DEVELOPMENT OF A MECHANISM FOR DUAL FUEL COMBUSTION

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Abstract
The pollutant emission limit requirements for marine engines and engines used in heavy-duty vehicles like railways and trucks, becoming stricter and more difficult to meet. The operation of engines in dual fuel mode, using the fuels natural gas and diesel, offers the possibility to significantly reduce pollutant emissions. In the development process of a new engine, simulation tools can reduce the required engine test bench time and therefore lower the total development costs. The reaction mechanism used for the simulation must therefore be able to correctly describe both the combustion of natural gas and diesel. In this study, n-heptane was chosen as diesel surrogate, a mixture of methane and propane considered natural gas. As basic mechanism, the Complete San Diego Mechanism with the heptane and nitrogen chemistry add-on was used. In order to reduce the deviation between the simulation results and the experimental values, an optimization of the reaction mechanism was performed. With a sensitivity analysis, influential reactions were identified and adapted by adjusting the Arrhenius parameters to improve the prediction accuracy of the simulation.

Introduction
In the transport sector, whether on land or on water, engines with a self-ignition concept play the dominant role due to their proven economy, rugged durability and reliability [1]. However, compared to gasoline engines, the increased emission of nitric oxides is one of the major drawbacks of diesel engines. In the case of operating the engine with heavy oil, a high proportion of sulfur compounds is additionally added to the exhaust gas. Due to the more stringent environmental directives such as Eurocode 5 and 6 for motor vehicles in Europe or the Tier II and III standards for maritime large engines, more sophisticated engine concepts are needed, or additional technologies such as selective catalytic reduction have to be applied to meet the limits. An approach to reduce the emission of pollutants from self-igniting engines is the operation in the dual fuel mode. Here, a gas-air mixture is directed into the combustion chamber and ignited by the injection of a diesel pilot jet. Compared to a conventional diesel engine, the NOx and SOx fraction can be reduced significantly [2]. To further optimize the efficiency of the engine and to keep the

emission of pollutants as low as possible, it is highly necessary to know and understand the processes in the combustion chamber precisely. Since the experimental investigation on an engine test stand is associated with high costs and a high time expenditure, it is desirable to develop a theoretical model for the simulation of the dual fuel combustion processes. Due to the injection of a diesel jet into a gas-air mixture in the dual fuel combustion process, the simulation tool must be able to accurately reflect the ignition and combustion kinetics in the diesel-poor as well as diesel-rich ranges. Furthermore, the knocking behavior must be correctly predicted. Diesel fuel is a complex mixture of thousands of hydrocarbon compounds with carbon numbers between 6 and 28 [3]. A consideration of every species would lead to an unmanageable calculation time. To ensure calculability, n-heptane was used as diesel surrogate in this study. The second fuel, natural gas, was substituted by a mixture of methane and propane.

Basic reaction mechanism
The basic mechanism is composed of the Complete San Diego Mechanism and the heptane and nitrogen chemistry add-on [4]. In order to assess the predictive accuracy of the mechanism, experimental data for gas mixtures, as well as gas-n-heptane mixtures were used for validation. Pachler et al. [5] investigated the ignition delay time of methane-propane mixtures with the composition 100 mol% methane and 0 mol% propane, 95 mol% methane and 5 mol% propane and 70 mol% methane and 30 mol% propane at a pressure of 100 bar and a λ-value of 1.9. In the study of Herzler et al. [6], the ignition behavior of a methane-n-heptane mixture with 95 mol% methane and 5 mol% n-heptane at a pressure of 30 bar and a λ-value of 0.5 was investigated. Figure 1 shows a comparison between experimental data, measured with a rapid compression machine and a shock tube, and the ignition delay time calculated with the basic mechanism. All simulations have been performed with the software LOGEresearch v1.10 [7]. The ignition delay time for pure methane is reproduced well by the mechanism in its basic configuration. Increasing the amount of propane leads to a reduction of the ignition delay time. As can be seen, the reducing effect of the propane addition [8] is overestimated, leading to a significant deviation between the experimental and calculated results for a mixture of 70 mol% methane and 30 mol% propane. In the case of the methane-n-heptane mixture, basically, a good approximation of the simulation results to the experimental data is already evident. However, for a temperature lower than 900 K and higher than 1100 K, the ignition delay time is underestimated. At around 1050 K, the calculated ignition delay time is too long.

