Analysis of Reaction Products After Ignition Process of 1-octanol/air Mixtures on a Hot Surface

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1-octanol is considered an alternative to conventional diesel. In order to know the ignition parameters of 1-octanol, an experimental study of the explosive combustion of 1-octanol/air mixtures at ambient pressure and various initial temperatures was performed on a hot stainless-steel surface in a closed vessel. The ignition temperatures of 1-octanol/air mixtures at different initial conditions were determined. Using gas chromatography-mass spectrometry (GC-MS) and gas chromatography with flame ionisation detector (GC-FID) methods, the composition of the reaction products was investigated.

Keywords: ignition, hot stainless-steel rod, 1-octanol, reaction products

Hot surfaces have the potential to ignite explosive gases and vapour/air mixtures. Surfaces may become hot in a number of ways: during the normal operation of plants and processes or as the result of equipment failures (e.g. machinery, parts of combustion engines, electrically heated equipment, including rods and wires, and the hot surfaces and sparks produced by friction between surfaces [1]. With respect to the initiation of explosions, hot surfaces are characterised by the auto ignition temperature defined in standardised methods [2-5].

Ignition due to hot surfaces depends on the initial properties of the flammable gas/air mixture (e.g. composition, concentration, flow pattern, flow velocity) as well as on the material, size and shape of the hot surface [1, 6-14]. In this context, ignition temperatures are particularly useful and have been determined for different combustible mixtures [13,15]. Generally, when the ignition temperatures of combustible mixtures are determined by means of heated wires, rods or cylinders, the temperatures increase with decreasing contact times and heat source dimensions [1, 16-17]. As is well–known, the ability of a flammable mixture to ignite increases significantly with increasing particle temperature [1,18]; however, conditions exist under which an increase in the particle temperature inhibits the ignition of a given mixture. This can happen via reactant depletion in the case of catalytic surfaces [19,21].

The utilisation of hot catalytic surfaces in the combustion of fuels has recently received considerable attention, primarily as a means of reducing pollutant emissions and improving combustion by providing combustion efficiencies. Studies concerning ignition on platinum wires have been reported in [12-14, 20-25].

The need to reduce greenhouse gas emissions and dependence on fossil fuels has driven the search for alternative and renewable fuel sources. Alcohols are regarded as alternative fuels and blending fuel components for internal combustion engines. In the field of diesel engines, alcohols have generated a considerable amount of interest, as their increased oxygenated content can significantly stimulate combustion [26,27]. Many experimental studies about safety characteristics have addressed short-chain alcohols, e.g. [28-31]. Recently, 1-octanol has generated a considerable amount of interest because it can be obtained from biomass. 1-octanol is promising as a new fuel that could be considered an alternative to conventional diesel [26,27]. To date, very few studies have been carried out concerning the combustion behaviour of 1-octanol. A better understanding requires knowledge of its fundamental combustion characteristics. Studies concerning the combustion of 1-octanol mixtures have been reported in [26,27,32,33].

1-octanol can be considered representative of temperature class T3 [34] substances (200°C < autoignition temperature < 300°C). 1-octanol is manufactured for the synthesis of esters used in perfumes and flavourings. Esters of octanol such as octyl acetate occur as components of essential oils. Octyl acetate is used to evaluate the lipophilicity of pharmaceutical products.

In [1,35,36], a description is given of the fundamental aspects of the initiation of the combustion processes in homogeneous fuel/air mixtures by means of local ignition sources, in addition to a description of the most important notions concerning the explosivity of gaseous mixtures as well as the definitions used in research. Studies concerning the flammability of 1-octanol and other liquid fuel mixtures have been reported in [37-40].

This paper describes the reaction products after ignition of premixed flammable 1-octanol/air mixtures at ambient pressure and different initial temperatures, as well as fuel/air ratios within the explosion limits. The experiments were performed in a closed vessel using a stainless-steel rod as a hot surface. The compositions of the reaction products were investigated using the gas chromatography-mass spectrometry (GC-MS) and the gas chromatography with flame ionisation detector (GC-FID) methods.

