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A global combustion model for simulation of *n*-heptane and iso-octane self ignition

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HIGHLIGHTS

- ▶ Development of a global model for gasoline fuel combustion simulation.
- ▶ Simulation of self ignition of iso-octane and *n*-heptane surrogates.
- ▶ Ignition delay time and species histories validation.
- ▶ Simulation of HCCI engines.

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ABSTRACT

For CFD-simulations, superposed with combustion phenomena, simplified reaction models are needed to reduce calculation times. In the present study, a global kinetic model for gasoline fuels was developed, whereby the focus was on the simulation of self ignition and estimation of main off-gas components (CO_2, H_2O, CO and H_2). The developed reaction system, consisting of 18 species (8 molecules, 10 species classes) and 19 mostly global reactions was validated for $T = 600–1250$ K and for $p = 13–40$ bars for equivalence ratios of $\Phi = 0.5$ to $\Phi = 2$ for combustion simulation of iso-octane, *n*-heptane and mixtures of both. Simulated ignition delay times were compared to shock-tube data and validated by a detailed combustion mechanism; these were then compared to approved reduced mechanisms. Species histories of different ideal reactor simulations were compared to literature data and detailed simulation results.

1. Introduction

Chemical kinetic mechanisms for simulation of iso-octane and *n*-heptane mixtures have been developed by different research groups. The requirements on a combustion mechanism can on the one hand be to describe the chemistry in a detailed way and on the other hand to be an application oriented kinetic model. For scientific research, each chemical step proceeding during combustion is of interest, but the so obtained detailed models are too large to be implemented to CFD-applications. Therefore, it is possible to reduce the detailed mechanisms to obtain less detailed systems which are suitable for CFD-simulations, yet are still accurate for application.

Curran et al. [1] developed a detailed combustion mechanism for primary reference fuels; this very extensive kinetic description is able to describe the *n*-heptane and iso-octane mixtures combustion. Detailed and semi detailed mechanisms for combustion of *n*-heptane, iso-octane and mixtures of both, have been developed by [2–7]. These kinetic models are interesting from the combustion scientific point of view, but are numerically too expensive for applications. Reduced combustion mechanisms have been developed by [3,8–22], in which the focus during the reduction process was on achieving a mechanism usable for CFD-simulation applications.

Different systematic strategies of mechanism reduction from a detailed to a reduced model are described in [10,23–27]. The methods for mechanism simplification and saving computational costs for simulations can be classified in the following way: dimensions reduction, reduction of detailed diffusion and chemical stiffness removal [25]. Only the first method yields to a reduction of the species and reactions in the combustion model. Different techniques have been developed for reduction of the number of species of combustion mechanisms. The direct relation graph method (DRG) is based on the fact that some species are strongly coupled to a few major species [25]; this knowledge makes it possible to exclude those species that are of minor influence to the combustion mechanism. Using DRG for mechanism reduction does not yield a minimal number of species. Therefore, optimized methods based on DRG have been developed which show more powerful error-propagation analyses, whereby the computational costs are higher compared to the DRG (e.g. DRGEP and DRGADSA [25]). These

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Nomenclature

CFD	computational fluid dynamics
DRG	direct relation graph method
DRGASA	direct relation graph-aided sensitivity analysis
DRGEP	error-propagation based direct relation graph method
EF	element flux analysis
HCCI	homogeneous charge compression ignition
I0-1/I0-2/I100-1/I100-2	chain branching products of *n*-heptane/iso-octane
JSR	jet stirred reactor
max	maximum
NTC	negative temperature coefficient of ignition delay times
PFR	plug flow reactor
PRF	primary reference fuel
PRF0/PRF100	*n*-heptane/iso-octane
QSSA	quasi-steady-state assumption
R-1/R-100	initiation product of *n*-heptane/iso-octane
RO0-1/RO100-1	oxygenated reaction inition product of *n*-heptane/iso-octane
RO0-2/RO100-2	product of internal oxygen abstraction of *n*-heptane/iso-octane
0	index, starting conditions
Φ	equivalence ratio