Reaction selection
In order to determine the reactions, which have a significant influence on the ignition delay time, the individual reactions were investigated with respect to their sensitivity
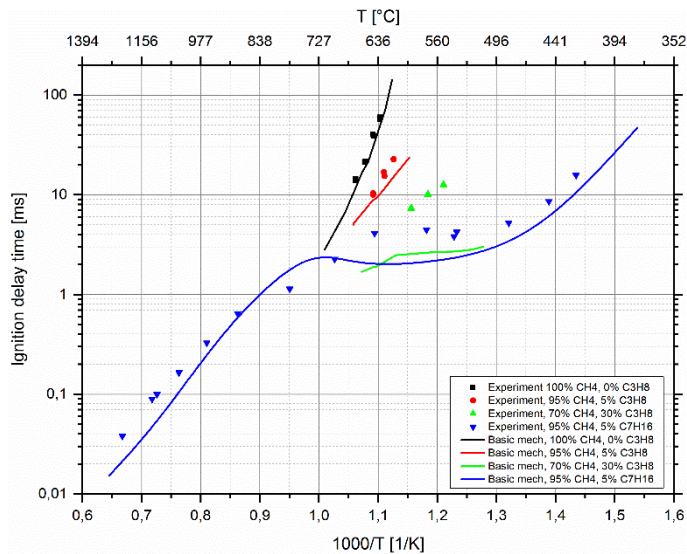
Figure 1. Measured and calculated ignition delay time of methane-propane mixtures with a mol% mixing ratio of 100 to 0, 95 to 5 and 70 to 30, as well as a methane-n-heptane mixture with a mol% mixing ratio of 95 to 5.

on the ignition process. Due to the fact, that the concentration of CH-radicals shows a sharp increase shortly before the ignition event as presented in Figure 2, they can be used as an ignition trigger. Therefore, the elementary reactions of the mechanism were investigated concerning their influence on the formation of CH-radical. Based on this analysis, 12 of 354 reactions have been selected for optimizing the mechanism.
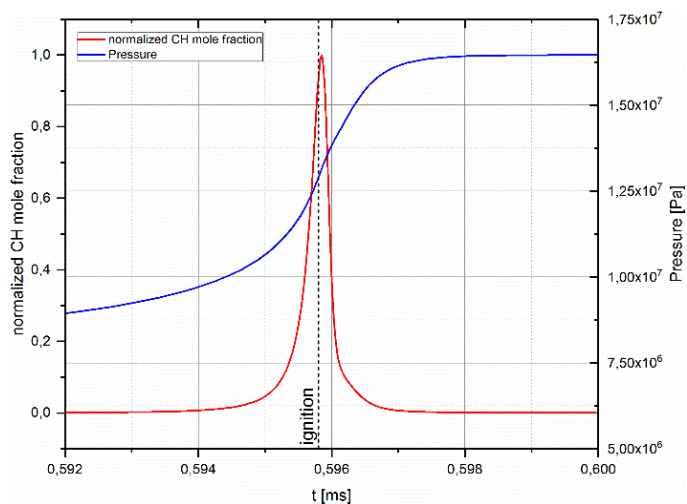

Figure 2. Normalized mole fraction of CH-radicals during the ignition process.

Reaction adaption

The reaction rate coefficients of the elementary reactions are calculated using the extended Arrhenius approach

$$k = A \cdot T^\beta \cdot e^{\frac{-E_A}{R \cdot T}} \tag{1}$$

with the frequency factor A, the temperature T, the temperature exponent β, the universal gas constant R and the activation energy E_A. By adapting the Arrhenius parameters of the 12 selected reactions, the mechanism was optimized. The adaptation of the reaction 233 will be described in the following exemplarily. The reaction and the associated Arrhenius parameters in the basic configuration are shown in Table 1.

Table 1. Arrhenius parameter overview of reaction 233 in its basic configuration.

