

# Test methods for determining explosion characteristics re-examined

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## Abstract

Detailed knowledge about the explosion indices is essential for safe and efficient operation. For optimal operation, explosion indices should be known under realistic process conditions, in other words under the prevailing temperature, pressure and turbulence levels of the process. The equipment described in this paper allows experiments to be carried out under actual process conditions within the following ranges: initial temperatures up to 400 °C, initial pressures up to 35 bar, oxygen enriched mixtures up to mixtures involving pure oxygen and under known and adjustable turbulence levels. The explosion indices can thus be determined under realistic conditions avoiding any uncertainties in extrapolation from data obtained under ambient conditions. Another major issue is to design proper safety measures. A typical example, involving the safe engineering of processes handling ethylene oxide, is illustrated with some preliminary experimental results.

## 1. Introduction.

In the chemical process industry, most processes are operated under non-ambient conditions. High pressures and temperatures are needed to maximise yields and profitability. Typical processes include the manufacture of petrochemicals, foods, pharmaceuticals, polymers and many other products. A crucial point in these processes is safety. Safe operation requires that explosion indices be known under realistic process conditions, thus at the same (high) temperature, (high) pressure and (sometimes high) turbulence levels as encountered in the process. In general, equipment and test procedures exist for measuring gas and dust explosion characteristics in air at ambient pressure and temperature. However, for conditions of high pressure and temperature, high oxygen concentration, and, in particular, known levels of turbulence, both equipment and design methods are lacking. This article describes the operation of equipment allowing gas and dust explosion measurements to be carried out under strongly non-ambient process conditions. Explosion indices, including explosion limits, Limiting Oxygen Concentration (LOC), ignition energy, maximum explosion pressure and the explosion severity index, can thus be reliably determined under realistic conditions, avoiding uncertainties in extrapolation from data obtained under ambient conditions. Additionally it is shown that previous results presented in literature by Siwek and Rosenberg [1,2] regarding the decomposition of ethylene oxide can not be satisfactorily explained using the cube-root-law as suggested.

## 2. The explosion severity index.

An example of the pressure evolution of a dust explosion in a test sphere is given in Figure 1. This explosion is obtained by injecting a dust from the dust storage canister into the explosion chamber. The pressure-time recording consists therefore of three parts, each related to a different step in the experiment. Part one represents the pressure in the explosion chamber before the injection; the pre-injection pressure of the chamber is below one bar due to the evacuation. In the second part of the curve, the pressure increases from the pre-injection pressure up to the required initial pressure. This region is bounded from the beginning of the injection process to the moment of ignition. The time elapsed between those two events is known as the ignition delay time. The injection process, roughly 30 ms, should be completed within this time interval. The delay time results in decay of turbulence: the longer the decay time, the more the initial turbulence of the mixture has decayed. Too large a delay time causes dust to settle; this is of course not preferred. The final part of the pressure time curve is generated by the explosion and will therefore be called the explosion curve (Figure 1). The explosion index  $P_{max}$  is easily found by determining the maximum pressure at the end the explosion curve. The determination of the maximum pressure rise,  $(dP/dt)_{max}$ , is found by taking the derivative of the pressure over time.

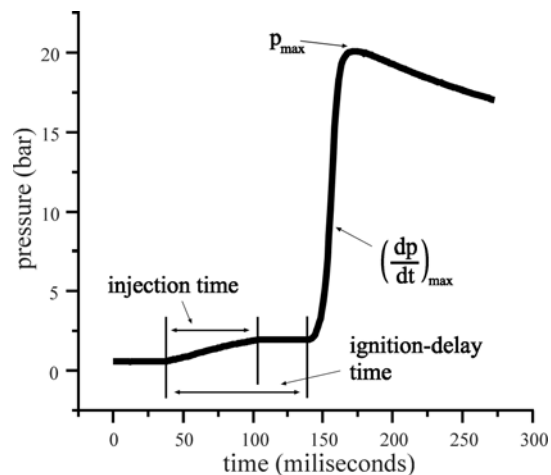


Figure 1: Pressure time recording of a dust explosion.