optimized tools are able to derive higher grades of mechanism reduction; however, DRG is commonly used as a first-step tool for mechanism simplification. The element-flux analysis (EF) [26] calculates the atomic fluxes (C, H, N, O, etc.) between sources and sinks. Sink-source pairs showing a flux lower than a user defined cut-off are neglected, while pairs above this value are implemented in a reduced mechanism. Advantages of this approach are low computational costs and the possibility for application to on-the-fly reduction [27], although a major shortcoming is the definition of the user defined cut-off value. By configuring this value the complexity of the reduced mechanism is defined; experienced knowledge on the combustion system is necessary for defining this limit. A widely used method for mechanism simplification is the time-scale analysis which yields knowledge about steady-state species which can be applied for mechanism simplification (e.g. QSSA [26]). More techniques for systematic mechanism analysis and reduction such as the sensitivity- and Jacobian-analysis and others are mentioned in [10,24–28].

Peters et al. [8,9] developed different reduced chemical-kinetic mechanisms for *n*-heptane; the simplification was achieved by fundamental analysis of the proceeding combustion chemistry and by applying approved techniques such as steady-state assumptions. The mechanism published in [8] consists of 27 species (Peters 27), the one described in [9] includes 17 species (Peters 17) and 14 partly global reactions with user defined kinetic descriptions (number of species for [8] and [9] including N_2). In [19], Ra and Reitz published a kinetic model for gasoline PRF-fuels, whereby the mechanism was developed by combining reduced *n*-heptane and iso-octane kinetics. The model was then optimized further by updating and tuning rate parameters.

In cases of very complex simulations, even further reduction is advisable; therefore even global reaction sets have been developed [29–34]. For global kinetic models a different method for mechanism development than the systematic reduction is sometimes applied, known as "ad hoc-reduction" [8,32]. The knowledge of the major ignition steps is used to define a set of global reactions, commonly based on species classes instead of real species. Due to the high grade of investigations on gasoline fuels, these basic steps are well known and can be sourced from literature; however, the challenge is to select accurate descriptions of species–classes and global reactions and of course to provide a useful kinetic description. For kinetic models developed by the "ad hoc method" extensive analysis and validation is of importance to confirm the suitability of the designed reactions.

In [32,34], models for fitting ignition delay times are published, without calculating species distribution. Zheng et al. investigated global mechanisms by using species classes instead of single species [30,31]. These kinetic descriptions are able to simulate the time dependent formation of some major species and the ignition delay times of a fixed gasoline surrogate mixture. Global combustion mechanisms are designed for special investigation cases and of course compromises between levels of detail (which extends simulation times) and accuracy of experimental data are unavoidable.

Within the present work, a global combustion model for simulation of self ignition was developed.

The present kinetic model is based on the chemical descriptions of [31,34]; the advantage of these models is, on the one hand, the description of the kinetic parameters in the Chemkin® – format [35] (standard format, not user defined). On the other hand, the present model is able to calculate ignition delay and species histories of the off-gas products (CO_2, H_2O, CO, H_2) for varying gasoline mixtures (varying *n*-heptane + iso-octane), using the same set of kinetic parameters.

2. Mechanism specification

A combustion mechanism for mixtures of *n*-heptane and iso-octane was designed for simulation of numerically extensive cases, while this mechanism should satisfy the following specifications:

- Global Combustion mechanism for variable iso-octane and *n*-heptane mixtures in Chemkin® – format [35], 50 or fewer species.
- Rate parameter adaption for ignition delay time simulations
- Validation of off-gas -temperatures, -pressure and -molar-fractions of the main off-gas species (CO_2, H_2O, CO, H_2)
- Simulation of varying PRF-mixtures by using the same set of kinetic parameters, contrary to [31] and [34] where mixture dependent kinetics are used.

To develop reaction kinetic models for combination with CFD-cases the focus is on including the most significant reaction steps only and designing the kinetic description for an actual simulation case to be as simple as possible. The problem dimensions of the simulation that the present mechanism is created for are: challenging flow phenomena such as multiphase flow, supersonic flow and shock waves combined with combustion chemistry. The fluid-flow case on its own is numerically challenging (a very dense grid is needed and an optimized solver for shock-waves), furthermore a certain number of simulations using varying starting parameters are necessary. Therefore, the intention was to develop a highly reduced combustion model (global model) to minimize simulation times, which is usable for CFD-simulations in which self-ignition is important.

3. Global mechanism development

The global chemical reactions described are sourced from [31,34]; the kinetic parameters were fitted to enable the