Experimental parts

The experimental setup was previously described in detail in [15]. The experimental setup consists of a 2.63* 10^{-3} m^3 vertical cylindrical explosion vessel, an evaporator tube, a mixing vessel, metering devices for fuel and air, and a heating chamber. The mixture preparation unit designed according to [41] is connected to the explosion vessel. The cylindrical hot surface (stainless-steel rod, surface 2.5*10^{-2} m^2, maximum temperature 750°C) equipped with tightly fitting thermocouples is placed in the centre of the explosion vessel. The initial working temperatures were 150 and 175°C. Figure 1 presents the scheme of the experimental equipment.

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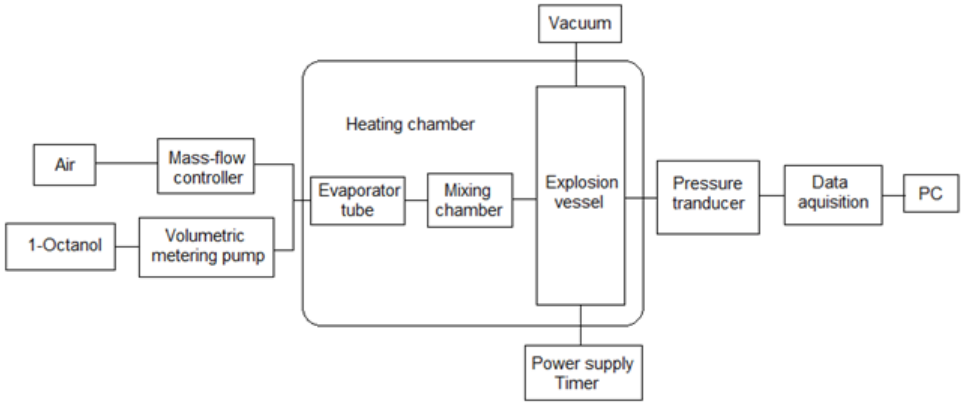

Fig. 1. Scheme of the experimental setup

After ignition takes place, a sample is taken from the end mixture for gas chromatographic analysis using a syringe heated to the starting temperature (150, 175°C). The concentration of n-octanol in the starting vapour/air mixture is varied from 6.0 vol% to 18.0 vol% of n-octanol. Each mixture concentration was investigated at least three times at each temperature.

After each ignition of 1-octanol/air mixtures at ambient pressure and different initial temperatures of these mixtures (150, 175°C), the composition of the combustion products was analysed using gas chromatography-mass spectrometry (GC-MS) and gas chromatography with flame ionisation detector (GC-FID) methods.

Relevant data and safety characteristics of 1-octanol:

- Boiling point, Bp.: 195°C [6];
- Vapor pressure at T_0 = 20°C, p_{22}: 1.3 mbar [42];
- Flash point, Fp: 84°C [6];
- Lower explosion point, LEP: 77.5 °C [38];
- Lower explosive limit at T_0 = 100°C, LEL_{100}: 0.7Vol% [6];
- Upper limit of explosiveness at T_0 = 150°C, UEL_{150}: 6.7 Vol% [6];
- Auto-ignition temperature, AIT: 245°C [6].

Results and discussions

The ignition of flammable gas mixtures on hot surfaces constitutes a hazard in many industries and is a function not only of the type and temperature of the hot surface, but also of the properties of the gas mixture. This study presents results of the ignition process of 1-octanol/air mixtures on a hot stainless-steel rod located in a vertical cylindrical explosion vessel, which differs from ignition on extended surfaces such as heated vessels.

The ignition process occurred at surface temperatures between 330 and 365°C (estimated uncertainty 20°C), which is higher than the auto-ignition temperature (245°C [6]) determined according to a standardised determination method [2-5].