If the explosion occurs adiabatically, the  $P_{max}$  is independent of the volume of the tested vessel. However it must be mentioned that a vessel which is too small ( $V < 16$  litres [2]) will result in substantial heat losses and therefore in a lower measured  $P_{max}$  than that would be expected from an explosion in a larger volume. Heat losses are also the reason why the last part of the explosion curve decreases after having reached the maximum pressure. The  $(dP/dt)_{max}$  strongly depends on the volume of the vessel. When the flame thickness is negligible with respect to the radius of the test vessel, the maximum rate of pressure rise obeys the so-called ‘cube-root-law’:

$$K_{\#} = \left( \frac{dP}{dt} \right)_{\max} V^{\frac{1}{3}} \quad [ 1 ]$$

The # denotes ‘g’ for a gas explosion and ‘st’ for a dust explosion (German: staub). Although the cube-root-law is the most widely used explosion scale-up rule, its scientific value is under debate. One of the reasons is that the thickness of the flame is not taken into account; i.e. direct transition from unburned to burned is assumed. Another deficiency is that turbulence is not explicitly taken into account. Gases are tested under quiescent circumstances (no injection) and dusts only at one, not-quantified turbulence level.

The validity of the cube-root-law as a scale-up relationship between differently sized vessels is based on the following restrictions:

- The vessels in question are geometrically similar and basically spherical in form
- The flame thickness is negligible with respect to the vessel radius
- The burning velocity is the same in all volumes
- Point ignition occurs at the centre of the vessels

Crucial in the derivation of the cube-root-law is that the maximum rate of pressure rise,  $(dP/dt)_{\max}$ , occurs when the pressure attains its maximum value,  $P_{\max}$ . Such behaviour, however, is rarely found in practice. More usually, the pressure-time curve of explosions in closed spherical vessels exhibits an inflection point, with the maximum rate of pressure rise occurring before the end of the explosion. This can be explained as follows. When the flame has a finite thickness, a front and a rear of the flame can be distinguished. As the flame starts propagating, after ignition, radially from the centre of the sphere to the vessel wall, the flame will reach its maximum surface as the front of the flame reaches the wall. At this moment the rate of pressure rise attains its maximum value. However, the rear of the flame still needs to travel a certain distance to the vessel wall; this distance is equal to the flame thickness. As this happens, the combustion will continue for a time equal to the flame thickness divided by the flame speed. During this time period the temperature and thus the pressure in the vessel will continue to increase. Only when the rear of the flame reaches the vessel wall the maximum pressure of the explosion is attained.

The cube-root-law can be derived using the so-called Thin Flame Model [3]. In this model two regions (unburned and burned mixtures) are separated by an infinitely thin spherical flame front ( $r_{\text{flame}}$ ). The flame front is then a surface where a discontinuous transition takes place from unburned to burned mixture and propagates radially from the point of ignition towards the vessel wall. This model shows that the rate of pressure rise  $(dP/dt)$  increases monotonically with  $P$  and hence the maximum rate of pressure rise is attained when pressure attains its end pressure. By multiplying the maximum rate of pressure rise by the cube root of the vessel volume it is normalised with respect to the vessel volume. In practice however, gas flames, let alone dust flames, do not have an “infinitely thin” flame. A stoichiometric hydrogen/oxygen mixture under initially quiescent conditions comes closest to having an infinitely thin flame (i.e. flame thickness in the order of micrometers).

### **3. Turbulence.**

As mentioned previously, turbulence is not explicitly taken into account in the current testing methods and use of the K-factor. Gases are tested under quiescent circumstances (no injection) and dusts only at one, not-quantified turbulence level. These conditions will rarely be encountered in the process units of the process industry. In our research the turbulence levels after injection existing in the 20-litre explosion sphere were characterised using Laser Doppler Anemometry (LDA) [4]. Laser Doppler Anemometry is a technique to measure velocities of (small) particles. Since small particles ( $\pm 300$  nm) follow the flow without slip, the fluid velocity is known. Hence the turbulent nature of the flow field can be quantified. With this knowledge, one of two major missing links, turbulence, is now incorporated into the explosion science and realistic explosion indices can now be measured. The other missing link being a detailed kinetic scheme applicable for the temperature and pressure interval in question.

