Investigation of Reaction Products Obtained from Ignition Process of n-Heptane / Air Mixtures on Free Hot Surface

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The ignition behaviour at ambient pressure (p_0 between 98.0 kPa and 101.3 kPa) of different concentrations of homogenous n-heptane/air mixtures on stainless steel hot surface as well as the composition of the reaction products have been investigated. Although all reaction products are present in each burned n-heptane/air mixture, a correlation between the lowest ignition temperature and the quantitve composition of the reaction products is not obvious.

Keywords: ignition, hot surface, n-heptane, reaction products

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: 2.63×10^{-3} m³) 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 2.5×10^{-2} m², 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 homogenous 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
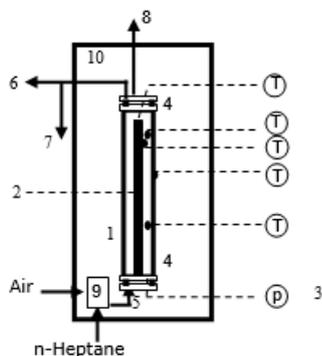
Fig.1. Schematic view of the experimental set up: (1) explosion vessel, (2) free hot surface, (3) pressure transducer, (4) pressure release, (5) mixture inlet, (6) mixture outlet, (7) vacuum line, (8) sampling, (9) mixture preparation unit, (10) oven, (T) thermocouple

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 N_2, O_2, CO, 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 CO, 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.

(were: 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 H_2.

Relevant data and safety characteristics of n-Heptane [6]:

- Boiling point, Bp.: 98 °C;
- Vapor pressure at T_0 = 20°C, p_{20}: 4.7 kPa;
- Flash point, Fp: -7 °C;
- Lower explosive limit at T_0 = 20°C, LEL_{20}: 0.8 Vol%;
- Upper limit of explosiveness at T_0 = 20°C, UEL_{20}: 6.7Vol%;
- Auto-ignition temperature, 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 [6]) 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
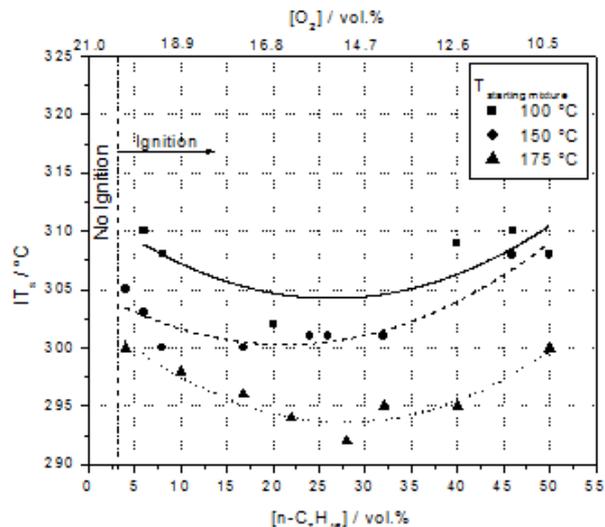

Fig.2. Ignition temperature of n-heptane/air mixtures on free hot surface (stainless steel) at different starting temperatures and different concentrations of the n-heptane/air mixtures
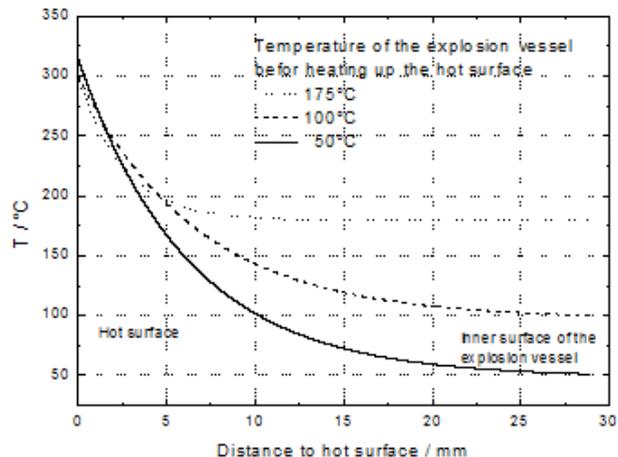

Fig.3. Temperature gradient between the free hot surface and the wall of the explosion vessel

