# Rapid compression machine (RCM) studies on the production of unsaturated hydrocarbons from methane

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# 1 Introduction

Methane (CH<sub>4</sub>), a main component of natural gas, is a cheap and widely available substance. Its current use in technical applications is dominated by its role as a fuel for combustion; currently, at least 65 % of methane are burned for heating, electric power generation and transportation purposes [7]. 35 % of natural gas are used in the industrial sector, where it is either burned for heating and power systems or used as feedstock to produce chemicals [7].

Some studies on the latter type of use, i.e., employing methane as a basis for producing other chemically and/or energetically more valuable substances, can be found in literature, though. For instance, Happel and Kramer [4] report high methane conversion in a tubular quartz reactor heated by an electric furnace. They found conversion rates up to nearly 100 % at a low pressure of 119 hPa. At a similar pressure, Holmen et al. [5] also reached methane conversion rates up to 90 % in an electrically heated graphite reactor. Fau et al. [1] give a survey on works in this field. Besides different types of flow reactors, there are also investigations in shock tubes, such as Agafonov [2] for kinetic modeling of soot formation. Chakraborty et al. [3] investigated the pyrolysis of n-heptane under typical engine conditions, for a pressure of p = 29.3 bar at a low temperature range from T = 793 - 953 K.

In this paper, we investigate the conversion of methane to other substances, notably unsaturated hydrocarbons, by pyrolysis under engine-like conditions in a raid compression expansion machine (RCEM). The RCEM allows to study the conversion process under similar conditions like in a motored piston engine, but with better controlled initial- and boundary conditions.

The aim of this study is to understand the formation and yield of higher valuable and energetic species that can be created in an internal combustion engine.

# 2 Experimental

The experiments have been performed in a rapid compression expansion machine (RCEM), described in detail in Werler et al. [8]; slight modifications of this setup have been performed, as described below.

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## 2.1 RCM Setup

The RCM is a cylinder-piston device in which a gas mixture can be compressed by pushing the piston into the cylinder. Additionally, after an adjustable hold time during which the piston is held fixed at TDC position, the piston can be pushed outwards again, thus causing a controlled rapid expansion. Figure 1 demonstrates this by showing an exemplary pressure and volume curve with the compression (between  $\tau \approx -50$  to 0 ms), the isochoric phase at TDC (hold time  $\tau \approx 130$  ms), and the subsequent expansion phase. The pressure drop during the hold time is caused by heat losses, while the pressure drop after  $\tau \approx 130$  ms is caused by the expansion.



The pre-compression pressure is measured by absolute pressure meter (MKS Baratron 121A), and

Figure 1: Sample pressure/volume curve of an RCEM process. End of compression is defined at time  $\tau \approx 0$ .

the initial temperature is measured by a type K thermocouple. The time-resolved pressure trace during compression, hold period and expansion is measured by a quartz pressure sensor (Kistler 6061B). The piston position is detected by a potentiometric position sensor (Burster type 8710). From the known initial volume, bore and timne-resolved piston position, the volume trace of the combustion chamber can be calculated. After an experiment, the chemical composition of the cooled-down gas mixture is analyzed by a micro gas chromatograph (Agilent 490 Micro GC equipped with following columns: PoraPLOT U, Molsieve 5A, CP-Sil 5 CB). The focus is set on the species  $C_2H_2$ ,  $C_2H_4$  and  $H_2$ .

## 2.2 RCM experiments

The thermodynamic properties of the compressed state can be varied by the initial values of temperature and pressure and/or the compression ratio. In a series of experiments, the compression pressure varies from  $p_C = 10.2 - 30.6$  bar and the compression temperature varies from  $T_C = 1370 - 1850$  K, respectively. The values of  $T_C$  are computed from the measured  $p_C$  and the pre-compression values of pressure and temperature using the isentropic relation between T and p [9–11]. Two different gas mixtures have been investigated. The mole fraction of CH<sub>4</sub> was adjusted to 1 and 5 mol-%, respectively. In both gas mixtures, 5 mol-% helium (He) by mole were added as a reference gas for the GC measurements. The remaining 94/90 mol-% were argon (Ar). The purity of these gases were: Ar ( $\geq$  99.996 Vol.-%), He ( $\geq$  99.996 Vol.-%) and CH<sub>4</sub> ( $\geq$  99.995 Vol.-%).