Reaction 233	A [-]	β [-]	E_A [kJ/mol]
$C_3H_8 + OH \rightarrow nC_3H_7 + H_2O$	$1 \cdot 10^{10}$	1	6.69

The reaction 233 shows a significant influence on the mechanism's underestimating behavior on the ignition delay time when adding propane. The faster this reaction takes place, the shorter is the total ignition delay time. The adaptation of the reaction was carried out by a reduction of the reaction rate constant. The reduction was not uniform, but increased with decreasing temperature. Figure 3 shows the temperature-dependent reaction rate coefficient of reaction 233 in its basic and adapted configuration. The other 11 selected reactions were adjusted in the same or similar way.
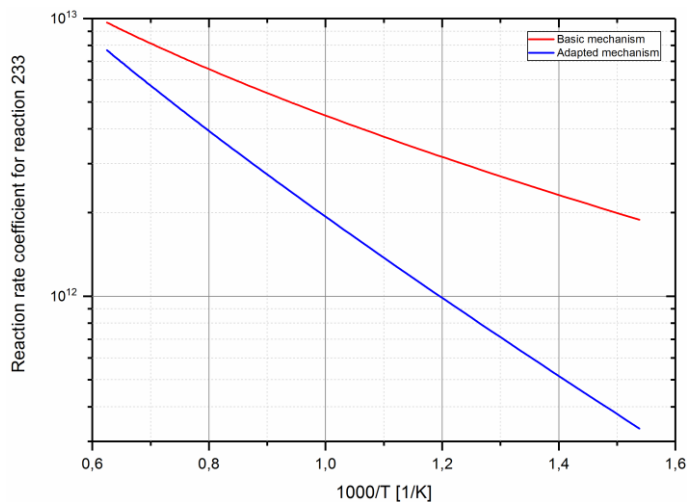

Figure 3. Temperature-dependent reaction rate coefficient of reaction 233.

Optimized mechanism

The impact of the mechanism adaptation is shown in Figure 4. In addition to the simulation result with the new mechanism and the experimental data, the simulation result of the basic mechanism is shown for comparative purposes.
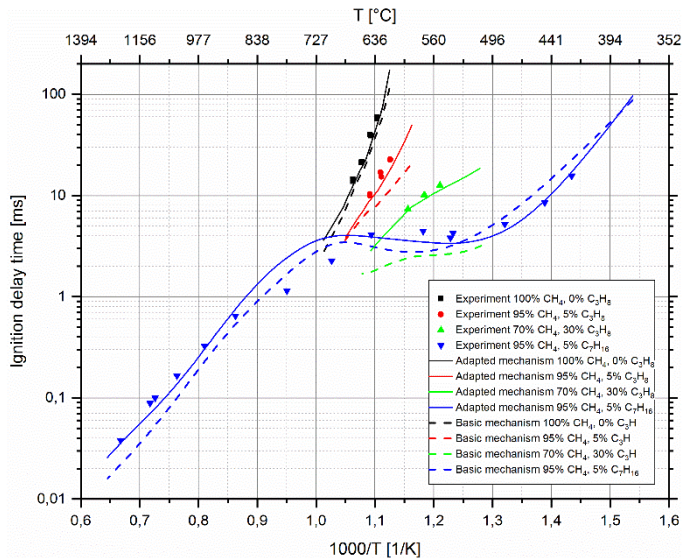

Figure 4. Comparison of experimental data and simulation results using the basic and adapted reaction mechanism.

As a result of the mechanism adaptation, the influence of propane addition on the ignition delay time is reproduced well. In the case of the methane-n-heptane mixture, a good approximation of the simulation results to the experimental values is evident both in the temperature range 700 to 900 K and in 1150 to 1500 K. In the temperature range 900 to 1050 K, an overestimation of the ignition delay time is obvious, where further adaption of the mechanism is necessary.

Conclusion

In this study, the optimization of a mechanism for simulation of a dual fuel combustion process is presented. The basic mechanism is composed of the Complete San Diego Mechanism with the heptane and nitrogen chemistry add-on. Comparison of the simulation results with experimental data from a rapid compression machine and a shock tube showed a wrong assessment of the propane influence on the ignition delay time. With a sensitivity analysis, reactions with a significant influence on the rate of the reaction process were identified and adapted by changing the corresponding Arrhenius parameter. With the optimized mechanism, the propane influence on the ignition delay time is reproduced well. For the methane-n-heptane mixture, the simulation shows a good approximation to the experimental values over a large temperature range. Between 900 to 1150 K, however, the ignition delay time

is still overestimated and indicates potential for further optimization.

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