Reaction Products of n-Heptane /Air Mixtures after Ignition on Free Hot Surfaces

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1 Summary

The composition of the combustion products of n-heptane/air mixtures after ignition by free hot surfaces at ambient pressure (p_0 = 1013 mbar) and different initial temperatures of these mixtures (from 100°C to 175°C) was analysed with gas chromatography-mass spectrometry (GC-MS) and gas chromatography with flame ionization detector (GC-FID) methods.

2 Introduction

Hot surfaces are one of the most common ignition sources. At ambient pressure they are characterised by the auto ignition temperature determined according standardised methods [1 - 5]. Within the frame of investigations on the influence of different parameters (starting pressure temperature of the flammable mixture, concentration of the flammable mixture, turbulence etc.) on auto ignition temperature [see also 5 – 11], gas chromatographic analyses of the end mixtures have been carried out, to see whether the variation of the influencing parameters are represented by the reaction products. This paper deals with the combustion products for of n-heptane/air mixtures when ignited in a closed vessel by free hot surfaces at ambient pressure, at mixture temperatures lower than the auto ignition temperature according to a standard.

3 Experimental set up

The upright cylindrical explosion vessel (mixture volume: $2{,}63 \ast 10^{-3}$ m³) is made of glass and had a pressure release opening . The vessel was equipped with thermocouples mounted in the area between the hot surface and the glass wall, with gas inlet and gas outlet lines, a pressure transducer, a vacuum line and a sampling valve. The cylindrical hot surface (stainless steel rod, surface $2{,}5 \ast 10^{-2}$ m², maximum temperature 750°C) equipped with tightly fitting thermocouples was placed in the centre of the explosion vessel. A mixture preparation according to [12] was connected to the explosion vessel. The explosion vessel and parts of the mixture preparation unit were placed in a heating device. After filling the explosion vessel with the vapour/air mixture the hot surface was heated at a rate of 5 K/s, till an ignition of the vapour/air mixture occurred. In this case the heating process was stopped. A visible flame and a mixture temperature rise of at least 20 K was taken as ignition criterion, as indicated by one of the thermocouples mounted between the hot surface and the wall. After ignition has occurred

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a sample was taken from the burnt end mixture for gas chromatographic analyses using a syringe which was heated to the oven temperature. In the case of non-ignition the heating process was stopped at 500°C and a sample was taken from the unburnt mixture for gas chromatographic analyses. The concentration of n-heptane was varied from 1,0 vol% to 36 vol% in the starting mixture, mixture temperatures were 100°C, 150°C and 175°C.

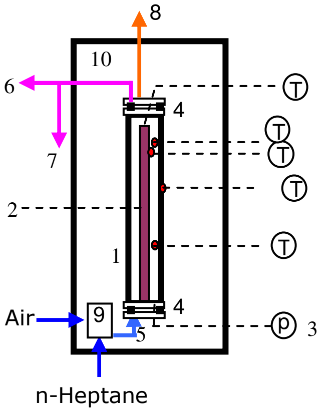

Figure 1 Schematic view of the apparatus

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

For the gas chromatographic analyses the following condition have been used:

GC 1: column: MN-Optima 5. 60 m, ∅0,32 mm, He: detector: FID
temperatures: T_i: 33 °C for 10 min; dT/dt: 20 K/min, T_f: 280°C
GC 2: column: CP-Sil 5 CB. 48 m, ∅0,32 mm, He: detector: MS [13]
temperatures: T_i: 33 °C for 4 min; dT/dt: 9 K/min, T_f: 205°C
GC 3: column: Mol sieve 5A. 30 m, ∅0,32 mm, He: detector: MS [13]
temperaturs: T_i: 33 °C for 7 min; dT/dt: 9 K/min, T_f: 205°C

4 Results

Ignition was observed for n-heptane concentrations of above 3 vol%. Ignition occured at surface temperatures between 298 °C and 330°C. Table 1 summarizes the substances identified in the end mixture (unburnt or burnt). There are n-heptane and oxygen, oxidized reaction products containing one or two oxygen atoms (CxHyOz, CO, CO_2), methane and unsaturated hydrocarbons.

All reaction products are present in every unburnt (1 vol% to 3 vol%) and burnt end mixture independently of the n-heptane concentration and the initial mixture temperature but their absolute and relative amount vary, however, with mixture concentration and initial temperature. The uncertainty of the concentration of the reaction products is estimated to be 20 % relative.

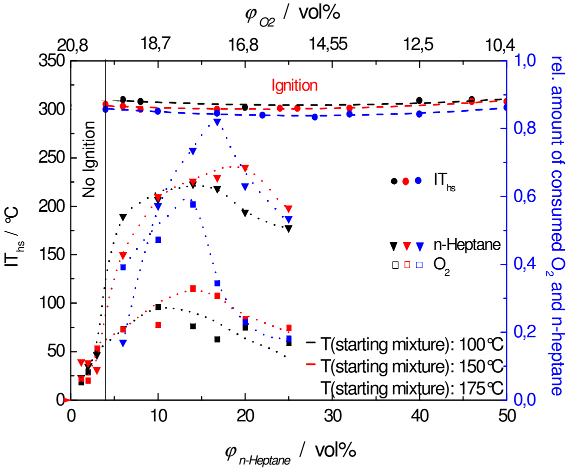

Fig. 2: Consumed amount of n-heptane and O_2 compared to the respective amounts of the starting mixtures

Figure 2 shows the consumed relative amount of n-heptane and oxygen in the burnt and unburnt end mixtures. The consumed relative amount of n-heptane as well as of oxygen increases with increasing temperature of the starting mixture. It shows a maximum between 6 vol% and 10 vol% n-heptane in the starting mixture.