The ignition temperatures of various compositions of the 1-octanol/air mixture were measured at ambient initial pressure and at different initial temperatures of the vapour/air mixtures (150, 175°C). The experimental data at an initial temperature of the 1-octanol/air mixtures of 150°C are given in figure 2 at ambient pressure and different initial compositions. It can be observed that the ignition temperature decreases when the 1-octanol concentration increases.

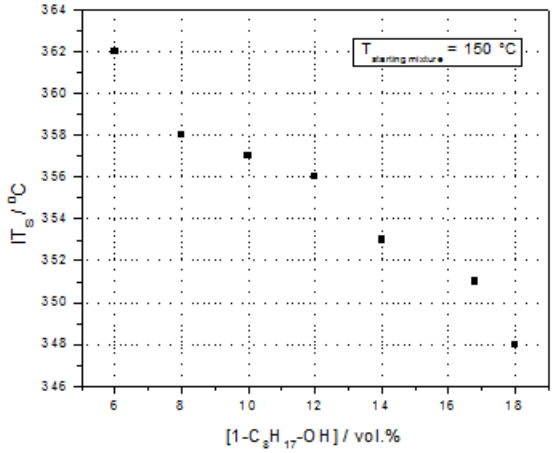

Fig. 2. Ignition temperature of homogenous1-octanol/air mixtures on a free hot surface (stainless steel) at different initial concentrations and T_0 = 150 °C.

Figure 3 and table 1 show the main substances identified in the mixture after ignition: reaction products, N_2, O_2 and 1-octanol. The identification is based on the NIST database [43]. CO, CO_2 H_2O and other substances with oxygen atoms in the molecule ($C_xH_yO_z$), saturated hydrocarbons and mostly unsaturated hydrocarbons (alkene, diene, alkine etc.) were identified.

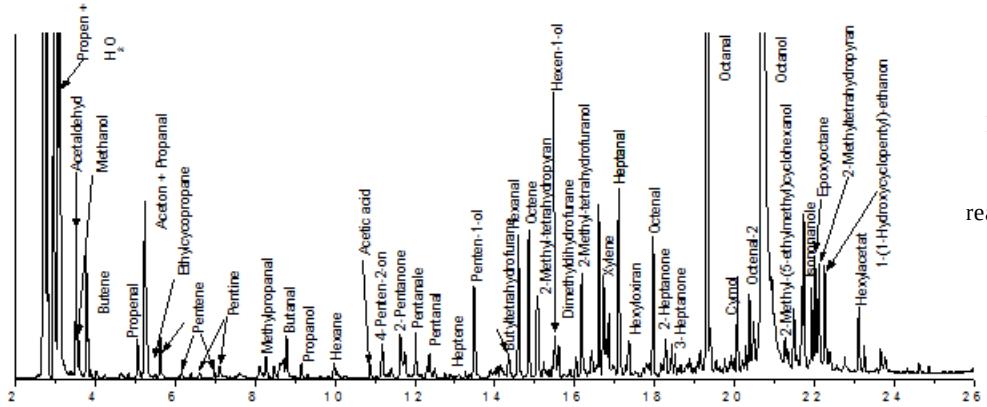

Fig. 3. A typical chromatogram (gas chromatography-mass spectrometry apparatus) of reaction products identified in the mixture after ignition of a 1-octanol/air mixture

Unoxidised reaction products (C_xH_y) in mixture after ignition	
- methane	- pentadiene (isomers)
- ethene	- hexane
- ethyne	- hexene (isomers)
- propene	- hexadiene
- butene (isomers)	- heptene (isomers)
- butadiene	- heptadiene
- pentane	- benzene
- pentene (isomers)	- toluene
- pentene (isomers)	
Oxidised reaction products ($C_xH_yO_z$ + CO +CO_2) in mixture after ignition	
- carbon monoxide	- n-pentanal
- carbon dioxide	- n-pentenol
- formaldehyde	- pentanone
- methanol	- propanoic acid
- ethanal	- epoxipentene
- ethoxipropane	- dimethyldihydrofuranone
- acetic acid	- hexanone
- propenol	- tetrahydromethylpyranone
- propanol	- heptanone (isomers)
- propenal	- butyltetrahydrofurane
- propanal	- hexanal
- acetone	- heptanal
- epoxibutane	- octene
- 2-butenone	- octadiene
- 2-butanone	- octanal
- butanal	- nonanol
- butenole	- butylcyclopentanol
- methylfuran	- water
- tetrahydrofuran	

