Chemically Unstable Gases – MITD of Ethylene Oxide Mixtures

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1 Introduction
Ethylene oxide (EO) is among the top 3% of high volume chemicals. Because of its several hazardous characteristics, safe handling of EO is an important industrial issue. Besides its toxicity EO is extremely flammable and furthermore chemically unstable. This means pure EO is explosive even without any amount of an oxidizer like air. Using flammable gases like ethylene oxide information on safety characteristics like flammability limits or ignition temperatures is necessarily required for an adequate concept of explosion prevention.

In a previous work it was determined in which concentrations mixtures with EO can be ignited with an effective ignition source. For this purpose, flammability limits of mixtures with EO, inert gases and air were determined experimentally in dependence of the temperature and the pressure. Furthermore a semi-empirical method for the calculation of the flammability regions was presented [1]. Methods for the calculation of safety characteristics can help to reduce laborious and expensive experimental work even if it can not replace experimental work completely.

In this work the ignition of EO and EO-mixtures by hot surfaces was studied. Hot surfaces are typical ignition sources in industrial processes. In the past, EO explosions have already been caused by hot surfaces [2][3]. Besides the avoidance of flammable mixtures the avoidance of ignition sources is another important method for explosion prevention in industrial processes.

Firstly the minimum ignition temperatures of decomposition (MITD) of pure ethylene oxide and mixtures of ethylene oxide with nitrogen and carbon dioxide were determined experimentally in closed systems without air and in dependence of the vessel volume and the pressure. The usual standards for the experimental determination of ignition temperatures [4][5] are not appropriate for this purpose because they only can be applied with air and at atmospheric pressure.
Secondly a model for calculating of MITD was developed by simulating the pressure and temperature course inside the vessel. The experimental data were used for validation. For the simulations the time dependent zero dimensional heat and mass balance equations were solved numerically.

2 Experimental Set-Up

The MITD of EO at certain pressures and of mixtures of EO with nitrogen and carbon dioxide were determined experimentally. The experiments were carried out in closed pressure resistant ignition vessels made of stainless steel. Two different cylindrical vessels with volumes of 0.2 dm$^3$ and 3 dm$^3$ were used as ignition vessels. For preparing the mixtures an additional mixing vessel of 6 dm$^3$ equipped with a fan was used. The experimental set-up for the determination of the MITD of EO is shown in figure 1.

Figure 1. Experimental set-up of the experiments.

For safety reasons the experiments were carried out in a separate shelter. The control panel (left side in figure 1) and the experimental set-up (right side in figure 1) were separated by a concrete wall. The gas mixtures were prepared in the mixing vessel according to the manometric method [6]. Then the test gas was charged in the pre-heated and evacuated ignition vessel. The pressure in the mixing vessel was adjusted in such a way, that the desired pressure in the ignition vessel was reached after pressure balance in both mixtures. The mixing vessel was closed after the filling procedure. During the filling procedure and for additional 10 minutes the pressure in the ignition vessel was measured and recorded. The criterion for an ignition was a sudden pressure rise in the pressure-time curve. After each experiment both vessels were purged with nitrogen and evacuated again. The temperature of the ignition vessel was varied in steps of 10 K until the lowest temperature was found, at which an
ignition occurs. The highest temperature at which no ignition occurs was affirmed with altogether three experiments.

### 3 Calculation Methods

The MITD of ethylene oxide was calculated by simulating pressure-time-curves. For that purpose the time dependent zero dimensional heat and mass balance equations (Equations 1 and 2) were solved numerically using COMSOL Reaction Engineering Lab.

\[
\frac{dc_i}{dt} = v_i r \\
V \sum (c_i C_{p,i}) \frac{dT}{dt} = V \Delta H - U A (T - T_0) + V \frac{dp}{dt}
\]

- \(c_i\): concentration of species i
- \(t\): time
- \(v_i\): stoichiometric factor of species i
- \(r\): reaction rate
- \(V\): vessel volume
- \(C_{p,i}\): heat capacity of species i
- \(\Delta H\): reaction enthalpy
- \(U\): heat transfer coefficient
- \(A\): heat exchange area
- \(T\): temperature
- \(T_0\): wall temperature or initial temperature

The wall temperature \(T_0\) is constant and equal to the initial temperature. In accordance to the experiments this temperature was varied in steps of 10 K in order to determine the MITD. Similar to the experiments a characteristic pressure peak occurs in the simulated pressure time curve above a certain initial temperature.

