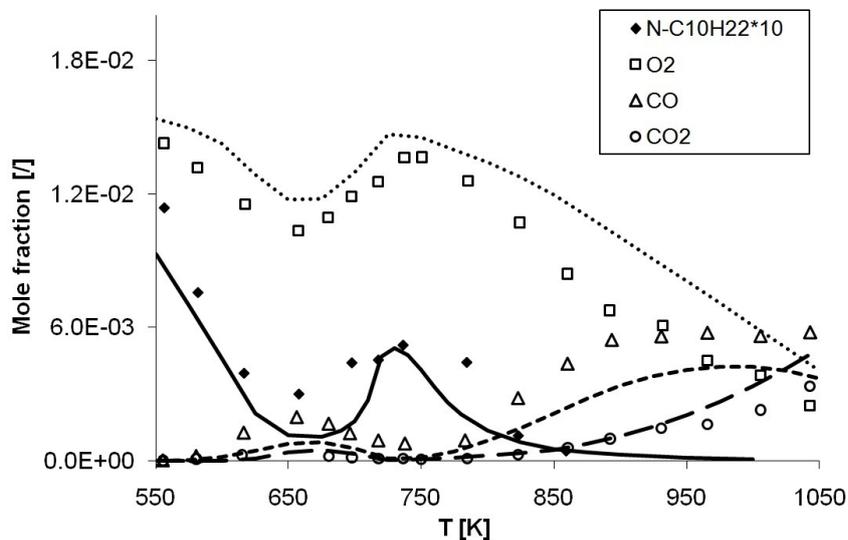

Figure 1: Concentrations of n-Decane, O_2, CO and CO_2 in a Jet Stirred Reactor at p=10 bar, ϕ=1.0, 0.1% fuel and τ=1 sec [10].
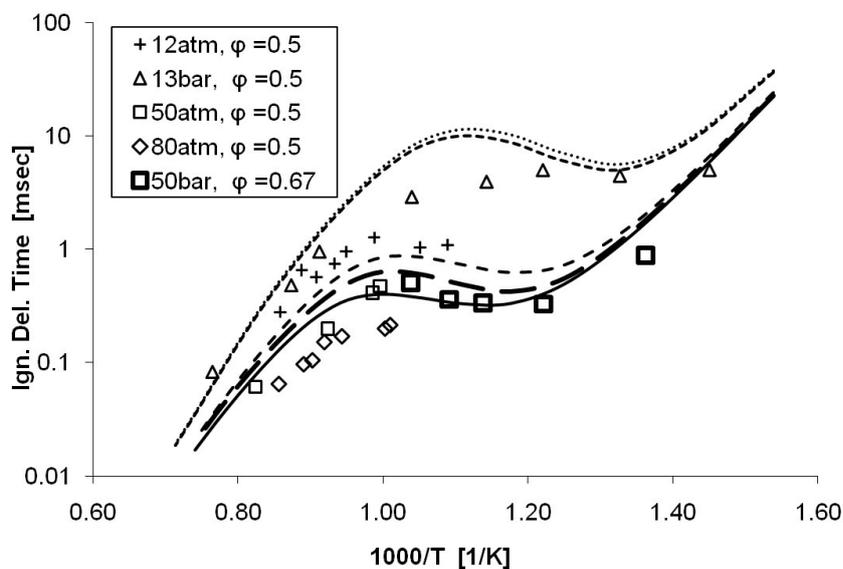

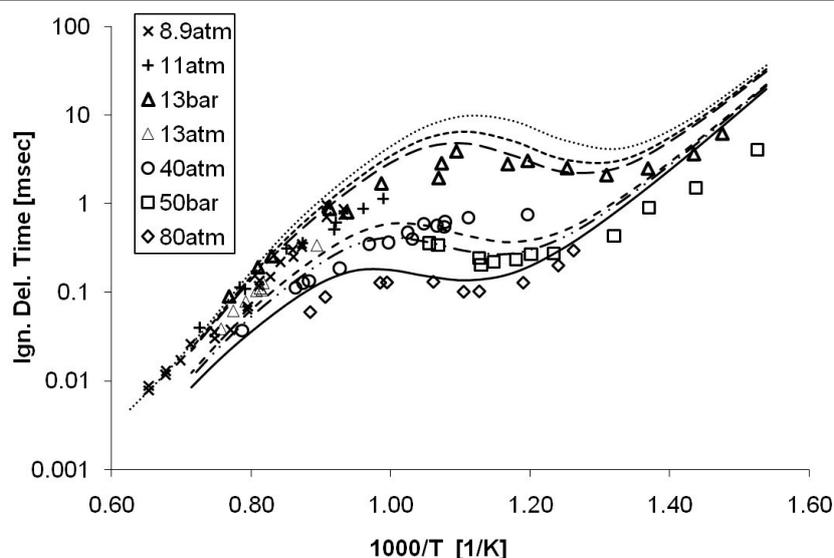Figure 2: Ignition delay time for n-decane/air mixture at 12 atm, 50 atm [7] , 13 bar, 50 bar [6], 80 atm [8]