According to the computed compression temperature  $T_C$ , the input variables are initial pressure  $p_0$ , compression pressure  $p_C$  and initial temperature  $T_0$ . With the uncertainties of the employed measurement devices, the overall uncertainty is calculated by a numerical error propagation analysis. For each input variable, a Gaussian-shaped probability density functions (PDFs) is calculated. This results in a uncertainty of  $\pm 5$  K in compression temperature and  $\pm 200$  mbar for compression pressure with  $\pm 2$  standard deviation.

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## **2.3** Evaluation of the results

We define the conversion U of  $CH_4$  as the ratio of the masses of methane after (Index 1) and before (Index 0) reaction:

$$U = 1 - \left(\frac{m_1}{m_0}\right)_{CH_4} = 1 - \left(\frac{X_0}{X_1}\right)_{He} \left(\frac{X_1}{X_0}\right)_{CH_4}$$
(1)

Because the mass of He does not change during the course of reaction, the mass fraction can be expressed by mole fractions (variable X) of CH<sub>4</sub> and He, before and after reaction, respectively (eq.1). This conversion is done, since masses of species are not directly measurable, however, mole fractions are.

In a similar way, the yield Y of a target species S is defined as the ratio of the observed mass of this species and its maximally possible mass as given by atom balance. The maximally possible amount is calculated as the amount of substance of  $CH_4$  in the initial mixture and a species-dependent factor F. For instance, from one  $CH_4$  molecule, maximally two  $H_2$  molecules can be formed, so  $F_{H_2} = 2$ .

In eq. 2, Y is the yield, X is a mole fraction, indices 0, 1 denote the state before and after reaction, respectively. Index S is a wildcard for any product.

$$Y_S = \frac{m_{S,1}}{\max(m_S)} = \frac{n_{S,1}}{F_S n_{\rm CH_4,0}} = \left(\frac{X_0}{X_1}\right)_{\rm He} \frac{X_{S,1}}{X_{\rm CH_4,0} F_S}$$
(2)

## **3** Results



Figure 2: Time dependence of conversion and yield in the RCEM. Open symbols: Temporally resolved hold times; Full symbols: No expansion (corresponding to the limit of infinite hold time).

#### **3.1** Dependence on hold time

The dependence of conversion and yield on hold time was studied for post-compression conditions  $p_C = 21$  bar,  $T_C = 1530$  K. Figure 2a shows CH<sub>4</sub> conversion as a function of the hold time (circles). Conversion first increases with  $\tau$ , indicating it takes some time span on the order of several 10 ms to complete. After about 50 ms, the conversion no longer increases with  $\tau$ ; this is also evident by data from an experiment

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without expansion (bullets), corresponding to the limit of an infinitely large hold time Figure 2b exhibits that the yields of target species  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$  also first increase with increasing hold time, until reaching a nearly constant value near 50 ms.

The calculated H/C ratio in the product species is between 4.1 and 6.3; it should be 4 based on element conservation of the initial substance methane. Equilibrium calculations for this gas mixture and temperature show that, beside the species we can detect in our setup, also benzene  $(C_6H_6)$  can be produced in significant amounts. It is a potential course for the observed mismatching ratio of H/C-atoms; especially, because it has an low H/C ratio of 1. For this reason, homogeneous reactor simulations are performed (Fig. 3). The mole fractions are normalized to the initial methane mole fraction (5 mol-%). Besides the investigated species, C<sub>6</sub>H<sub>6</sub> is also taken into account. After 100 ms, the sum of the shown mole fractions and argon is 99.94 mol-%. In this constellation, the lack of C6H6 causes an relative er-



Figure 3: Homogeneous reactor simulation with  $T_0 = 1530$  K and p = 21 bar. Simulations are performed with PolyMech [12]

ror of 8.9 %. However, in the RCM, this high  $CH_4$  conversion for the 5 mol-% mixture is not reached. The error at a conversion after 50 ms is 4.6 %.