The gas mixtures were assumed to be mixed ideally, which means temperature gradients inside the vessel were neglected. Heat loss is determined by the overall heat transfer through the wall, which is characterized by the heat transfer coefficient \(U\). It is calculated from the temperature dependent material properties according to [7], which gives an empirical approach for the calculation of heat transfer coefficients at vertical curved plates taking into account natural convection. The heat transfer coefficient is also dependent on the temperature difference of the vessel wall and the gas.

The rate of heat production is mainly determined by the reaction rate. Only the decomposition of EO to the main products methane and carbon monoxide was considered using a simplified reaction kinetic according to Lifshitz et al. [8]. The physical properties of the mixtures were calculated with data from [9][10] according to [11]. Moreover an ideal behaviour of the gas phase was assumed.

### 4 Results and Discussion

The ignition criterion was very sharp in all experiments. Either there was a clear pressure peak a few seconds after the filling procedure or there was no visible pressure peak over the whole time period. In this case the pressure rises continuously and slowly indicating that a slow decomposition reaction takes place.

In figure 2 the experimentally determined MITD of EO in dependence of the initial pressure compared to the calculations are shown. In figure 3 the experimentally determined and calculated MITD of EO in
dependence of the vessel volume is shown. The experimental results in a spherical vessel of 0.55 dm$^3$ were taken from [12].

Figure 2. Experimentally determined and calculated MITD of pure EO in dependence of initial pressure for vessel volume of 3 dm$^3$.

Figure 3. Experimentally determined and calculated MITD of pure EO in dependence of vessel volume for initial pressure of 2 bara.

The MITD of EO falls with rising pressure as the concentration and thus the reaction rate rises. It also drops down with rising vessel volume as the ratio of vessel surface to vessel volume falls. The calculated results deviate from the experimental results by 10 K at the most, which correspond to one
step size at the experiments. All in all the calculations deliver results with good accuracy for the MITD of EO at pressures between 1 bar and 10 bar and for vessel volumes between 0.2 dm$^3$ and 3 dm$^3$. The calculated MITD for larger vessels are plausible, but experiments for validation were not made yet.

The good accuracy of the calculations in spite of neglecting local dependencies inside the vessel indicates natural convection is sufficiently considered through the calculation of the heat transfer coefficient in the zero-dimensional calculations. For more complex geometries, for example with built-in components, a two or even a three dimensional approach might be necessary. An accordant extension of the model is possible without greater efforts.

The simplified kinetic model [8] is obviously appropriate for the calculation of the MITD of EO. For mixtures with air or other oxidizers reaction kinetics can not be described with a simple overall decomposition reaction, but only with more complex reaction mechanisms. This can also be true for the decomposition of other chemically unstable gases like TFE without air. An implementation of such reaction mechanisms would be possible within this model without further efforts. A more complex kinetic model for the decomposition of EO that could possibly be used for mixtures of EO with air is given by [13]. Further experimental data for such mixtures are not available for validation yet.

Just as pure EO, mixtures of EO with carbon dioxide or with nitrogen play an important role in industrial processes. These gases are often used for inertisation of EO. In figure 4 the MITD of certain mixtures of EO and nitrogen as well as EO and carbon dioxide determined in a vessel of 3 dm$^3$ at an initial pressure of 1 bar are shown.

As expected the MITD rises with rising dilution of EO. But whereas the influence of a dilution with nitrogen is humble and only noticeable from fractions of 50 mole% on, dilution with carbon dioxide is much more effective. Even at fractions of 25 mole% an effect can be observed. The MITD of a mixture of 60 mole% carbon dioxide and 40 mole% EO lies 70 K higher than of pure EO. Mixtures with 75 mole% carbon dioxide could not be ignited even at temperatures up to 680 °C.
For the calculations it makes no difference whether nitrogen or carbon dioxide is used as diluents. The calculated MITD is the same in both cases. It accords well with the experimental results for EO/nitrogen-mixtures. The influence of fractions of carbon dioxide can not be expressed correctly by these calculations. Apparently the model fails using inert gases with higher heat capacities. Therefore the criterion for ignition (pressure rise peak) in the simplified model seems to be incomplete. Additionally it has to be regarded that realistic ignition is associated with flame propagation and consequently with heating up the gas mixture to the flame temperature.

References


