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Reduction and validation of a chemical kinetic mechanism including necessity analysis and investigation of CH_4/C_3H_8 oxidation at pressures up to 120 bar using a rapid compression machine

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ABSTRACT

Cost efficiency and the ecological footprint are becoming more important in the locomotive and maritime business. To overcome these needs, manufacturers are forced to develop highly efficient internal combustion engines suitable for alternative fuel, such as biogas. In the development process of a new engine, simulation tools offer economic benefits compared to engine bench tests. To manage the trade-off between enhanced efficiency by increasing the compression ratio and knocking combustion, a reaction mechanism is necessary to capture the ignition behavior of various fuel blends and conditions during the simulation. Since previous studies only investigated methane/propane oxidation at pressures up to 50 bar, experimental investigations have been conducted to include pressure regimes, which are similar to those of a knocking combustion. Therefore, rapid compression machine (RCM) experiments were performed using methane/propane mixtures at lean conditions with air-to-fuel ratios of 1.5, 1.7 and 1.9. Furthermore a range of compression temperatures from 800 to 1000 K at pressures of 80, 100 and 120 bar were conducted. The experiments for mixtures containing 30 mol% propane showed a negative temperature coefficient (NTC) behavior, which is consistent with experiments for other alkane fuels presented in the literature. In addition, the experimental results were compared with the recently published detailed chemical mechanism Aramco Mech 1.3. This mechanism was used to simulate the ignition delay times with consideration of the facility effects of the rapid compression machine. The simulation results, based on a zero-dimensional homogeneous batch reactor showed good agreement with the measurements over a wide range of the investigated conditions. In a further step the detailed mechanism has been reduced by necessity analysis in order to minimize computational efforts for future combined CFD (Computational Fluid Dynamics) and kinetic simulations. The results of this novel work show the first set of high pressure screening experiments in a RCM for CH_4/C_3H_8 mixtures combined with a systematic method for mechanism reduction.

1. Introduction

The rising demand for emission reduction, especially CO_2 and NO_X will lead to a further decrease of emission limits e.g. EURO 6 or IMO Tier III. Therefore, the complexity of conventional internal combustion engines will increase in order to meet these limits [1]. In so-called ECA regions (Emission Control Areas), such as coastal zones, limits for the sulfur content in the fuel and speed related nitric oxide emissions are required. Especially in the maritime or locomotive sector, fuel gases such as biogas are popular to be used due to the content of shorter hydrocarbons compared to heavy fuel oil (HFO) and the high knocking resistance. The advantage of a large gas engine with an extremely lean combustion is the lower raw emission with at the same time similar power outputs and thermal efficiencies comparable to a diesel engine [2,3]. Further, increase in combustion efficiency by e.g. higher compression ratios, increased charge pressure stands in the foreground of the developments, but is rather limited by knocking combustion [4,5]. The self-ignition behavior of fuel gas is strongly dominated by the mixture of its components like methane, propane as well as substantially amounts of inert gases [6]. The conventional procedures for optimizing large gas engines are engine bench tests, which are very resource consuming and expensive. Therefore, the demand for detailed numerical methods is increasing. The most common methods are 1D-modeling approaches to predict the load exchange and the burn rate. They are implemented with empirical

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knock models which are based on fuel properties such as the octane- or methane number in order to predict the knock limit [4,7]. To get deeper insight of knocking combustion, there is still a need for more detailed approaches to predict the knock behavior of different gas mixtures at lean conditions [8].

In this paper, the oxidation of methane–propane blends at very high pressures of up to 120 bar in a rapid compression machine was studied. While previous research [Table 1] investigated CH_4/C_3H_8 ignition at pressures only up to 50 bar, the range in this work included pressure regimes that are similar to those of a knocking combustion. Further, the generated data was used to compare with a detailed kinetic model.

To investigate and understand knocking combustion inside the engine cylinder, a transient CFD[1]-analysis has to be made, where for each time step the chemistry, the heat transfer and the turbulent mixing process has to be solved [9]. To reduce the computational complexity while at the same time retain good accuracy in predicting the ignition behavior, established methods such as sensitivity and flow analysis [10–13] have been used in this paper to reduce a detailed chemical mechanism.

2. Experimental

2.1. Rapid compression machine

A detailed description of the construction of rapid compression machine (RCM) used in this study can be found in Lee et al. [14]. The facility utilizes a creviced piston head to reduce the effect of roll up vortex by containing the boundary layer inside the crevice volume [15,16]. The RCM used for this study facilitates compression times of the order of less than 20 ms. The end of compression temperature can be varied using a moveable end wall which changes the compression ratio. This increases the flexibility and range of conditions achievable with one diluent gas. However, in the current study the diluent gas was varied to achieve the conditions in the test matrix. The reported experimental work on methane conducted in other RCM facilities have been in the operating ranges of 16 [17], 10 and 25 bar [18] and some studies have used the facility up to 80 bar. Table 1 shows a list of experimental work carried out in shock tubes and RCM's with relevance to the current study. To our knowledge, this is the first experimental work carried out for CH_4/C_3H_8 mixtures at pressures of 80, 100 and 120 bar in a RCM.