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 CO, CO_2 H_2O and further components containing one on two oxygen atoms in the molecule ($C_xH_yO_z$) 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 reactions products and the hydrocarbons as unoxidized reaction products (C_xH_y). CO and C_2H_4 have been chosen as representatives of the short chain reaction products. The uncertainty of the

products starting mixture	unoxidized reaction products (CxHy) end mixture	oxidized reaction products (CxHyOz, CO, CO₂, H₂O) end mixture	
nitrogen	methane	Water	1-propylmethylketone
oxygen	ethene	carbon monoxide	1-pentanal
n-heptane	propene	carbon dioxide	dimethyldihydrofuranone
	butene (isomers)	formaldehyd	dimethyltetrahydrofuranone
	butadiene	ethanal	2-methylbutyloxirane
	ethyne	methanol	propyloxiranemethanol
	pentene (isomers)	propenal	tetrahydrofurfuryl alcohol
	pentadiene (isomers)	propanal	furanone
	hexene	acetone	hexenone
	1-hexene	methyloxirane	tetrahydromethylpyranone
	heptene (isomers)	2-butenone	heptanone (isomers)
	heptadiene	butanal	butyltetrahydrofurane
	dimethylcyclopentene	2-butanone	hexanal
	dimethylpentene	methylfuran	1-heptenol
	allylcyclohexene	tetrahydropyrancarbinol	heptanal
	methylcyclohexane	tetrahydrofuran	2,5-hexandione
	benzene	2-methyltetrahydrofuran	methylhexylhydroperoxide

Table 1
IDENTIFIED MAIN REACTION PRODUCTS IN THE STARTING AND IN THE END MIXTURE

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 to 150 °C is however less distinct compared to the increase from 150 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 ration 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 C_2H_4 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% and a maximum at about 10 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 the oxidized reaction products with n-heptane concentration in the starting mixture at different starting temperatures.

As with the C_2H_4/C_xH_y 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 ($C_xH_yO_z$) decreases clearly due to increasing ratio of n-heptane to O_2 in the starting mixture.

The temperature of the starting mixture has more or less no influence on both ratios.
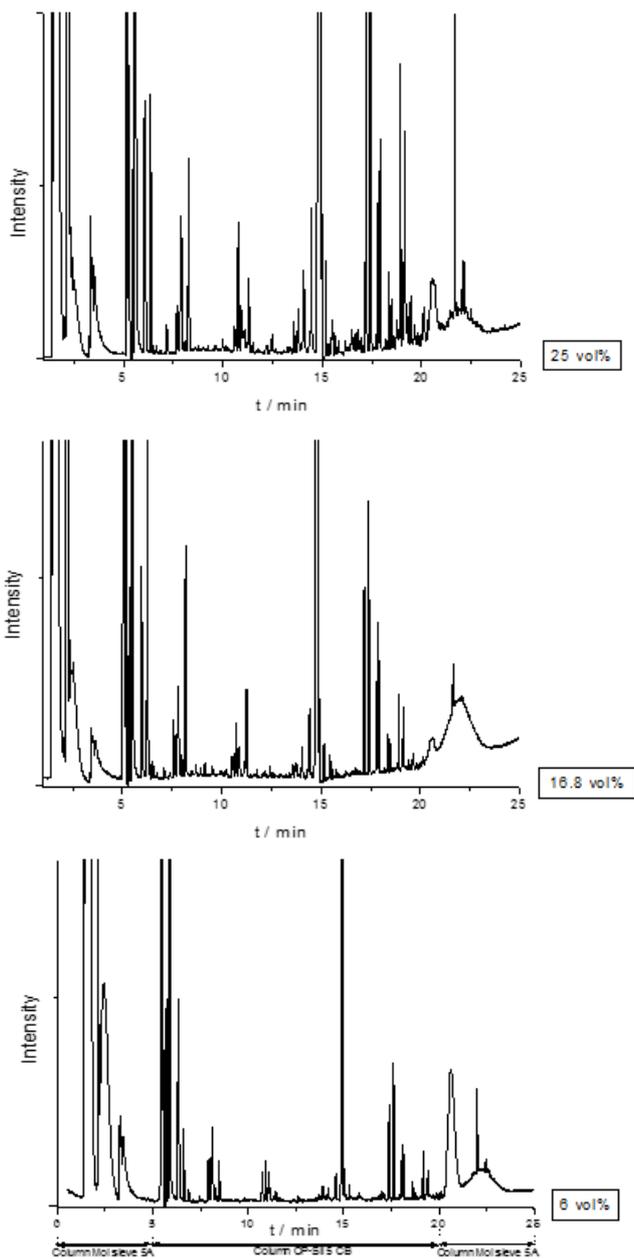
Fig. 4. Reaction products of n-heptane/air mixtures
(6 vol%, 16.8 vol%, 20 vol%) after ignition, starting temperature
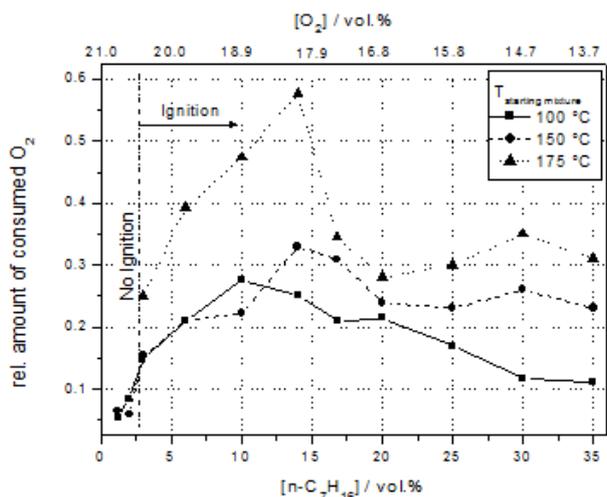of the mixture: 100 °C

