

Limiting Oxygen Concentrations - Process Safety by Oxygen Monitoring

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1. Introduction

A simple and cost-saving way to avoid explosive atmospheres in chemical processes is the monitoring of the oxygen content in the respective gas mixture. Such a monitoring is easily achieved by installing oxygen detectors also in closed systems. The determination of the amount of fuel gas, which was very often a complex procedure, is no longer necessary. The main requirement for the use of oxygen detectors is of course the knowledge of the so called limiting oxygen concentration (LOC). The LOC is defined as maximum oxygen concentration in a mixture of a flammable substance, air and an inert gas, in which an explosion will not occur, determined under specified test conditions. If the mole fraction of oxygen in a gas mixture is below the LOC value, even the arbitrary addition of fuel gas cannot lead to explosive atmospheres. The LOC does not only depend on the test substance but also on the type of inert gas.

Since 1997, the European standard EN 1127-1 gives a definition for the limiting oxygen concentration. Furthermore a new European standard EN 14756:2006 [1] for the determination of LOC values of gases and vapours was developed. Unfortunately these standards only cover atmospheric conditions. This is why LOC values are mainly published for these conditions and not for elevated values of initial pressure and initial temperature. Since in chemical production most processes are not operated under atmospheric conditions, the data basis for applying the protective measure of not exceeding the LOC value is highly unsatisfactory.

The EU project SAFEKINEX [2] was directed towards process safety of hydrocarbon oxidation by investigating and modelling oxidation kinetics and collecting data on gas explosion properties at ambient and elevated conditions. The fuels comprised methane, ethylene, propane and propylene, and n-butane. To obtain a better insight such fuels as ammonia, carbon monoxide and hydrogen were also included. Conditions covered temperatures up to 250 °C and initial pressures up to 30 bara. The data on various explosion indices were acquired by experiments carried out at different locations by different partners of the consortium over a range of vessel volumes making it a unique exercise. The operating procedure was standardised. The data were assembled in a data base.

The objective of the project was to study and possibly enhance yield while conserving safety of hydrocarbon oxidation processes for the manufacture of intermediates for polymers and other products: these processes are performed with excess of fuel. Beside the typical safety characteristics like explosion limits and self-ignition temperatures the emphasis was also to expand the knowledge about pressure and/or temperature dependencies of the LOC values.

2. Experimental

A new European standard EN 14756:2006 “Determination of limiting oxygen concentrations of gases and vapours” was developed. This standard describes very well two procedures in order to determine the LOC value of ternary gas systems. The term LOC is directly linked to gas systems consisting of a fuel, nitrogen and air. For other inert gases and/or oxygen the safety related property is called maximum oxygen content (MOC).

In the European standard a short procedure and an extended procedure was described. The LOC is calculated from the limiting air concentration (LAC) according to the following equation:

$$\text{LOC} = \text{LAC} * 0.209 \quad (1)$$

Pre-assumption is the determination of the explosion area of the ternary gas system. The explosion area is the area inside the boundary curve formed by the lower and upper explosion limits of the system (see Figure 1).

The standard test apparatuses for determination of the explosion area respectively the LOC values are described in EN 1839 [3] completely. For practical reasons there are two methods to determine explosion limits, a tube method (T) and a bomb method (B). In each method a specific apparatus is described. Both devices are suitable to determine LOC. It has clearly to be stated, which of the two methods has been used, because the apparatus and test procedure may influence the LOC value. For the need of this standard the oxygen concentration has to be measured by means of a calibrated oxygen analyser with a sensitivity of 0.1 mol% oxygen (e.g. paramagnetic analyser, gas chromatography etc.).