In this study, the auto ignition delay measurements were carried out for a defined test matrix which can be categorized into two sections. The first section involves the study of CH_4/C_3H_8 mixtures, at $\lambda = 1.9$ for varying pressures of 80, 100 and 120 bar for a temperature range of 825 –940 K. The second section comprises of the study of the mixtures for varying lambda at an end of compression pressure of 100 bar for a temperature range of 880–920 K. Table 2 shows a comprehensive overview of the test matrix.

The test gases used in the present study were supplied by Praxair and Westfalen with a high level of purity [CH_4, C_3H_8 – 99.99% and for diluent gases Ar – 99.996%, N_2 and O_2 – 99.999%]. The mixture is prepared in a stainless steel mixing vessel which is controlled by two different pressure gauges ranging from 0 to 500 mbar (Co. STS, ATM. 1st) and 0 to 10 bar (Co. STS, ATM. 1st). Both gauges show temperature compensated pressures with an uncertainty of 0.05% of full scale for temperatures below 125 °C ensuring good accuracy in the mixture composition. The initial temperature is measured using a several T type thermocouples mounted over the reaction chamber. The pressure in the reaction chamber during compression and any post compression event including ignition is measured using a dynamic pressure transducer (PCB 113B22). However, the non-reactive experiments were measured using two pressure transducers Kistler 6125C-U20 and PCB 113B22 in order to quantify the effect of heat shock [32]. The uncertainty of these pressure transducers are 0.07% of full scale and ±0.04% of full scale respectively. As the end of compression temperature influences the chemistry and ignition delay time, the uncertainties leading to its calculation is estimated. By taking into account uncertainties in initial temperature, initial pressure, change in air–fuel ratio and possible uncertainty in thermal data of species; the combined uncertainty of the measurements leads to a deviation of ±5 K in the end of compression temperature [33].

[1] Computational Fluid Dynamics.

Table 1
List of specific literature.

No	Condition	P (bar)	ϕ	Facility	Ref.
1	C_1–C_5 natural gas based mixtures	20	0.5	ST	[19]
2	C_3H_8 mixtures	21, 27, 37	0.5, 1.0, 2.0	RCM	[20]
3	CH_4/C_2H_6/C_3H_8 mixtures	13–21	0.625, 1.0	RCM	[21]
4	CH_4/C_2H_6 and CH_4/C_3H_8	16, 40	1	ST	[22]
5	CH_4/C_2H_6/C_3H_8 mixtures	1–50	0.5, 1.0, 2.0	ST/RCM	[23]
6	CH_4/C_3H_8 mixtures	10, 20, 30	0.3–3.0	ST/RCM	[24]
7	CH_4/C_3H_8 mixtures	5.3–31.4	0.5–3.0	ST	[25]
8	C_1–C_5 alkane mixtures	8–30	0.5, 1.0, 2.0	ST/RCM	[26]
9	C_1–C_4 mixtures	3–15	0.45–1.25	ST	[27]
10	CH_4 air mixtures	16–40	0.7–1.3	ST	[28]
11	CH_4/n-C_4H_{10} mixtures	10–30	0.32–2.31	ST/RCM	[29]
12	H_2/CH_4/CO mixtures	20–80	0.5	RCM	[30]
13	CH_4/H_2 mixtures	15–70	1	RCM	[31]

ST – Shock Tube; RCM – Rapid Compression Machine.

Table 2
Overview of the test matrix [P_c – end of compression pressure; T_c – end of compression temperature].

No	C_3H_8 (mol%)	lambda (–)	CO_2 (mol%)	T_c range (K)	P_c (bar)
1	0/5/30	1.9	0	825–940	80/100/120
2	5	1.9/1.5	0	880–920	100

The Fig. 1 shows the pressure trace for the condition of 100 bar end of compression, 850 K end of compression temperature with 5% propane at lean condition of $\lambda = 1.9$. Target end of compression temperature was achieved by varying the percentage of Argon in the diluent gas. It is important to mention that pre-ignition was observed in some of the conditions tested and were regarded as failed experiments. Pre-ignition is characterized by a gradual increase of pressure before main ignition resulting from a local ignition and flame propagation in contrast to a homogeneous ignition in the entire reactor.

The initial temperature T_i, initial pressure P_i along with the reactant composition and the experimentally measured compressed gas pressure P_c were used to calculate the end of compression temperature T_c in Gaseq. It employs the adiabatic compression/expansion routine and uses the temperature dependence of the ratio of specific heats, ɣ according to the equation

$$ln\left(\frac{P_c}{P_i}\right) = \int_{T_i}^{T_c} \frac{\gamma}{\gamma - 1}\frac{dT}{T}$$

while assuming frozen chemistry during compression.

3. Results and discussion

3.1. Rapid compression machine

Experiments on lean mixtures of methane were carried out at 80, 100 and 120 bar end of compression pressures P_c, for various targeted end of compression temperatures T_c based on the test