### **4. Equipment.**

At the Delft University of Technology a strengthened 20-litre sphere is operated (Figure 5) [5]. The strengthened sphere is a reinforced and upgraded standard 20-litre explosion sphere. In comparison with the standard 20-litre sphere, it handles a wider range of operating conditions: high initial pressures up to 35 bar (maximum final pressure 350 bar), high initial temperatures up to 400 °C and oxygen-enriched mixtures up to mixtures involving pure oxygen. This is in contrast to the internationally standardised 20 litre sphere, which is capable of withstanding a maximum pressure of 39 barg at a maximum temperature of 60 °C. The explosion chamber and storage canisters of the strengthened sphere have double walls to allow the circulation of a thermofluid for heating and cooling. The heating/cooling system is constructed in such a way, that it enables simultaneous heating or cooling of the explosion chamber and storage canister to the same temperature in an accurate way. It is also possible to heat or cool the two vessels to temperatures different from one another. The temperature of the vessels is monitored by thermocouples. The development of the explosion in the explosion chamber is traced independently by two piezo-electrical pressure transducers. For the preparation of the flammable mixtures in the equipment prior to injection and ignition, a pressure sensor is used with an accuracy of 1.5 mbar. The explosion chamber is connected to a storage canister through a duct. Three different storage canisters, depending on the amount of dust or gas that has to be injected, can be used; their volumes are 0.6, 2.0 and 6.5 litres. For standardised testing the 0.6 litre storage canister is used. A fast acting valve opens and closes the aperture of the duct within an adjustable time, called the injection time. The fast action valve should allow injection in a brief period of time and more critically, be capable of withstanding the resulting impact of an explosion. The opening and closing of the fast action valve is controlled by the working of an auxiliary piston actuated by compressed air and electromagnetic valves. The compressed air for opening and closing the fast action valve is stored in a buffer vessel. The movement of the piston is controlled by two electromagnetic valves. As mentioned earlier, the decay of turbulence after injection inside the 20-litre sphere was measured as function of time. Since we have

measured turbulence as a function of delay time, the explosion characteristics of the flammable mixture can therefore be studied under known and adjustable turbulence levels as they exist in industrial equipment by appropriately choosing the ignition delay time.

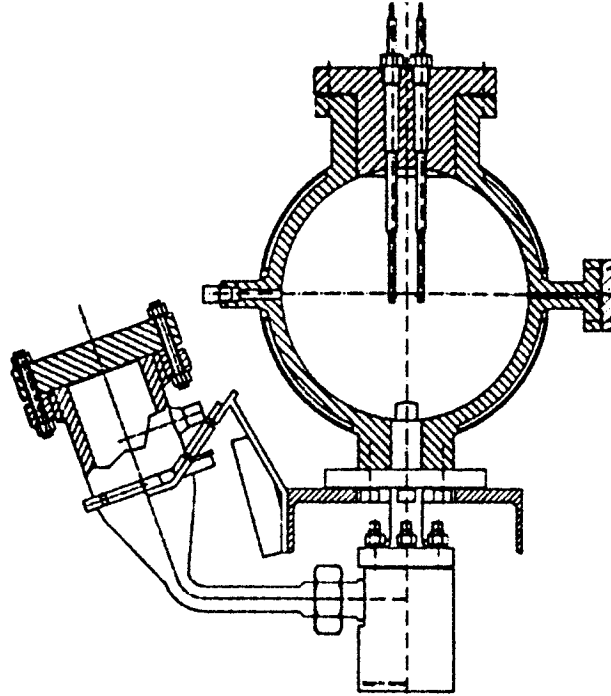


Figure 5: Schematic diagram of the strengthened 20-litre sphere.

## 5. Ethylene oxide decomposition.

Ethylene oxide is certainly one of the most versatile petrochemicals at the disposal of the process industry today. The most important uses for ethylene oxide are in the manufacture of derivatives such as ethylene glycol, ethanolamines, and surfactants. The explosive decomposition nature of ethylene oxide vapour is also well recognised. When ethylene oxide vapour is exposed to a sufficiently strong ignition source it can decompose explosively. Several studies were dedicated to the decomposition of ethylene oxide vapour and special attention was paid to the decomposition limits in diluents, most notably in nitrogen [6,7]. Other work focussed on the decomposition kinetics [8,9], thermal decomposition limits [10], and venting of decomposing ethylene oxide [11,12].

