Hot surfaces have to be considered as potential ignition sources for explosive fuel-air mixtures. They occur in normal operation of plants and processes (e.g., heating systems, dryers, electrical equipment, heated pipes). Furthermore, equipment failures generating hot surfaces (e.g., overheating of bearings, friction processes, or failures of temperature control) can lead to an ignition of explosive gas-air mixture [1]. In all these cases the question must be answered whether or not hot surfaces can be effective ignition sources under the prevailing conditions. This depends, for example, on the composition, the concentration, the flow pattern, and flow velocity of the explosive mixture, as well as on the material, size, and shape of the hot surface. At ambient pressure hot surfaces are characterised by the auto ignition temperature determined according standardised methods [2-6]. To see whether the variation of the parameters influencing the ignition temperature like starting pressure, concentration of the flammable mixture, turbulence, system configuration, geometrical configuration of the hot surface as well as of the volume etc. [1, 6-14] are mirrored by the reaction products, gas chromatographic analyses of the end mixtures have been carried out (end mixture means the mixture either after ignition or after having stopped the heating up of the hot surface in case no ignition occurred).

This paper deals with the combustion products of homogenous n-heptane/air mixtures when ignited in a closed vessel by free hot surfaces at ambient pressure (experimental setup see below). Free hot surface means that the vapour/air mixture surrounds the hot surface which leads to a remarkable temperature gradient between the hot surface and the wall of the explosion vessel. This experimental setup was chosen to represent industrial conditions where a hot surface may be surrounded by explosive vapour/air mixtures having lower temperature than the hot surface. This is in contrary to the configuration used by the standardized determination methods where the explosive vapour/air mixture is surrounded by the hot surface. n-Heptane was chosen as a representative of temperature class T3 [15] substances (200°C ≤ autoignition temperature ≤ 300°C) having a vapour pressure high enough to cover a wide concentration range in mixture with air and because of its importance as component of solvents and fuels (n-Heptane is an important primary reference fuel for gasoline and diesel fuels).

**Experimental part**

The experimental set up consists of: (1) an upright cylindrical explosion vessel, (2) a mixture preparation unit and (3) a heating chamber. In figure 1 is presented the schematic view of the apparatus.

The explosion vessel (mixture volume: 2.63 x 10^3 m^3) is made of glass with a pressure release opening. The vessel is equipped with thermocouples mounted in the space between the hot surface and the glass wall, with gas inlet and gas outlet lines, a pressure transducer and a sampling valve. The cylindrical hot surface (stainless steel rod, surface 2.5 x 10^-2 m^2, maximum temperature 750°C) equipped with tightly fitting thermocouples is placed in the centre of the explosion vessel.

The mixture preparation unit designed according to [16] is connected to the explosion vessel.

The explosion vessel and parts of the mixture preparation unit were placed in a heating device and heated to the desired starting temperature (100, 150, 175°C).

After filling the explosion vessel with the homogeneous vapour/air mixture and after the temperature equilibrium within the n-heptane/air mixture was reached (approx. 1 min. after having completed the filling) the cylindrical hot surface was heated up at a rate of 5 K/s, till an ignition of the vapour/air mixture occurred. The heating up of the stainless steel rod was stopped at that moment. A visible flame and a temperature rise of at least 20 K, as indicated by one of the thermocouples placed between the hot surface and the wall of the ignition vessel was taken as ignition criterion. After an ignition has occurred a sample was taken from the end mixture for gas chromatographic analyses using a syringe which was heated to the starting temperature (100, 150 resp. 175°C). In case of non-ignition the heating of the hot surface was stopped at app. 500°C and a sample was taken from the mixture which was not ignited for gas chromatographic analyses as well. The concentration of n-heptane in the starting vapour/air mixture was varied from 1.0 to 36 vol%. This corresponds to a n-heptane/O_2 ratio from 0.05 to 2.56 (for the stoichiometric mixture, the n-heptane/O_2 ratio is 0.097).

The starting temperatures were 100, 150 and 175°C. Each
mixture concentration was investigated at least 3 times at each temperature.

The composition of the combustion products of n-heptane/air mixtures after ignition at ambient pressure and different initial temperatures of these mixtures (from 100 to 175°C) was analysed with gas chromatography-mass spectrometry (GC-MS) and gas chromatography with flame ionization detector (GC-FID) methods.

For the gas chromatographic analyses the following three different gas chromatography (GC) conditions have been used for the separation, identification and quantification of the reaction products.