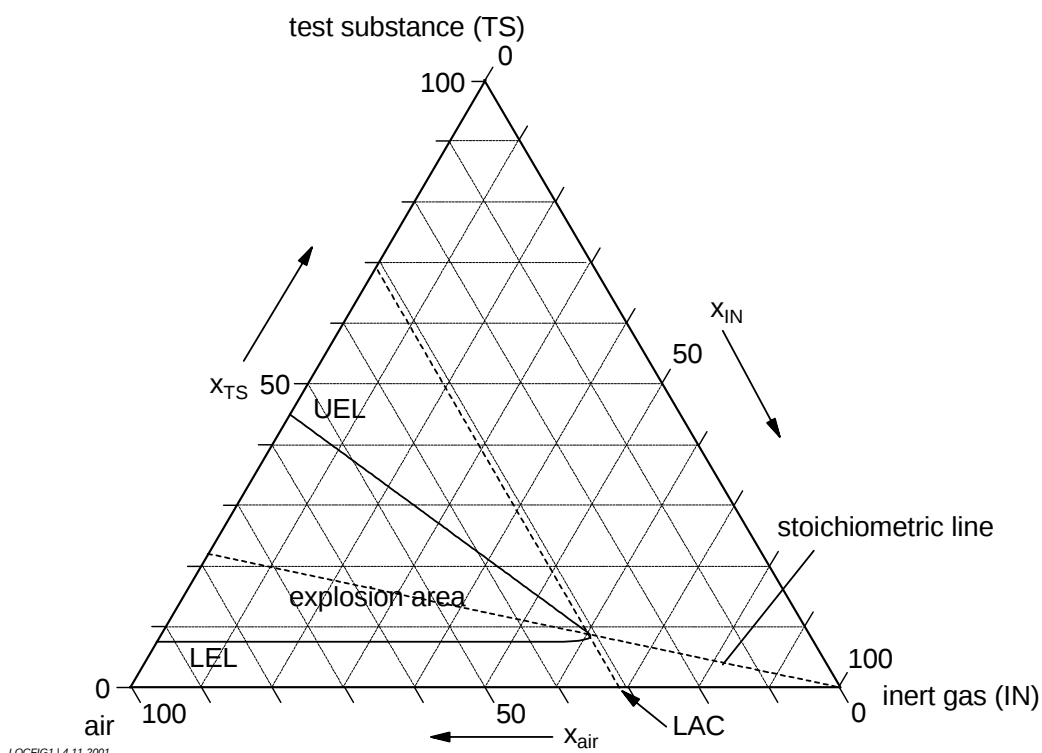


Figure 1: Explosion area for a ternary gas system consisting of a test substance (TS), air and an inert gas (IN) [01]

For many fuels especially hydrocarbons the explosion area determined at atmospheric conditions has an apex (“nose”), which leads to the limiting air concentration (LAC). But the reason for the description of a short and an extended procedure for the LOC determination is that some exceptions are possible, e.g. for hydrogen/nitrogen/air mixtures. The LAC results from the course of the upper explosion limit and not from the apex. This is also the case for hydrocarbons at non-atmospheric conditions where the course of the upper explosion limit is shifted to high fuel gas amount (see Figure 2).

3. Results

In order to gain a better understanding of the LOC behaviour at elevated conditions a literature study was carried out to find explosion areas from commonly and industrial used fuels in mixture with inert gases and air or oxygen. These data were finally compared to those published by Zabetakis in 1949 [4]. These values show a clear linear dependency on the log scale. Due to great influences of the experimental set-up used for the determination of the explosion areas it was feared that this linear dependency could not be validated. And the comparison to other data [5-8] then showed that this dependency is not evident in experimental data from other sources, where a mirrored ‘c’ shaped dependence is observed. The small number of experimental points prevents the possibility of rejection of outliers without a large consequence for data interpretation.