Fig.5. Relative amount of consumed O_2 compared to the respective
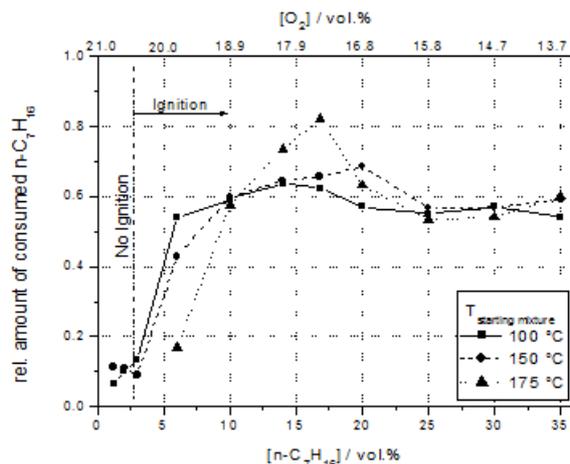composition of the starting mixtures

Fig.6. Relative amount of consumed n-heptane compared
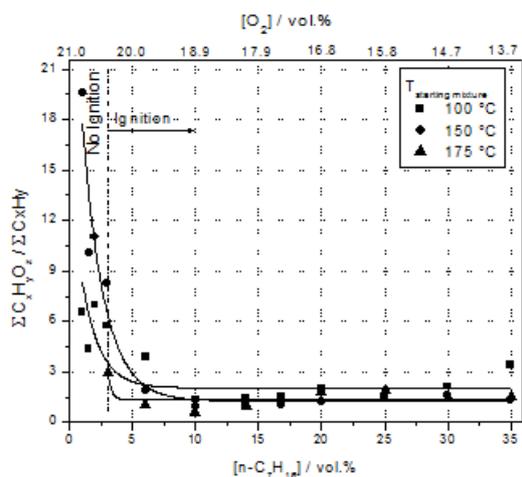to the respective composition of the starting mixtures

Fig.7. Ratio of $\Sigma C_xH_yO_z/\Sigma C_xH_y$ compared to the respective
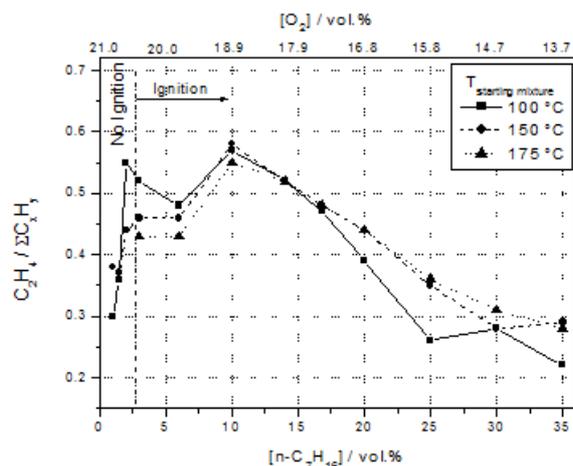composition of the starting mixtures

Fig.8. Ratio of $C_2H_4 / \Sigma C_xH_y$ compared to the respective
composition of the starting mixtures

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
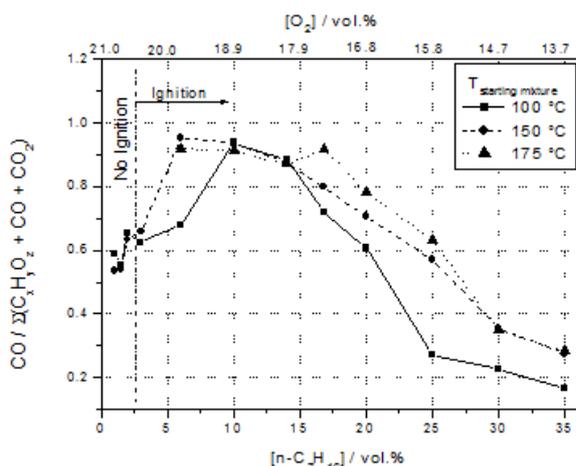of the combustion processes in homogeneous fuel-air

Fig.9. Ratio of CO / $\Sigma(C_xH_yO_z + CO + CO_2)$ compared to the respective composition of the starting mixtures

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 O_2 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/O_2 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/$\Sigma C_xH_yO_z$ and C_2H_4/C_xH_y ratios 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 C_3 and higher.

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