Separation and identification of the reaction products:
GC 1: - column typ: CP-Sil 5 CB, \( l = 48 \) m, \( \varnothing = 0.32 \) mm
- carrier gas: He
- detector: MS
- temperatures: \( T_i: 33 \) °C for 4 min; \( dT/dt: 9 \) K/min, \( T_f: 205 \) °C.

Separation and quantification of \( \text{N}_2, \text{O}_2, \text{CO}, \text{CO}_2 \):
GC 2: - column typ: Mol sieve 5A, \( l = 30 \) m, \( \varnothing = 0.32 \) mm,
- carrier gas: He
- detector: MS
- temperatures: \( T_i: 33 \) °C for 7 min; \( dT/dt: 9 \) K/min, \( T_f: 205 \) °C.

Separation and quantification of the n-heptane and reaction products (except \( \text{CO}, \text{CO}_2 \)):
GC 3: - column typ: MN-Optima 5. \( l = 60 \) m, \( \varnothing = 0.32 \) mm
- carrier gas: He
- detector: FID
- temperatures: \( T_i: 33 \) °C for 10 min; \( dT/dt: 20 \) K/min, \( T_f: 280 \) °C.

(\( T_i: \) initial temperature, \( T_f: \) final temperature, \( dT/dt: \) temperature rise, \( l: \) length of the column, \( \varnothing: \) diameter of the column)

These conditions did however not allow to detect \( \text{H}_2 \).

Relevant data and safety characteristics of n-Heptane [16]:
- Boiling point, \( \text{Bp.} \): 98 °C;
- Vapor pressure at \( T_0 = 20 \) °C, \( \rho_{20}: 4.7 \) kPa;
- Flash point, \( F_p: 7 \) °C;
- Lower explosive limit at \( T_0 = 20 \) °C, \( \text{LEL}_{20}: 0.8 \) Vol.%;
- Upper limit of explosiveness at \( T_0 = 20 \) °C, \( \text{UEL}_{20}: 6.7 \) Vol.%;
- Auto-ignition temperature, \( \text{AIT}: 220 \) °C.

**Results and discussions**

**Ignition temperature**

Ignition was observed for n-heptane/air mixture concentrations higher than 3 vol% (fig. 2). Ignition occurred at surface temperatures between 280 and 320°C (estimated uncertainty 20°C), which is higher than the autoignition temperature (220°C [16]) determined according to a standardized determination method [2-5]. The main reason for this difference is that in case of the standardised determination method the vapour/air mixture is more or less completely surrounded by the hot surface and therefore the whole mixture inside the explosion vessel is at the temperature of the hot surface. In case of the experimental setup used for the experiments reported here only part of the explosive mixture is in contact with the hot surface and thus a temperature gradient is formed between the hot surface and the wall (fig. 3). Therefore more energy that means a higher temperature of the free hot surface is necessary to heat up the necessary ignition volume to the necessary ignition temperature.

**Reaction products**

As expected, apart from the n-heptane and the oxygen left, a great number of substances was found in the end mixture representing an incomplete combustion. Table 1 summarizes the main identified substances [17] in the end mixture (unburned or burnt). Apart from \( \text{CO}, \text{CO}_2, \text{H}_2 \text{O} \) and further components containing one or two oxygen atoms in the molecule (\( \text{CH}_2 \text{O} \)) hydrocarbons mostly unsaturated (alkene, diene, alkine, etc) but also saturated ones (methane and others) could be identified. For simplifying the quantification all oxygen containing products were grouped as oxidized reaction products and the hydrocarbons as unoxidized reaction products (\( \text{CxHy} \)). CO and \( \text{C}_2\text{H}_4 \) have been chosen as representatives of the short chain reaction products. The uncertainty of the
quantification of the reaction products in the end mixtures is estimated to be 20% relative.

All identified reaction products are present in every unburned (1 to 3 vol.) and burnt end mixture independent of the n-heptane concentration and the starting temperature. Burned mixture means an auto ignition below surface temperatures of the hot surface below 500°C was observed. Their absolute and relative amount varies, however, with the concentration and initial temperature of the vapour/air mixture. This is shown in figure 5, as an example for three different mixture compositions at a starting temperature of the mixture of 100°C.