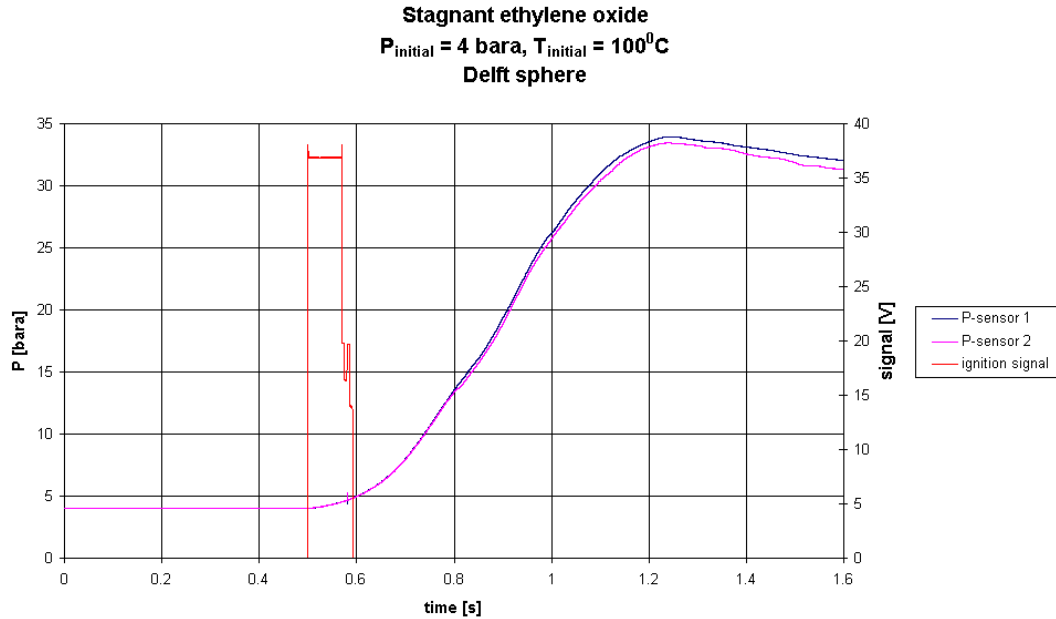
In this work special attention is paid to the work of Siwek [1,2]. Siwek performed ethylene oxide vapour decomposition experiments in three differently sized vessels (20 litre, 1 m<sup>3</sup> and 10 m<sup>3</sup>) in the initial temperature range of 40 – 200 °C and initial pressure range of 1 – 4 bara. The major conclusions from the work are:

- Maximum decomposition pressure is independent on the ignition energy applied and the vessel volume (for quiescent ethylene oxide vapour).
- The maximum rate of pressure is dependent on the ignition energy applied and the vessel volume (for quiescent ethylene oxide vapour).

- For turbulently decomposing ethylene oxide vapour the maximum decomposition pressure equals that of the quiescent decomposing ethylene oxide vapour (i.e. results independent of turbulence).
- The maximum rate of pressure rise under turbulent conditions is considerably larger than under quiescent conditions, but surprisingly independent of the turbulence intensity (high, medium or low turbulence intensity makes no difference).
- Under turbulent conditions the K value, calculated according to the cube-root-law, is independent of vessel size.

Before commenting on the above-mentioned conclusions, results are presented of some preliminary experiments conducted in the strengthened Delft sphere. The results obtained in this work are part of a large study dedicated to the decomposition of ethylene oxide. This study will include measurements of the maximum rate of pressure rise and maximum decomposition pressure as function of turbulence levels, pressure, temperature and vessel volume, effect of the location of the ignition source, effect of additives (nitrogen, argon, carbon dioxide, etc) on the decomposition characteristics, studies of the decomposition kinetics, measurement of species during and after decomposition, and modelling of the decomposition by means of computational fluid dynamics. At the end of the study, different safety systems, most notably venting, will be tested and modelled under the given conditions, including anomalies of relief and suppression devices. Furthermore, the effect of a combined gas-liquid phase on the mitigation of the decomposition reaction will be studied.

The decomposition of initially quiescent ethylene oxide was studied at 100 °C and 4 bara initial pressure. To initiate the decomposition reaction, a tungsten fused wire (0.72 J) as well as pyrotechnic ignitors of 180 Joule and 540 Joules were applied. The decomposition of pure ethylene oxide was also studied under non-quiescent conditions. The filling procedure started with the subsequent evacuation and filling with ethylene oxide of the sphere, repeated several times, to minimize the oxygen content (< 0.001%) in the sphere. After each explosion, the sphere was thoroughly cleaned and prepared for the next experiment. An example of an explosion of quiescent ethylene oxide is given in Figure 6. The results of all the quiescent experiments are summarised in Table 1. For the turbulent ethylene oxide explosions the 20-litre sphere was filled up to 3.8 bara with ethylene oxide according to the methodology described above. From the storage canister 0.2 bara of nitrogen was injected to create a turbulent flow field in the sphere, while ensuring homogeneous mixing. Ignition was, in this case, accomplished by a pyrotechnic ignitor of 180 J. The storage canister was also at 100 °C. For safety reasons, nitrogen instead of ethylene oxide was used as the injection fluid.



