Journal of Hazardous Materials

Explosive decomposition of ethylene oxide at elevated condition: effect of ignition energy, nitrogen dilution, and turbulence

A.A. Pekalski[a,*], J.F. Zevenbergen[a], M. Braithwaite[b], S.M. Lemkowitz[a], H.J. Pasman[a]

[a] *Delft University of Technology, DelfChemTech, Explosion Group, Julianalaan 136, 2628 BL Delft, The Netherlands*
[b] *RMCS, Cranfield University, Shrivenham SN6 8LA, UK*

Abstract

Experimental and theoretical investigation of explosive decomposition of ethylene oxide (EO) at fixed initial experimental parameters ($T = 100\,^\circ C$, $P = 4\,bar$) in a 20-l sphere was conducted. Safety-related parameters, namely the maximum explosion pressure, the maximum rate of pressure rise, and the K_d values, were experimentally determined for pure ethylene oxide and ethylene oxide diluted with nitrogen. The influence of the ignition energy on the explosion parameters was also studied. All these dependencies are quantified in empirical formulas. Additionally, the effect of turbulence on explosive decomposition of ethylene oxide was investigated. In contrast to previous studies, it is found that turbulence significantly influences the explosion severity parameters, mostly the rate of pressure rise. Thermodynamic models are used to calculate the maximum explosion pressure of pure and of nitrogen-diluted ethylene oxide, at different initial temperatures. Soot formation was experimentally observed. Relation between the amounts of soot formed and the explosion pressure was experimentally observed and was calculated.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Explosive decomposition of ethylene oxide; Turbulence; Explosion parameters; Nitrogen dilution; Safety; Ignition energy

1. Introduction

Ethylene oxide (EO) is a major chemical intermediate in the manufacturing of ethylene glycols. These, in turn, are the starting points for processes making a wide range of surfactants and emulsifiers. The EO molecule contains oxygen connected in a triangular structure of which the C–C bond is short and the bond angles strained. These make the EO molecule unstable, very reactive and cause serious hazards.

EO has been involved in a number of accidents, discussed by various authors [16,10,34,12,31,22,35,26].

Processes that handle EO typically operate in the region of 100–200 °C at pressures up to 15 bar in large process vessels [3,16].

The design of safe processes for the manufacture and use of EO requires considerable care and understanding of the chemistry and thermodynamics of this hazardous molecule, both in the condensed phase [28,17,11] and in the gas phase. In the gas phase, EO can decompose rapidly in the absence of air at modest temperatures and pressures. When mixed with air it can form gas mixtures that can detonate [33], a situation exacerbated by its comparatively high vapour density. However, if the ignition source is weak, the decomposition of ethylene oxide occurs as a deflagration. Several studies were dedicated to understanding the deflagrative decomposition of ethylene oxide vapour. Special attention was paid to the flammability limits of EO and its decomposition limits in diluents. Amongst other, gases like nitrogen, propylene oxide and methane were studied as diluents [17,15,8,29,30,32,2,6,19,25,4]. Other research focussed on, thermal decomposition limits [5] and venting of decomposing ethylene oxide [9,3].

* Corresponding author. Tel.: +31 15 2783725; fax: +31 15 2784945.
  E-mail address: Pekalski@tnw.tudelft.nl (A.A. Pekalski).

For safe and efficient operation involving ethylene oxide, it is essential to know the explosion indices as a function of process conditions.

The minimum amount of energy able to initiate EO vapour decomposition (minimum ignition energy, MIE) as a function of pressure, temperature and volume was investigated [14,18]. After successful ignition, the EO decomposition flame propagates causing an explosion. Its severity is described by the maximum explosion pressure (P_{max}), the maximum rate of pressure rise $(dP/dt)_{max}$, and is scaled up by the empirical cube-root-law explosion parameter K_d ($K_d = (dP/dt)_{max} V^{1/3}$). EO explosion severity indices depend on many factors, like initial pressure, temperature, turbulence level, ignition energy (IE) and concentration of an inert gas. If the concentration of the inert gas is increased and other variables are kept constant, there is a critical concentration of the inert gas above which no sustained decomposition flame propagation is possible. This concentration, in case of nitrogen, is called the limiting nitrogen concentration for EO decomposition. This value changes if one of the above-mentioned factors is varied. Increasing the ignition energy in the range from MIE up to 50 J causes a noticeable increase in the limiting nitrogen concentration for EO decomposition. A further increase, beyond 50 J, has no significant effect [32,19]. The importance of the limiting nitrogen concentration for EO decomposition is emphasized due to its application in the process industry. The most commonly used inert gas is nitrogen. However, several authors [16,14,19,32] pointed out that the presence of high nitrogen concentrations in an ethoxylation reactor gas phase reduces the reaction rate, and therefore, plant productivity. Excessive nitrogen concentration increases the production costs, while insufficient nitrogen concentration compromises safe plant operation. For processes operating at nitrogen concentrations lower than the limiting nitrogen concentration, additional safety measures must be installed, e.g., venting panels and/or pressure relief systems [3]. For their proper design, explosion severity indices are needed. Such data on EO–nitrogen mixtures at EO-concentrations in the range from pure EO vapour up to the limiting nitrogen concentration for EO decomposition, although needed for the design of explosion safety protection measures, are not available in the literature.