Table 1
MAIN REACTION PRODUCTS IDENTIFIED IN THE MIXTURES AFTER IGNITION

In all experiments, the same reaction products were found (albeit in different proportions). This is also valid for previous experiments carried out with 1-octanol at ambient pressure during the determination of the auto-ignition temperature according to EN 14522 [2] or at higher pressures (determination of autoignition temperature in a 0.5 l autoclave); thus, the conclusion can be drawn that the basic reaction mechanism of the oxidation reactions [44] did not change.

Compared to the reaction product of n-Heptane /air mixtures that had comparable compositions and starting temperatures [15], more oxidised species, especially short-chain alcohols, were detected in the burnt 1-octanol/air mixtures as expected, whereas more cyclic and unsaturated compounds were detected with n-Heptane/ air mixtures.

In order to simplify the quantification, all reaction products containing oxygen were grouped as oxidised reaction products, while the hydrocarbons were grouped as unoxidised reaction products (C_xH_y). CO and C_2H_4 were chosen to represent the short-chain reaction products. The relative uncertainty of the quantification of the reaction products in the end mixtures is estimated to be 20%.

For each experimental test, all reaction products identified were present in every burnt end mixture independent of the 1-octanol concentration and the starting temperature.

Figure 4 shows the variation of the relative amount of O_2 consumed and the relative amount of 1-octanol consumed.

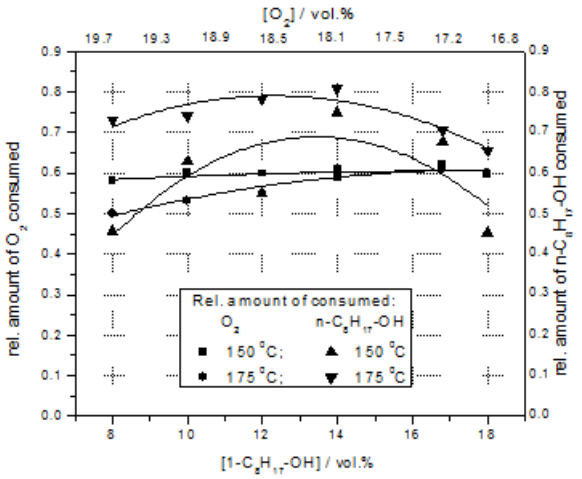

Fig. 4. Relative amount of O_2 consumed and of 1-octanol consumed, compared to the respective composition of the starting 1-octanol/air mixtures.

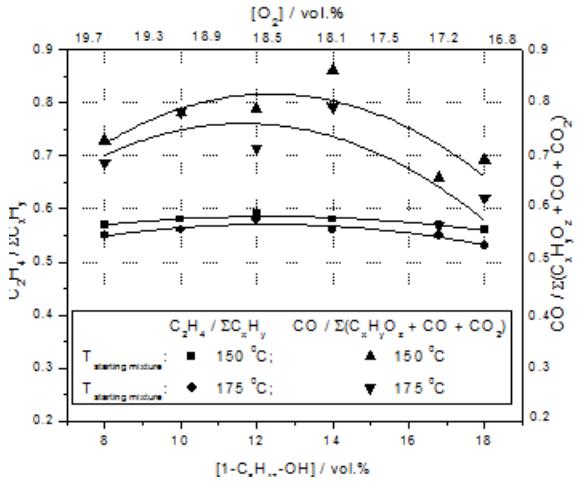

Fig. 5. Ratio of C_2H_4 / ΣC_xH_y and of CO / $\Sigma(C_xH_yO_z$ + CO + CO_2) compared to the respective composition of the starting 1-octanol/ air mixtures

