# AUTOMATIC GENERATION OF A DETAILED MECHANISM FOR THE OXIDATION OF *n*-DECANE

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## Introduction

Practical fuels such as gasoline, diesel or kerosene are complex mixtures of different hydrocarbons. To best predict the behavior of such fuels in combustion systems, it is important to develop and validate suitable detailed oxidation mechanisms. The mechanisms used to describe the oxidation of such practical fuel contain several hydrocarbons such as high linear alkanes (*n*-decane, dodecane). To build such comprehensive chemical models manually can be very difficult and the use of an automatic generator of mechanisms is almost a prerequisite.

In the present work a detailed mechanism for the oxidation of *n*-decane of 485 species and 3684 reactions has been built automatically by using the REACTION mechanism generator [1]. This mechanism has been validated against a wide range of experimental data including ignition delay times.

#### *n*-Decane oxidation mechanisms

Few kinetic modeling studies describing the *n*-decane oxidation are available in the literature. Dagaut et al. [2] have developed a detailed mechanism for the oxidation of *n*-decane in a jet stirred reactor at atmospheric pressure, from 550 to 1150 K and for a range of equivalence ratios from 0.1 to 1.5. The global reactivity of this mechanism is quite satisfactory. Nevertheless, the model is not able to simulate the consumption profiles of some 1-alkenes from C<sub>5</sub> to C<sub>8</sub>. The model is in good agreement with experimental data obtained in jet stirred reactor especially at high temperatures (>800K). The semi-detailed mechanism developed by Bikas and Peters [3] contains about 600 reactions with 67 species. This model includes a detailed C<sub>4</sub> chemistry. In addition H-abstraction, decomposition, simple 1-alkene chemistry for the  $C_6$ - $C_7$  and  $C_{10}$  and a lumped C<sub>10</sub> low temperature chemistry are included. The validation has been performed against experimental data obtained on a stabilized premixed flame, shock tube, jet stirred reactor and propagating premixed flame. The transition between low and high temperatures is well reproduced. Glaude et al. [4, 5] and Battin-Leclerc et al. [6] have generated automatically a detailed mechanism of 7920 reactions and 1216 species. The validation of this mechanism against experimental data obtained in jet stirred reactor at high temperatures (922-1033 K) at atmospheric pressure shows a good agreement. Semi-detailed mechanisms for the combustion and pyrolysis of different hydrocarbons in a wide range of operating conditions have been generated by Ranzi et al. [7].

In this study, we have generated automatically a detailed *n*-decane mechanism. It includes all the low and high temperature chemistry outlined by the reaction classes from Curran et al. [8, 9]. It nevertheless has a reasonable size of 485 species and 3684 reactions.

#### Chemical model

The key to the building of the *n*-decane mechanism was doing it automatically using the REACTION [1] tool. The goal of this tool is to simulate the techniques used for building mechanisms by hand. It is, in essence, a formalization of the procedures used to generate and manipulate all objects associated with mechanism development. The fundamental concept in generating mechanisms is the reaction class. Reaction classes are founded on the basic principle that reactivity of a species is based solely on the structural features immediately around the reaction center. Whenever these structures are found in reactant species, products can be generated.

The key to avoiding the combinatorial explosion of generated reactions and species is the definition of reactive pathways, sequences of reaction classes. From a 'seed' species and the first set of reaction classes in the sequence a set of reactions producing a set of product species is generated. However, only the generated products are used in the next step in the sequence. This continues through the entire sequence generating a sub-mechanism representing a given reactive pathway. A complete mechanism is defined by merging a complete set of these sub-mechanisms.

The reaction class definitions within REACTION allow for a wide variety of bonding (single, double and triple), valence (including radicals, resonance and aromatic atoms), branched structures (primary, secondary and tertiary centers) and cyclic structures. For example, the entire set of chemistry defined by the twenty-five Curran et al. reactive types has been described with the REACTION reaction classes.

All the detailed mechanisms for the oxidation of alkanes consist of two parts, a validated base sub-mechanism, produced manually and a generated sub-mechanism. In this study, the base mechanism consisted of a validated  $C_1$ - $C_4$  mechanism [10]. The  $C_5$ - $C_{10}$  sub-mechanism has been generated. The 25 oxidation rules defined by Curran et al. [8, 9] for the oxidation of *n*-alkanes were translated into reaction classes used by REACTION [11]. In addition, to deal with the products of the 25 reaction classes, an additional set of classes were defined for the oxidation of alkenes, aldehydes and ketones [12]. In the *n*-decane mechanism, all reaction classes are used for the  $C_7$  and  $C_{10}$  chemistry. Extensive high temperature and alkene oxidation chemistry has been generated for all  $C_5$  through  $C_{10}$  mechanisms.

#### Validation of the mechanism

Simulations were performed by using the Ignition code developed in the kinetics group from Lund [13]. Perfectly stirred reactor, plug-flow reactor as well as a shock tube experiments can be simulated using this code.

All the calculations presented in this article have been obtained with the same oxidation mechanism. No specific changes have been done in the mechanism to match the experimental data. The generation of the mechanisms for the oxidation of n-decane and lower alkane, such as n-heptane has been performed by using the same set of parameters for the low and high chemistry.

Pfahl et al. [14] have studied the autoignition of *n*-decane in shock tube experiments at 13 and 50 bar and for fuel/oxygen equivalence ratios from 0.5 to 2.0. We have used the *n*-decane mechanism in the Ignition code [13] assuming a constant-volume and homogeneous adiabatic conditions behind the reflected shock wave to reproduce the experiments from Pfahl et al. [14].

Figures 1 and 2 display the comparisons between the ignition delay times for the oxidation of *n*-decane respectively at 13 and 50 bar from experimental data [14] and the calculated values.



**Fig. 1** Ignition delay times for the oxidation of *n*-decane,  $\Phi=1$  at  $13 \pm 1.5$  bar. Shock tube experimental data from Pfahl et al.[14] (symbols). Calculations (line)



**Fig. 2** Ignition delay times for the oxidation of *n*-decane,  $\Phi=1$  at  $50 \pm 3$  bar. Shock tube experimental data from Pfahl et al.[14] (symbols). Calculations (line)

Though we obtained a good prediction of the ignition delay times for the oxidation of n-decane at 13 bar (Fig. 1), the calculations showed a slightly over-estimation of the delays at 50 bar for the low and intermediates temperatures (Fig. 2). Some of the reaction classes included in the mechanism are really sensitive in this range of temperatures at quite high pressure. The sensitivity analysis as well as other validations of the n-decane mechanism will be described in details in this work.

### Conclusion

A detailed mechanism for the oxidation of *n*-decane has been generated by using our automatic mechanism generator (REACTION). This mechanism has a reasonable size, 485 species and 3684 reactions, but nevertheless it has an extensive range of chemistry. The model

shows a good prediction of the ignition delay times for the oxidation of n-decane at 13 and 50 bar.

A validated *n*-decane oxidation mechanism has been produced using the reaction classes of a smaller hydrocarbon and a given base mechanism. For this reason the same set of reaction classes and the same base mechanism can be used to generate oxidation schemes for larger hydrocarbons, such as *n*-dodecane and *n*-tetradecane. In addition, reaction classes for branched species, cyclics and aromatics have been defined and can be used to produce oxidation mechanisms for further families of chemical species to describe the combustion of practical fuels.

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