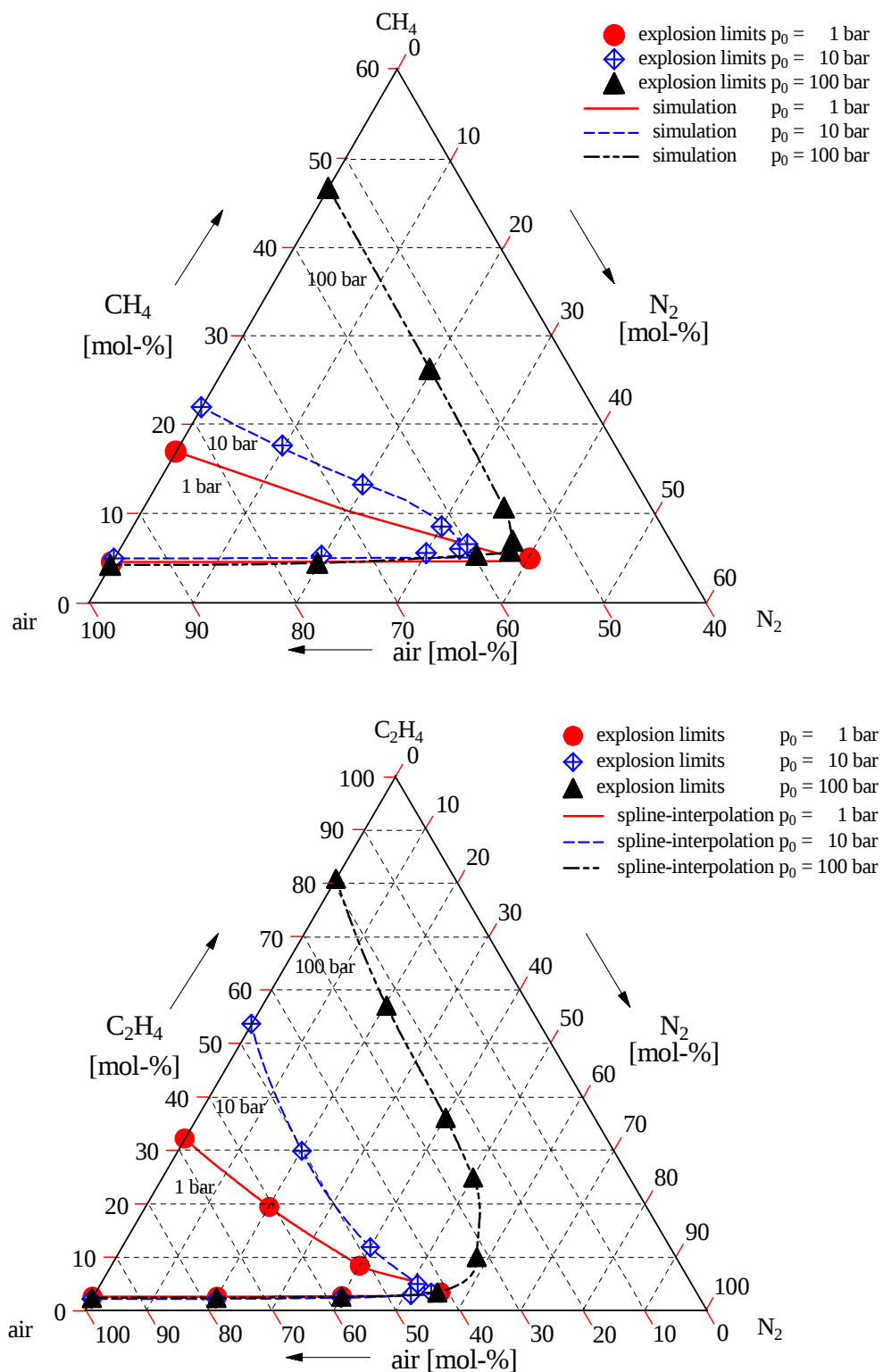


Figure 2: Explosion areas for CH₄/N₂/air (top picture [7]) and C₂H₄/N₂/air (bottom picture [8]) at atmospheric and elevated conditions

A more detailed analysis of the experimental procedure for CH₄-N₂-air mixtures revealed that the experiments at atmospheric pressure were done in a vessel of 14 litre, while the experiments at elevated pressures were done in a 2.7 litre vessel. Additionally for experiments at elevated pressure different ignition criterion (10% of pressure rise instead of 5%) and stronger ignition source (60-70 J instead of 10-20 J) were used.

It is likely that these changes in the experimental methodology modified the experimental factors that, in turn, affected the measurement resulting in the unexpected mirrored ‘c’ shape pressure dependency. For instance, it is expected that in larger vessel the cooling effect due to heat transfer to the vessel walls is less pronounced leading to lower values of the LOC. Less rigorous ignition criterion would lead to higher LOC values.

Indeed, a considerably lower LOC value is measured in the larger vessel at atmospheric pressure as compared to the results of Jones. When the measurements are done in a vessel with the same, volume as of Jones the same pressure dependency is observed, yielding a similar slope.