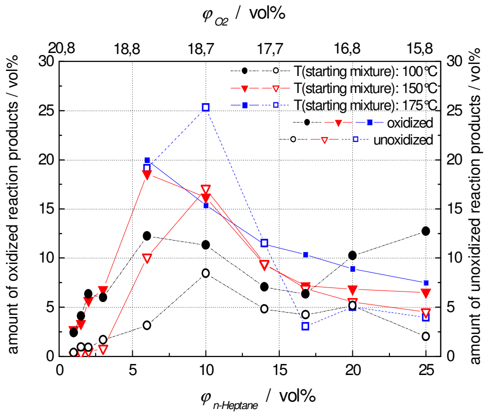

Fig. 3: Amount of oxidized and unoxidized reaction products compared to the n-heptane and O_2 amount in the starting mixture

Figure 3 shows the variation of molar amount of oxidized and unoxidized reaction products with the concentration of n-heptane in the starting mixture and the temperature of the starting mixture. The oxidized as well as the unoxidized reaction products show a maximum between 6 vol% and 10 vol% of n-heptane in the starting mixture. They increase with increasing temperature.

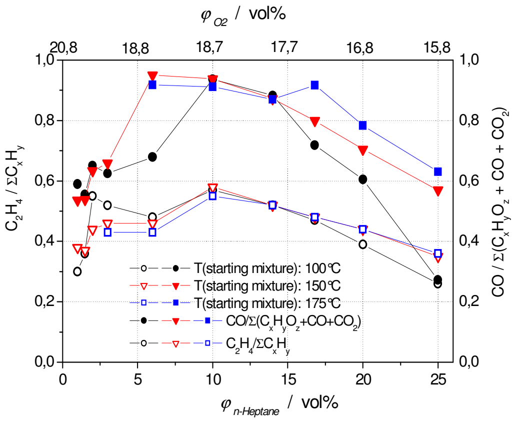

Fig. 4: Relative amount of CO compared to the total of the oxidized reaction products and relative amount of C_2H_4 to the total of the unoxidized reaction products compared to the n-heptane and O_2 amount in the starting mixture.

As figure 4 shows the CO maximum between 6 vol% and 10 vol% is not as distinct as the maximum of the sum of the oxidized and unoxidized reaction products. There seems to be no influence of the temperature of the starting mixture

Table 1. Identified reaction products in the starting and end mixture

products **starting mixture**	**unoxidized reaction products (CxHy)** **end mixture**	**oxidized reaction products (CxHyOz + CO +CO_2)** **end mixture**	
nitrogen	methane	carbon monoxide	i-propylmethylketone
oxygen	ethene	carbon dioxide	i-pentanal
n-heptane	propene	formaldehyd	dimethyldihydrofuranone
	butene (isomere)	water	dimethyltetrahydrofuranone
	butadiene	ethanal	2-methylbutyloxirane
	i-butene	methanol	propyloxiranemethanol
	pentene (isomere)	propenal	tetrahydrofurfuryl alcohol
	pentadiene	propanal	furanone
	hexene	acetone	isopropylmethylketone
	i-hexene	methyloxirane	isopentanal
	heptene (isomere)	2-butenone	heptanone (isomere)
	heptadiene	butanal	butyltetrahydrofurane
	dimethylcyclopentene	2-butanone	hexanol
	dimethylpentene	methylfuran	1-heptanol
	allylcyclohexene	tetrahydropyrancarbinol	heptanal
	methylcyclohexane	tetrahydrofuran	2,5-hexandione
	benzene	2-methyltetrahydrofuran	methylhexylhydroperoxide

5 Conclusion

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 determination of the standard auto ignition temperature) or at higher pressures (determination of auto ignition temperature), so one can conclude the basic reaction mechanism of the oxidation reactions did not change [14].

With the rise of the initial mixture temperature from 100°C to 175°C the amount of the reacted n-heptane increases over the whole concentration range investigated with a maximum at 10 vol% ; this corresponds to the beginning of range of the lowest ignition temperatures of the free hot surface measured in this series (see fig. 1).

At higher concentration2 of n-heptane the ratio of CO to the total of all oxidized reaction products (CO + CO_2 + CxHyOz) decreases because of increasing production of CxHyOz, caused by the lower O_2 contents in the starting mixture. The ratio of C_2H_4 to CxHy decreases too because of decreasing production of C_2H_4. The temperature of the starting mixture shows more or less no influence on the ratios.

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