**Figure 6:** Decomposition of stagnant ethylene oxide. Pyrotechnic ignitor of 180 J used as initiation source. Initial pressure 4 bara, temperature 100 °C.

**Table 1.** Maximum rate of pressure rise, decomposition severity index and maximum pressure of the decomposition of stagnant ethylene oxide as a function of ignition strength.

Ignition Energy [J]	$(dP/dt)_{\text{max}}$ [bar/s]	$K_d$ [bar m/s]	$P_{\text{max}}$ [bara]
0.72	41.98	11.40	31.83
180	77.80	21.12	33.65
540	169.6	46.04	36.38

The most striking feature of Figure 6 is the fact that the curve does not show one inflection point, as is the case in a dust or gas explosion, but multiple inflection points. In dust and gas explosions that inflection point corresponds, as discussed above, to the maximum rate of pressure rise. In dust and gas explosions the flame will tend to radially propagate from the centre of the sphere to the wall of the vessel, much like an expanding soap bubble. A stoichiometric methane – air explosion in the 20 litre sphere is completed in approximately 80 ms. The complete decomposition of ethylene oxide, however, takes place much more slowly, in about 700 ms. This means that buoyancy effects become appreciable. A reliable value for the maximum rate of pressure rise can therefore not be determined. The larger the vessel, the more pronounced the buoyancy effect will become. Therefore the severity index of differently sized vessels will vary, and any direct comparison is impossible due to the multiple inflection points arising in the pressure – time curve. This, apart from the fact that the decomposition of ethylene oxide is not a “normal” explosion. To fully describe the decomposition of ethylene oxide one needs to clarify the decomposition kinetics and solve the pressure evolution accordingly.

The ignition energy also has a significant effect on the maximum rate of pressure rise and hence the  $K_d$  value as well as on the maximum decomposition pressure.  $K_d$  roughly differs a factor 4 depending on the ignition source, indicating that the ethylene oxide explosions are very sensitive to different ignition strengths. This can be explained as follows. The ignitor strength and characteristics of the ignition influence the decomposition rate of ethylene oxide. The larger the ignition strength the larger the initial ignition kernel and the higher the flow disturbance of the initially quiescent ethylene oxide atmosphere and hence the greater the enhancement of the decomposition rate. Since the decomposition of pure ethylene oxide in the 20-litre sphere takes close to 0.7 seconds (Figure 6), the decomposition process will become more adiabatic as the decomposition rate increases, as can be seen from the results in Table 1. It is assumed here that the pyrotechnic ignitor does not, through the composition of its decomposition products (inorganic salts and nitric gas phase products after initiation of the ignitor), catalytically influence the decomposition of ethylene oxide. However, in our results a distinct difference in the maximum decomposition pressure can be noticed as a function of ignition strength. In case of the turbulent decomposition of ethylene oxide, maximum rates of pressure rise well over 2000 bar/s ( $K_d > 540$ ) were obtained, and the maximum decomposition pressure was in the order of 55 bar. The entire turbulent decomposition of ethylene oxide took place in less than 200 ms. Since the decomposition is faster than the quiescent decomposition, it is more nearly adiabatic and therefore the maximum decomposition pressure is higher. The maximum pressure measured also corresponds more closely to numerical calculations of the maximum decomposition pressure based on thermodynamic properties, where adiabatic behaviour is assumed [12]. We found the maximum rate of pressure rise to be very sensitive to turbulence intensity. Siwek and Rosenberg [1,2], however, stated that for ethylene oxide the actual degree of turbulence, adjusted by the ignition delay time, was found to have no recognisable influence on the decomposition characteristics, and hence the  $K$ -value, although turbulent ethylene oxide vapour decomposed faster than ethylene oxide in the quiescent state. The degree of turbulence in each of the vessels they used was not measured. As such a comparison between the  $K_d$  values they obtained in differently size vessels can not be justified. Turbulence levels can be adjusted by varying the ignition delay time to yield  $K_d$  values that correspond with the values obtained in other, differently sized vessels.

## 6. Conclusions.

In order to improve current processes and economically develop new processes, and to facilitate a more rational design of reliable explosion prevention and protection equipment and procedures, explosion characteristics should be known not only under ambient, but also under real process conditions. An improved version of the standard 20-litre sphere was demonstrated to be capable of measuring explosion characteristics at and above ambient conditions.

Literature data on the decomposition of ethylene oxide were expanded and improved upon. Rate of pressure rise and even maximum pressures resulting from the decomposition of ethylene oxide were found to be strong functions of both turbulence level and ignition strength.



## 7. Literature.

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