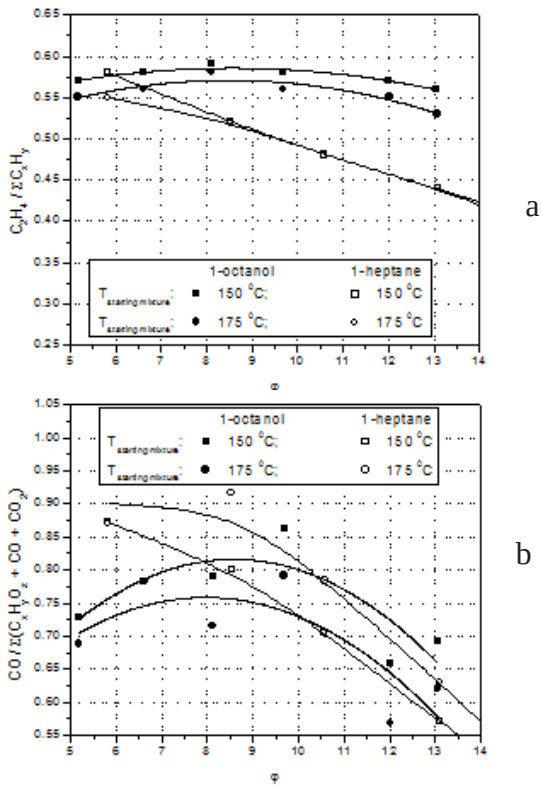

Fig. 6. Ratio of C_2H_4 / ΣC_xH_y of CO / $\Sigma(C_xH_yO_z$ + CO + CO_2) compared to the stoichiometric concentration of the starting 1-octanol/air mixtures and 1-heptane/air mixtures at different initial temperatures

The plots indicate that there is no real influence of the temperature on the ratios of C_2H_4 / ΣC_xH_y within the temperature range investigated, whereas the ratio of CO / $\Sigma(C_xH_yO_z$ + CO + CO_2) shows a clear maximum (fig. 5).

Comparing these ratios - C_2H_4 / ΣC_xH_y and CO / $\Sigma(C_xH_yO_z$ + CO + CO_2)-with the respective ratios of 1-heptane/air mixtures of the same equivalence ratio φ [15] (the equivalence ratio φ of any flammable mixture is defined as: $\varphi = \frac{[fuel]/[oxygen]}{[fuel]/[oxygen]_{st}}$, where the index *st* refers to the stoichiometric concentration of the fuel-air mixture), the following statements can be made:

-Although starting at similar C_2H_2 / ΣC_xH_y ratios, this ratio decreases with increasing 1-heptane concentration, whereas this ratio is more or less independent with 1-octanol (fig. 6a).

-Although the maximum ratio of CO / $\Sigma(C_xH_yO_z$ + CO + CO_2) (about 0.9) is comparable in both cases, the maximum appears at different starting compositions and the decrease is more distinct with 1-heptane mixtures.

Conclusions

This study investigated the reaction products of 1-octanol/air mixtures after ignition by a cylindrical hot surface (stainless-steel rod) in a cylindrical closed vessel at ambient pressure and different initial temperatures, as well as fuel/air ratios within the explosion limits. The ignition temperatures for various 1-octanol/air mixtures (6 vol% – 18 vol%) at 150°C were reported.

Using the gas chromatography-mass spectrometry (GC-MS) and the gas chromatography with flame ionisation detector (GC-FID) methods, the composition of the reaction products was investigated. In all the ignition-process experiments, the same reaction products were found in different proportions.

It has been observed that the amount of the 1-octanol and oxygen that undergoes the reactions is only slightly dependent on the initial starting temperature of the vapour/ air mixture over the whole concentration range. From the ratios of CO / $\Sigma C_xH_yO_z$ and C_2H_4 / ΣC_xH_y, it has been observed that, by increasing the 1-octanol 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. As expected, the number of oxidated reaction products is higher when compared to n-heptane/air mixtures.

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