

Ignition Temperature of Combustible Liquids in Mixtures of Air with Oxygen or Dinitrogen Oxide

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1 Introduction

A hot surface can become a potential ignition source in the presence of a combustible vapour/air mixture. Chemical and technical processes as well as cleaning operations are often carried out at temperatures high enough that such surfaces result. The autoignition temperature (AIT) is a safety characteristic used, on the one hand, to classify the combustible substances and, on the other hand, to classify the explosion-proof equipment according to the surface temperature. Under environmental conditions, the autoignition temperature is determined in accordance with standards such as DIN 51794 [1], ISO/IEC 80079-20-1 [2], DIN EN 14522 [3] and ASTM E 659-78 [4]. According to these standards, the autoignition temperature is measured at ambient pressure with air as the oxidizing gas. Oxidizing gases other than air may lead to significantly different ignition temperatures (IT). A considerable body of data has already been collected with pure oxygen as the oxidizer [5, 6]. Some substances show an ignition temperature in pure oxygen (IT_{Ox}) that is only a few degrees Kelvin lower than the AIT in air; however, for many other substances, it is lower by at least 100 K. For some substances that are not flammable in air at all, IT_{Ox} can be found in pure oxygen. Data on ignition temperatures in oxidants other than air or oxygen is rather sparse, while no data is available on the ignition temperatures of nitrogen/oxygen mixtures with an oxygen content between 21 vol% and 100 vol%, nor on such temperatures in dinitrogen monoxide (N_2O), despite its widespread industrial use. The aims of this work are to determine the ignition temperatures of the vapours of several combustible liquids in mixtures of air/oxygen or air/ N_2O under variation of the mixture composition and to find a correlation that allows the ignition temperature to be predicted with regard to the chemical structure.

2 Experiments

The experiments were performed at ambient pressure using the standard apparatus in accordance with IEC 80079-20-1 [2] and EN 14522 [3]. The apparatus was slightly modified to permit the use of oxidizers other than pure air. To inject the gaseous oxidizer mixtures, a thin tube reaching down to the bottom of the vessel was installed. The respective gas mixtures were prepared using two calibrated mass flow controllers (Figure 1) with a relative uncertainty of 1 %. An additional conical lid restricted the opening of the flask to

a diameter of 10 mm; an additional thermocouple was inserted into the vessel. Before each experiment, the test vessel was purged five times with the air/oxidizer mixture. The test itself was carried out in a quiescent gas mixture. After a stable temperature was reached within the vessel (indicated by thermocouple T3), the combustible liquid was dosed using a syringe in 25 μ l portions. All liquid chemicals were obtained from laboratory-grade commercial sources and used without further purification. The purity of oxygen and N₂O was 99.5 mol%. The surface temperature of the flask (measured by T1) at the beginning of the injection was taken as the measurement temperature. A visible flame was the ignition criterion. The measurement temperature was varied in steps of 2 K and the injected fuel volume was optimized. The lowest temperature where ignition occurred was taken as the ignition temperature.