The measurements of CH₄-N₂-air mixtures, presented by the CHEMSAFE database [5] were done by BAM. Therefore, it is likely that the same procedure was applied for the measurements of the CH₄-CO₂-air mixtures. If so, the mirrored ‘c’ shaped dependence for this system can be understood. Heat capacity of CO₂ is higher than of N₂, therefore the LOC assumes higher values when CO₂ is used as the inert gas.

To understand the difference in pressure dependence new experiments at elevated pressures were done at BAM and BASF AG under the funding of SAFEKINEX project [22,9]. The experiments were carried out in 6-dm³ respectively 20-dm³ volume according to the new European Standard EN 14756, test method “short procedure”. Furthermore values reported in a not published master thesis carried out at BAM were taken into account for a possible explanation of the different pressure dependencies of LOC values. The LOC values are summarized and plotted in Figure 3.

In a pressure range of 1 bara to 10 bara the results show a dependence of LOC value opposite to the one reported by Zabetakis. It could be attributed either to the limited pressure range, or to a volume effect at atmospheric pressures. However, the explanation of volume dependence does not fit the experimental results at elevated pressure where on the contrary lower values of LOC are found in a smaller experimental vessel.

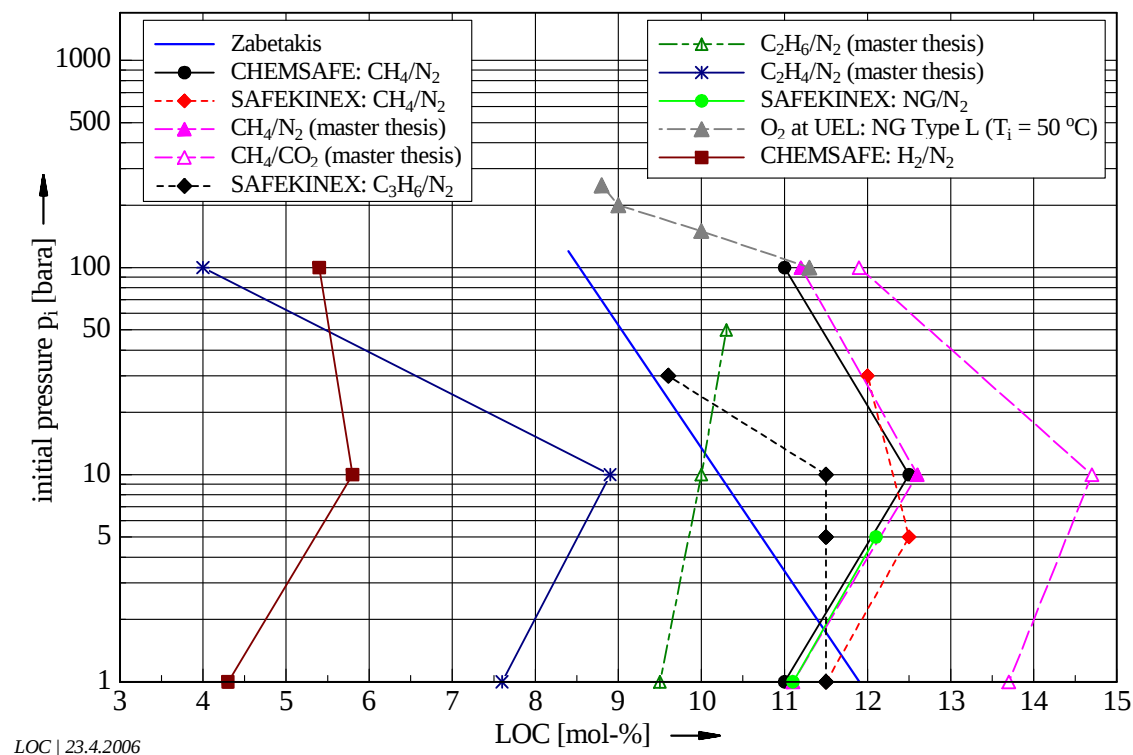


Figure 3: Pressure dependence of LOC values for different fuel/inert gas/oxidizer systems [9]

4. References

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