#### 3.2 Pressure dependence

In another series of experiments, the compression pressure was varied from 11 - 26 bar, with two compression temperatures ( $T_C = 1495(\pm 75)$  K and  $T_C = 1725(\pm 75)$  K). Both gas mixtures ( $X_{CH_4} = 1$  mol-% and  $X_{CH_4} = 5$  mol-%) were investigated. Hold time is set to  $\infty$ , meaning the engine is operated as a conventional RCM.

All experimental data exhibit a weak pressure dependence of the CH<sub>4</sub> conversion (Figure 4a). The target species  $C_2H_2$  shows a pressure dependence for both temperatures; the yield increases with decreasing pressure (Figure 4b). In contrast, the yields of H<sub>2</sub> and  $C_2H_4$  do not show a pressure dependence. The two data sets measured at high temperature show higher conversions than the low temperature data sets. The highest conversion ( $U \approx 52\%$ ) is seen for the gas mixture with  $X_{CH4} = 1$  mol-%.

The conversions achieved with the 5 mol-% mixture are significantly smaller than those with 1 mol-% mixture. This can be explained by the fact that the thermal decomposition of CH<sub>4</sub> is endothermic. When CH<sub>4</sub> conversion commences, the endothermal reaction causes a drop in temperature. with higher CH<sub>4</sub> mole fraction, this drop is larger, and therefore the chemical reactions for subsequent conversion get slower, according to Arrhenius' law.

## 3.3 Temperature dependence of pyrolysis reaction

The temperature dependence is investigated for the  $X_{CH_4} = 5 \text{ mol-}\%$  gas mixture, in the RCM operation mode. The temperature is varied from  $T_C = 1440 - 1700$  K for a compression pressures of

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Figure 4: Pressure dependence conversion of CH<sub>4</sub> at two different temperatures and dilutions

 $p_C = 18(\pm 0.5)$  bar. Figure 5a shows the conversion, which increases with temperature. Below 1500 K, there is just a small conversion.

Figure 5b shows the target species. The yields for the species  $H_2$  and  $C_2H_2$  increase with temperature. The yield of  $C_2H_4$  increases with higher temperatures as well, however, the slope decreases. The same behavior was found by Naik et al. [6], who investigated high pressure pyrolysis (340 - 1000 bar) of ethane.



Figure 5: Influence of temperature, studied with the 5 mol-% mixture at constant pressure

# 4 Conclusions

The conversion of methane to the unsaturated hydrocarbons  $C_2H_2$ ,  $C_2H_4$ , and to molecular hydrogen  $H_2$  was studied experimentally in a rapid compression-expansion machine (RCEM). It is shown that the conversion in the RCEM under the conditions of our study reaches a quasi steady state after 50 ms. Before this time, methane conversion and target species yield increase with increasing hold time.

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The highest conversion was found for a mixture consisting of 1 mol-%  $CH_4$  and 99 mol-% of noble gas (Ar + He). With increasing temperature, the yields of  $H_2$ ,  $C_2H_2$  and  $C_2H_4$  increase; however, the yield of  $C_2H_4$  reaches a saturation.

The conversion is almost independent of pressure, however, the yield of  $C_2H_2$  slightly drops with increasing pressure.

Overall, the observed yields are encouraging, demonstrating the potential of piston engines as means to produce substantial amounts of unsaturated hydrocarbons from methane. An important prerequisite for high yields are high post-compression temperatures and sufficiently long hold times (about 50 ms).

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