Kinetic model for surrogate diesel fuel comprising n-decane and α -methylnaphthalene

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1 Introduction

Conventional fuels are composed of a large variety of species; therefore surrogates are formulated to represent multi-component fuel blends by a limited number of species. The blend of 70% *n*-decane and 30% α -methylnaphthalene (mol percentage) was defined by the Integrated Diesel European Action (IDEA) program [1] as Diesel surrogate. Chemical mechanisms for this Diesel surrogate fuel have been formulated and validated by a number of experiments.

The autoignition of suspended liquid *n*-decane/ α -methylnaphthalene droplets was studied by Moriue et al. (2000) [2] in a pressurized combustion chamber at a pressure p = 3 bar and temperatures T = 600–750 K. The authors reported raised induction times with increased aromatic content. The chain breaking effect of α -methylnaphthalene reduces the reactivity of *n*-decane in the gas phase.

Ramirez et al. (2010) [3] measured species concentrations in a jet-stirred reactor at T = 560-1030 K, p = 6-10 atm, fuel air equivalence ratios $\varphi = 0.25-1.5$ and 1.03 % of carbon. They compared data gained from commercial Diesel fuel, with data resulting from the oxidation of IDEA surrogate fuel and proved the quality of this simple formulation.

The auto-ignition of *n*-decane/ α -methylnaphthalene in air with $\varphi = 1.0$ at p = 14-62 bar, and T = 848–1349 K was studied by Wang et al. (2010) [4]. These experiments were

simulated by the help of a detailed reaction mechanism with 662 species, 3864 reactions and major oxidation pathway have been elaborated.

The IDEA surrogate fuel was employed for the simulation of Diesel and HCCI engines by several authors, including Pitsch and Peters [5], Barths et al. [6] and Bounaceur et al. [7].

Haylett et al. [8] investigated alkanes of different chain lengths as surrogate for DF-2 diesel/ oxygen/ argon mixtures. Ignition delay times of the Diesel blend were measured in an aerosol shock tube at p=2.3–8 atm and φ =0.3–1.35 and T=900–1300 K. Haylett et al. added in their publication a specialized flow reactor experiment all with fully evaporated flows at p = 3-5 atm, φ = 0.2-1 from TeVelde and Spadaccini [9]. They simulated these experiments with different single component surrogate fuel models, i.e. propane-, *n*-heptane, *n*-dodecane and *n*-hexadodecane, using detailed reaction mechanisms from different authors. It was concluded that n-dodecane serves best as single component surrogate fuel.

Penzyakov et al. [10] investigated ignition times for Diesel/Air mixtures in shock tubes at pressures 4.7-10.4 atm and T=1065-1838 K and φ =0.5–2.

Synthetic Diesel fuel was studied by Dagaut et al. [11] in a jet stirred reactor (JSR) at p = 1-10 atm, T = 800-1400 K and $\varphi = 0.5-2.0$. This blend was modelled by a complex surrogate fuel blend consisting of *n*-hexadecane (36.1% by weight), *n*-propylcyclohexane (23.1% w), *n*-propylbenzene (18.7% w), iso-octane (14.7% w), and α -methylnaphthalene (7.4% w). A detailed reaction mechanism for this blend was presented, which could reproduce the experiments with high accuracy.

In this work, we present a detailed reaction mechanism for the IDEA Diesel surrogate fuel. The sub-mechanisms of *n*-decane and α -methylnaphthalene are comprehensively validated and the blend is also validated with available experiments.

2 Mechanism compilation

The reaction mechanism for the IDEA surrogate fuel consists of three submechanisms: 1) The base mechanism for smaller hydrocarbons described in an extended version (addition of alcoholic species) of the hand compiled mechanism by Hoyermann et al. [12], 2) the skeletal mechanism for *n*-decane, and 3) the detailed mechanism for α methylnapthalene. Each sub-mechanism has been validated individually, and perform with high accuracy for the available experiments. We are working with a modular mechanism structure, and do not include any fuel-fuel interaction reactions.

n-decane mechanism

The skeletal mechanism for *n*-decane includes both high and low temperature reactions, and was developed from an automatic generated reaction mechanism. The reaction rules follow the ones defined by Curran et al. for n-heptane. The rate coefficients are optimized and consistent with the coefficients used for n-heptane by Ahmed et al. [13]. The mechanism reduction was performed by the means of the Chemistry Guided Reduction (CGR) introduced in [14]. The resulting skeleton mechanism consists of 95 species and 480 reactions.

α -methylnaphthalene mechanism

The reaction mechanism for α -methylnapthalene is based on the reaction rules developed for toluene, which is part of our base mechanism by Oßwald at al. [15]. Since the validated model for toluene is part of the base chemistry the sub-mechanism for α -methylnapthalene consists of only 16 species and 122 reactions. The complete model for the Diesel surrogate fuel is composed of 328 species and 2004 reactions.

3 Validation and Analysis

The Diesel surrogate fuel model has been validated for experiments with both, the IDEA surrogate and commercial Diesel fuels.

Ignition delay times

Simulations have been performed for two different blends (30/70) and (70/30) mole percentage of α -methylnaphthalene and *n*-decane at $\varphi = 1.0$ and p = 10 bar and p = 40 bar using DARS [16] as shown in Fig. 1. Simulations agree well with the experiments at high temperatures for both pressures and mixtures. However the model predicts a higher sensitivity of the fuel blend on the ignition delay time in the NTC region. The possible reason for this could be a missing interaction of the fuel molecules in the modular fuel model. Ignition delay times for both pure n-decane and α -methylnaphtalene are very well predicted by the fuel model.



Fig. 1: Ignition delay time for *n*-decane and α-methylnaphthalene blends in comparison with pure fuels at a) 10 bar and b) 40 bar. Experimental data are shown as symbols: ● pure n-decane, 13bar and 50bar [16], ■ α-methylnaphthalene [4] ◆ 30/70 blend [4], □70/30 blend [4], and simulations as lines.



Fig. 2: Ignition delay time for Diesel in O_2/Ar at $\varphi = 0.5$ and p = 6 atm.

Figure 2 shows the comparison of simulation with the IDEA mixture and experiments [8], [9], [10] for the high and low temperature range of ignition delay times for a Diesel fuel. The model predicts the measured ignition delay times well, however the IDEA mixture was developed for European diesel and can not represent the variety of diesel fuels in all aspects.

Jet Stirred Reactor

Figure 3 shows the calculation of major species concentrations in JSR experiments at 10 atm [3] for the surrogate fuel blend at residence times $\tau = 1$ sec. The model predicts the species profiles for the main species *n*-decane, α -methylnaphthalene, CO, CO₂ and H₂O well at high, intermediate and low temperatures. The comparison indicates a slightly too low reactivity of n-decane in the NTC region. This is in contrast to the agreement of predictions with shock tube experiments. The JSR experiment indicates no sensitive fuel interaction reactions. Further research is needed to also increase the available experimental data base for surrogate fuel blends.



Fig. 3: IDEA surrogate Diesel fuel oxidation in a JSR at p = 10 atm, $\varphi = 1.0$ and $\tau = 1$ s. Experimental data are shown as symbols and simulations as lines.

4 Conclusions

In this work we present a reaction mechanism which compromises the existing experimental data base. The reaction mechanism was developed for *n*-decane and α -methylnaphthalene and shows a good agreement with experiments for pure fuels and for the IDEA mixture. Simulations show a stronger sensitivity of the temperature in the NTC region,

when compared to experiments. However the agreement is very good for JSR experiments in the same temperature window. We conclude that the experimental data base needs to be extended to allow conclusive mechanism development.

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