Almost over the whole range of investigated concentrations the relative amount of consumed oxygen (fig. 5) increases at identical concentrations of the mixture with increasing starting temperature with a maximum in the range of 6 - 15 vol% n-heptane in air and a steep increase between 3 and 6 vol% n-heptane in the starting mixture. The increase from 100°C to 150°C is however less distinct compared to the increase from 150°C to 175°C. The relative amount of the consumed n-heptane (fig. 6) shows a steep increase between 3 and 6 vol% as well, but seems to be less dependent on the starting temperature.

The sum of oxidized as well as the sum of the unoxidized reaction products show a maximum between 6 vol% and 10 vol% of n-heptane and a steep increase between 3 and 6 vol% n-heptane in the starting mixture. They increase with the increasing starting temperature. At mixture concentrations where no ignition was observed (1 to 3 vol%) the ratio of oxidized to unoxidized reaction products decreases from a high level (about 20 at 100°C and about 8 at 150°C) to about 1. For such mixture concentrations where an ignition was observed, the ratio of oxidized to unoxidized reaction products stays more or less unchanged at about 1 (fig. 7).

Figure 8 shows the variation of the ratio of C2H4 to the total of the unoxidized reaction products with the n-heptane concentration in the starting mixture at different starting temperatures. A steep increase between 3 and 6 vol% n-heptane in the starting mixture is to be seen as well. Figure 9 shows the variation of the ratio of CO to the total of all oxidized reaction products (CxHyOz) with n-heptane concentration in the starting mixture at different starting temperatures.

As with the C2H4/CxHy ratio, a steep increase occurs between 3 and 6 vol% n-heptane in the starting mixture. The maximum however is more broad (6 vol% n-heptane to 16 vol% n-heptane in the starting mixture) and remarkably higher. At higher concentrations of n-heptane in the starting mixture the ratio of CO to the total of all oxidized reaction products (C2H4O) decreases clearly due to increasing ratio of n-heptane to O2 in the starting mixture. The temperature of the starting mixture has more or less no influence on both ratios.

### Table 1

<table>
<thead>
<tr>
<th>Identified Main Reaction Products in the Starting and in the End Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>products starting mixture</strong></td>
</tr>
<tr>
<td>nitrogen</td>
</tr>
<tr>
<td>oxygen</td>
</tr>
<tr>
<td>n-heptane</td>
</tr>
<tr>
<td>butene (isomers)</td>
</tr>
<tr>
<td>butadiene</td>
</tr>
<tr>
<td>ethylene</td>
</tr>
<tr>
<td>pentene (isomers)</td>
</tr>
<tr>
<td>pentadiene (isomers)</td>
</tr>
<tr>
<td>hexene</td>
</tr>
<tr>
<td>1-hexene</td>
</tr>
<tr>
<td>heptene (isomers)</td>
</tr>
<tr>
<td>heptadiene</td>
</tr>
<tr>
<td>dimethylcyclopentene</td>
</tr>
<tr>
<td>dimethylpentene</td>
</tr>
<tr>
<td>allylcyclohexene</td>
</tr>
<tr>
<td>methyloclohexene</td>
</tr>
<tr>
<td>benzene</td>
</tr>
</tbody>
</table>
In all experiments with or without ignition the same reaction products although in different proportions were found. This is also valid for previous experiments carried out with n-heptane at ambient pressure during the determination of the auto ignition temperature according to the standard EN 14522 [2] or at higher pressures (determination of autoignition temperature in a 0.5L autoclave), so one can conclude the basic reaction mechanism of the oxidation reactions [18] did not change.

Description of the fundamental aspects of the initiation of the combustion processes in homogeneous fuel-air
mixtures by local ignition sources and the most important notions concerning the explosivity of gaseous mixtures as well as the definitions used in research are given in e.g. [1, 19-20].

Conclusions

In all experiments with or without ignition the same reaction products although in different proportions were found.

The amount of the n-heptane and O₂ undergoing reactions increases over the whole concentration range with increasing initial starting temperature of the vapour/air mixture. The effect is however more distinct with the oxygen than with the n-heptane and more obvious from 150 to 175°C.

The maximum near 10 vol.% (n-heptane/O₂ ratio: 0.53) corresponds to the beginning of the range of the lowest ignition temperatures of the free hot surface measured in this series (fig. 2).

The CO/Σ(C_H₅O₇ + CO + CO₂) ratio reflects clearly that with the increase of the n-heptane content in the starting mixture the amount of the short chain reaction products is reduced for the benefit of reaction products with a chain length of C₃ and higher.

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Manuscript received: 12.07.2016