Figure 3: Ignition delay time for n-decane/air mixture at ϕ=1.0, p = 8.9 atm [9], 11 atm, 40 atm [7], 13 bar, 50 bar [6], 13 atm, 80 atm [8].
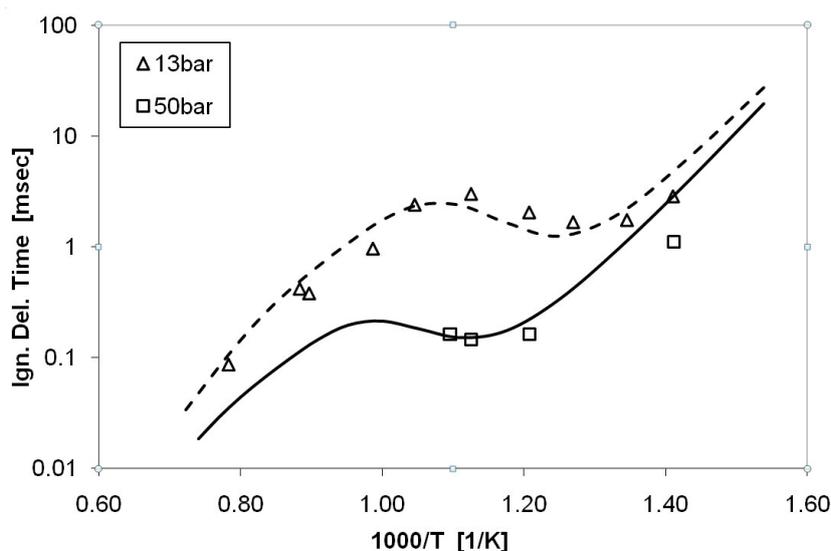

Figure 4: Ignition delay time for n-decane/air mixture at ϕ=2.0, p=13 bar, 50 bar [6].

2 Conclusions

This paper discusses the application of a new mechanism generator which is based on the object oriented data base CouchDB. This system allows efficient development of reaction mechanisms since it provides additional information, like reaction class sensitivity. The system is self-expanding, by adding newly defined species structures into the database of each defined working group. The generator has been trained by our prior work on n-heptane, based on the generation rules by Curran et al. . It was applied on n-decane, and the generated reaction mechanism was verified with JSR and shock tube experiments. In general the accuracy of the generated mechanism is comparable with the accuracy of the original mechanism for n-heptane. The provided reaction class sensitivity explains differences between
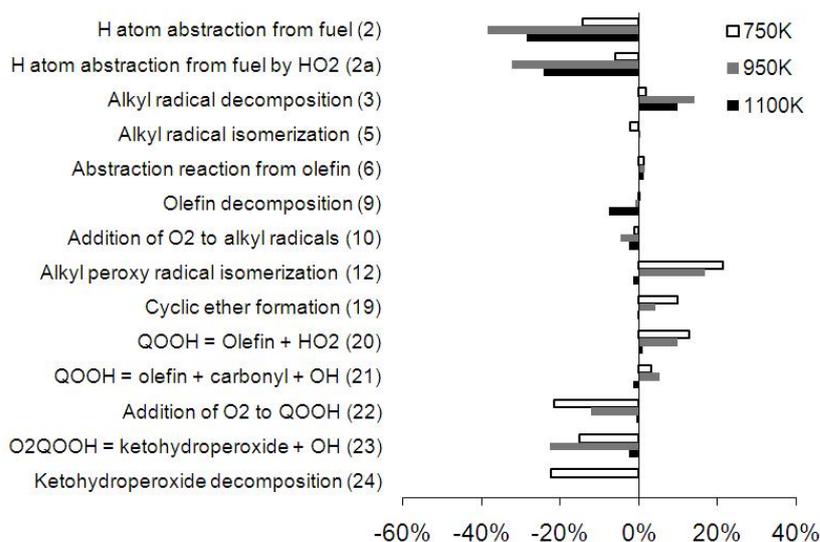
Figure 5: Sensitivity coefficients for ignition delay times for n-decane/air mixtures at three different temperatures (ϕ =1.0, p = 13.5bar).
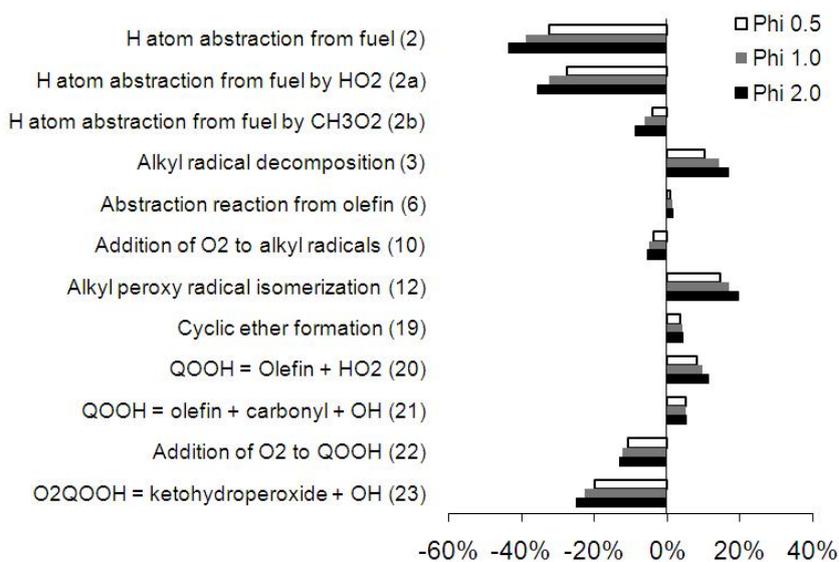
Figure 6: Sensitivity coefficients for ignition delay times for n-decane/air mixture at three different fuel air equivalence ratios (p = 13.5bar, T = 950K).

simulations and experiments at low temperature by too high rate coefficients for reaction class 24 (Ketohydroperoxide decomposition). Compared to our prior work the agreement of the model predictions with shock tube experiments has been improved. This can be explained by the improved n-heptane mechanism in reference [1]. We further demonstrate that the temperature dependence of species profiles in JSR experiments is well predicted.

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