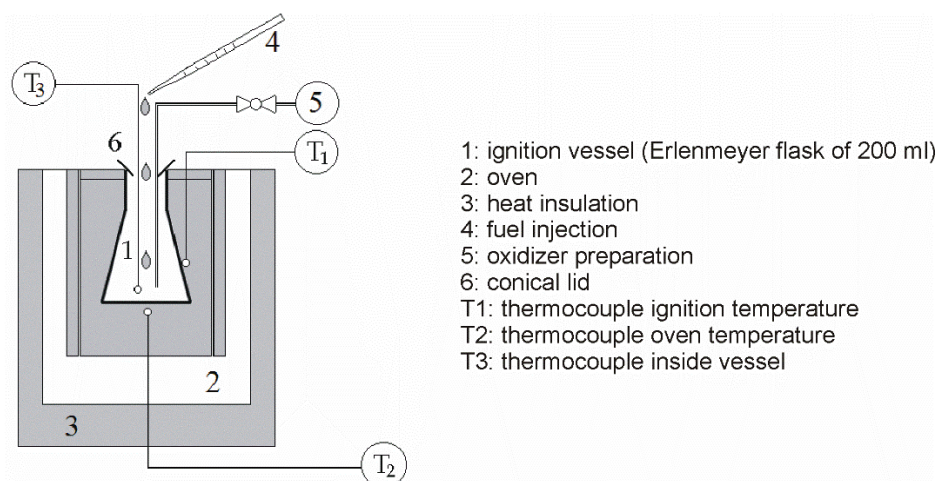


Figure 1: Experimental setup

3 Ignition temperatures in nitrogen/oxygen mixtures

The combustible liquids were chosen to cover different chemical classes; furthermore, they comprise cases in which the AIT in air and the ignition temperature in pure oxygen (IT_{ox}) have either a small or a large difference (Table 1). For all substances under investigation, the ignition temperature was found to decrease monotonically with increasing oxygen content, starting from the autoignition temperature in air down to the value in pure oxygen (Figure 2). The decrease was not linear in most cases. Linear behaviour was found only for Heptane and Butanal, where the difference between AIT and IT_{ox} was very small. For all other substances, the measured values were always lower than a linear interpolation would predict, and the liquids were subdivided into two categories: One group of substances displayed a gradual decrease of the ignition temperature with increasing oxygen content. Only when an oxygen content of 70 vol% was achieved did the ignition temperature of this group of substances reach the value in pure oxygen. Another group containing only esters and ketones showed a steep decrease in the IT with the oxygen content where the value in pure oxygen was reached even at 30 vol% of oxygen. These substances show a high $\Delta IT = (AIT - IT_{ox})$ of more than 110 K.

Table 1: AIT of the combustible liquids investigated and difference between AIT and the ignition temperature in pure oxygen IT_{ox} [5]

Substance	AIT (°C)	$\Delta IT = AIT - IT_{ox}$ (K)
<i>n</i> -Heptane	220	7
<i>n</i> -Butanal	190	11
Propanol-1	385	75
Ethanol	400	77
Heptanone-2	305	115
<i>iso</i> -Pentyl acetate	380	120
<i>iso</i> -Butanol	430	125
<i>n</i> -Butyl acetate	390	141
<i>n</i> -Butyl butyrate	395	152
2,4,4-Trimethylpentene-1	415	153
<i>n</i> -Propyl propionate	445	191
Heptanone-3	410	215
Heptanone-4	420	226

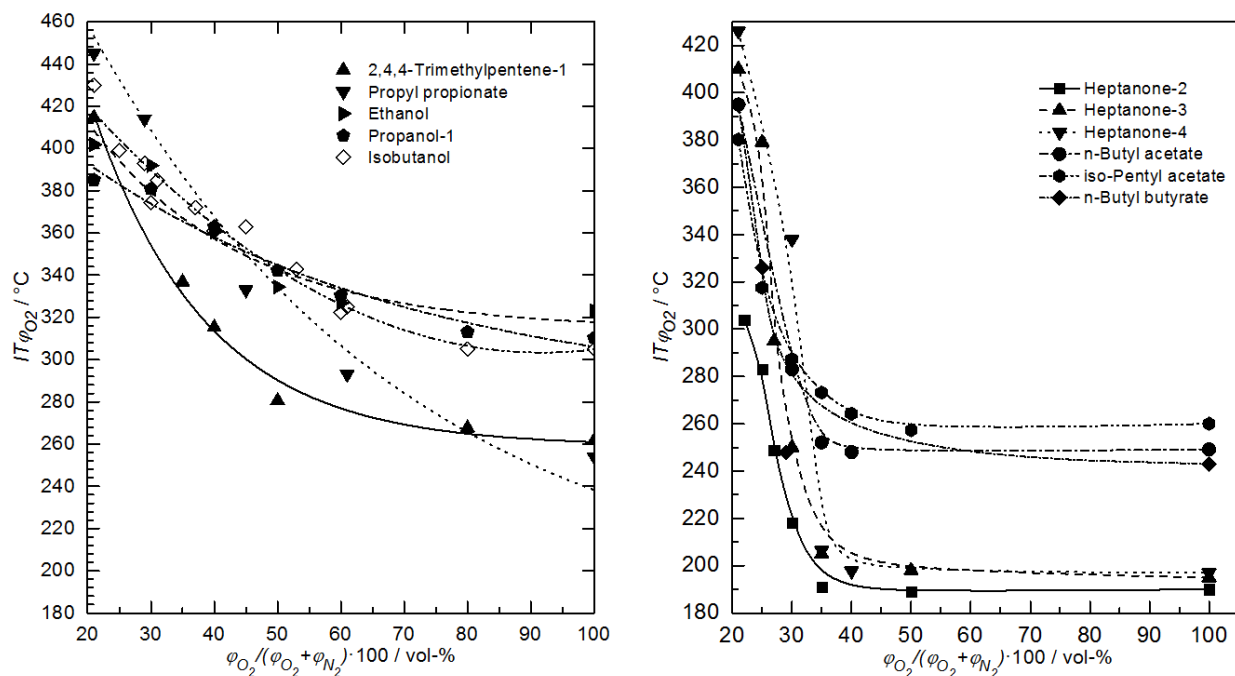


Figure 2: Measured decrease in the ignition temperature with increasing oxygen content in the oxidizing gas mixture (left: gradual, right: steep)

The IT of substances belonging to the first group can be approximated by a second-order polynomial starting with the AIT in air and reaching IT_{OX} at an oxygen content of 70 %. Ignition temperatures can be predicted safely in this manner if an additional 3 % relative uncertainty is subtracted in accordance with IEC/ISO 80079-20-1 [2] (Figure 3).

For substances with a steep decrease in the ignition temperature with decreasing oxygen content, it can be stated that the ignition temperature already reaches the value for pure oxygen at oxygen concentrations of 30 vol%. Ignition temperatures lower than the IT_{OX} were not found. For oxygen concentrations between 21 vol% and 30 vol%, a linear decrease in the IT can be assumed in safety assessments.

Predicting which of these two groups a substance belongs to is a complex task. Neither its AIT in air nor the difference between AIT and IT_{OX} are indicators of its behaviour. However, it may be noted that all substances displaying a "steep" decrease of the AIT have a chain of at least three consecutive methylene groups. For such substances, the formation of hydroperoxides followed by addition of a second oxygen molecule is energetically favourable. The involvement of a second oxygen molecule at the early stage of this mechanism makes the reaction path especially sensitive to the oxygen concentration within the mixture.

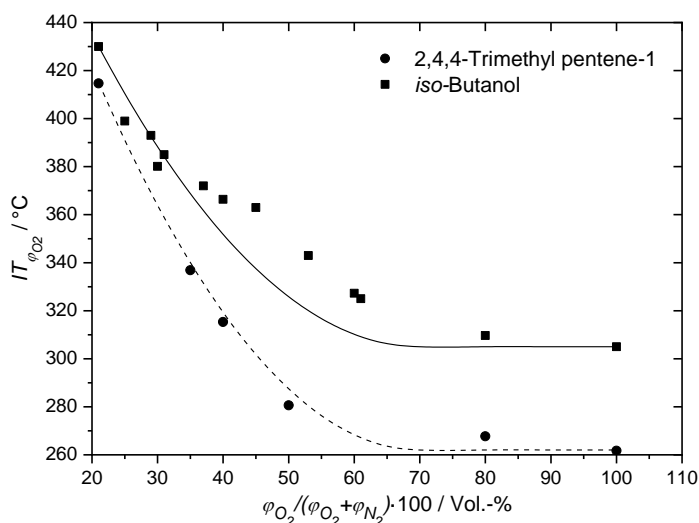


Figure 3: Prediction of the ignition temperature in oxidizing gas with increased oxygen content for substances displaying a gradual decrease of IT

4 Ignition temperatures in Dinitrogen oxide/air mixtures

Dinitrogen oxide (N₂O) is an endothermic gas ($\Delta H_f = 82.1$ kJ/mol) that may decompose under strong liberation of heat to form nitrogen and oxygen. Being a strong oxidant, it leads to a widening of the explosion regions [7, 8], higher explosion pressures and rates of pressure rise [9] and lower MESG values [10], and eases deflagration-to-detonation transitions [11]. Its coefficient of oxygen equivalency is 0.42 (compared to 0.21 for air) [12]. However, N₂O decomposition cannot be triggered at room temperature even by strong ignition sources [10]; N₂O auto-decomposes only at temperatures above 575 °C. Several combustible liquids with autoignition temperatures in air between 190 °C and 540 °C were chosen for this study and their

ignition temperatures in pure N₂O and in N₂O/air mixtures measured. None of the combustible liquids autoignited in pure dinitrogen oxide at temperatures below 580 °C.

With a N₂O/air mixture as an oxidizing gas, although autoignition occurred, the ignition temperature was always higher than in pure air. Furthermore, the ignition temperature increased with increasing dinitrogen oxide content (Figure 4). If the oxidizer contained more than 80 vol% N₂O, the ignition temperature rises to more than 580 °C even for substances with low autoignition temperatures in air. At higher N₂O concentrations, it was necessary to reduce the amount of injected liquid compared to measurements in air.

Regarding autoignition at ambient pressure, dinitrogen oxide acts more as an inert gas than as a powerful oxidant. The most recent results for 2-heptanone show that it is possible to compare the effects of N₂O and N₂. Here, adding similar amounts of each gas to air leads to a similar increase in ignition temperature. However, the similarity between dinitrogen oxide and inert gases is only true to a certain extent. If ignition takes place at higher N₂O concentrations, the subsequent explosion is very violent.

One tentative explanation is based on the fact that the first step in an autoignition reaction is the abstraction of hydrogen:



Adding N₂O inhibits this reaction by lowering the O₂ concentration. Thus, if N₂O itself is unable to trigger the decomposition of the fuel, it will act like an inert gas. However, if the temperature becomes high enough that the dinitrogen oxide starts to decompose, it can then act as a source of oxygen and add its decomposition energy to the total energy of the reaction.

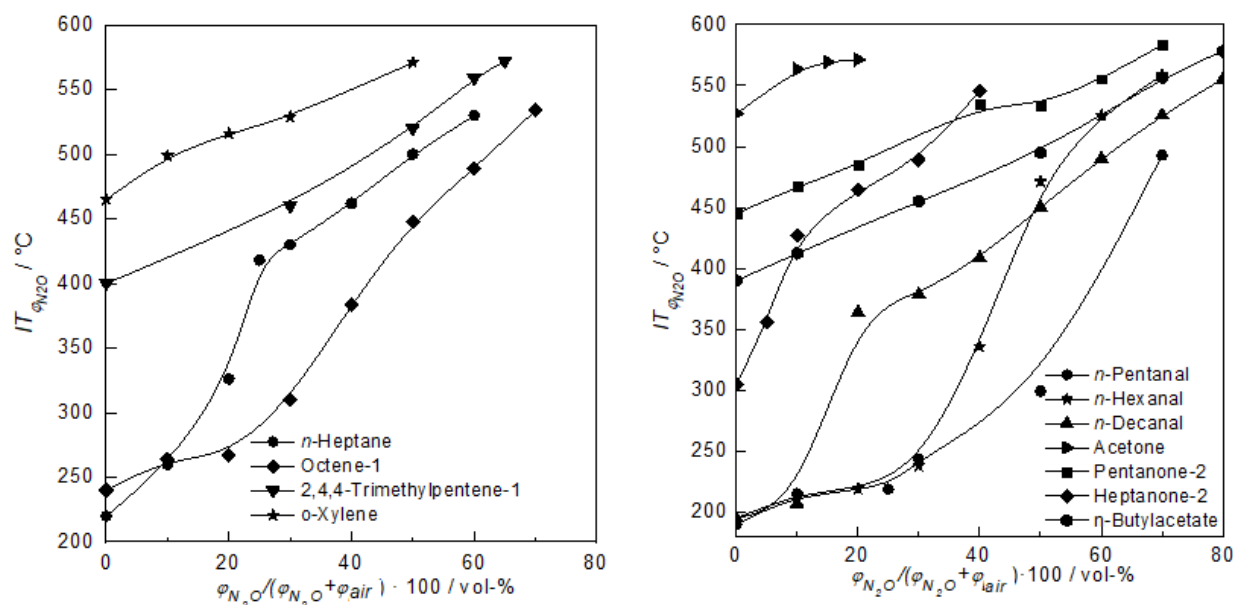


Figure 4: Ignition temperatures as a function of N₂O content of the oxidant (left: hydrocarbons, right: substances containing carbonyl group)

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