Proper determination of the explosion severity parameters (P_{max} and $(dP/dt)_{max}$) requires an apparatus with a volume greater than 16 l [2]. A vessel that is too small ($V < 16$ l) results in substantial heat losses, thus, affecting the measured values. Only Siwek and Rosenberg [32] performed experiments in vessels large enough to allow the determination of explosion severity indices whose values are not affected by too small size of the test apparatus. Their investigation was comprehensive and focused on establishing dependencies between the explosion severity indices (P_{max} and $(dP/dt)_{max}$) and the ignition energy, initial pressure, temperature and turbulence level. They experimentally studied pure ethylene oxide vapour decomposition in three differently sized vessels (20 l, 1 and 10 m³) in the initial temperature range of 40–200 °C and the

Table 1
Explosion severity data for pure EO

Mixture status	$(dP/dt)_{max}$ (bar/s)	K_d (bar m/s)
Quiescent	96	26
Turbulent	1500	407

$P = 4$ bar, $T = 100$ °C, IE = 250 J and $V = 0.02$ m³ [2].

initial pressure range of 1–4 bar. The major conclusions of the work are as follows:

- The maximum explosion pressure is independent of the ignition energy applied, the degree of turbulence and vessel volume.
- The maximum rate of pressure rise is dependent on the ignition energy, the degree of turbulence, temperature and vessel volume.
- For turbulently decomposing ethylene oxide vapour, the maximum decomposition pressure equals that of the quiescent decomposing ethylene oxide vapour (i.e., results are independent of turbulence).
- Under turbulent conditions, the K_d value, calculated according to the cube-root-law, is independent of vessel size.
- The initial turbulence level has no recognizable influence on EO decomposition characteristics.

Bartknecht [2] analysed the data of Siwek and Rosenberg [32], of stagnant and turbulent EO decomposition, and also concluded that turbulence had no noticeable influence. The conclusion that the initial turbulence level has no noticeable effect on the explosion characteristics is, however, very unusual, especially in view of Siwek's statement on the effect of turbulence level on the maximum rate of pressure rise. Careful re-evaluation of the experimental data presented by Bartknecht at an initial pressure of 4 bar, initial temperature of 100 °C, and ignition strength of 250 J, shows a significant difference between quiescent and turbulent EO decomposition. The measured values differ by a factor 15 (Table 1) and are therefore in conflict with the original conclusions.

Incorrect K_d values will result in an improper dimensioning of the safety protection measures in the EO handling chemical industry and thus needless financial loss.

2. Problem formulation

The aforementioned reasons prompted this research programme. The work is aimed at resolving the inconsistencies discussed and should be useful for operations involving EO processing in which the vapour space is partly or fully diluted with nitrogen. The goals were:

1. to investigate the influence of nitrogen dilution (20, 40%, v/v) on the explosion severity indices (P_{max} and $(dP/dt)_{max}$) of quiescent EO nitrogen mixtures and pure EO vapour;
2. to investigate the influence of the ignition energy on the explosion severity indices (P_{max} and $(dP/dt)_{max}$)

of quiescent pure EO vapour. Initiation of a flammable mixture by means of pyrotechnic igniters disturbs the quiescent mixture in the neighbourhood of the igniters. This disturbance creates a turbulence level at the beginning of the decomposition flame propagation process resulting in, depending on the ignition energy and mixture reactivity, a variation in the value of various explosion parameters [36]. Therefore, if a dependence of the ignition energy on the explosion severity parameters is found, it will prompt the need for further studies; and

3. to investigate the explosion severity indices (P_{max} and $(dP/dt)_{max}$) of pure EO vapour at very high turbulence levels, which would be beyond those present in industrial practice. Such data would define the highest limiting value of the severity parameters for deflagration of EO vapour.

The decomposition of initially quiescent ethylene oxide and mixtures of EO with nitrogen was studied at 100 °C and 4 bar initial pressure. To initiate the decomposition reaction, a tungsten-fused wire (0.72 J) was applied as ignition source as well as pyrotechnic igniters of 180 and 540 J.

3. Theoretical calculations

If EO vapour is ignited by a low energy ignition source, its decomposition process may be described as a deflagration. Under these conditions, explosion pressures can be readily estimated utilising routine equilibrium thermodynamics procedures to determine maximum explosion pressures for ideal gas phase and ideal condensed phase products. Thermodynamic calculations were done at different initial mixture compositions (EO and N_2), temperatures, pressures and post-decomposition products.

3.1. Species present in post explosion mixture

The set of considered species should be comprehensive and complete. Unimportant species, i.e., species present only at a very low concentration at the equilibrium stage, might be neglected, but omission of an important compound would result in incorrectly calculated values. A review was conducted to find all reported EO post-decomposition products. There is no agreement between researchers concerning the presence of soot in the post-decomposition mixture of ethylene oxide. The presence of soot was experimentally found [13,7] and included in theoretical calculations. Soot in the calculations is represented as a carbon in a solid phase, i.e., graphite (C(S)) [4,3,28]. Other species, like acetaldehyde, C_2H_2, C_3H_6, and C_4H_8, were found [23,24,21,1]. The final list of species considered in the computations consists of: C, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_8, C_2H_4O, CH_3, CH_2O, H, H_2, OH, H_2O, O, O_2, HCHO, CH_3CHO, C_2H_2, C_3H_6, C_4H_8, C_4H_8-trans, C_4H_8-cis and C(S).

3.2. Calculations

The thermodynamics of gas mixtures as well as post-explosion products at modest pressures (up to 50 bar) can be described with sufficient accuracy by ideal gas behaviour. Thermochemical equilibrium calculations have been carried out with an Equil subroutine of the Chemkin 3.6 [41]. Due to the uncertainty regarding the presence of soot in the post explosion EO-mixture, two thermodynamic models were assumed: one with and the other without soot presence.

The equilibrium pressure was calculated as a function of initial temperature for different EO–nitrogen mixtures to illustrate the change of the final to initial pressure ratio with changing of the initial temperature. In the past, a constant pressure rise ratio has been assumed for all initial temperatures. Results are presented in Figs. 1 and 2. It can be seen that
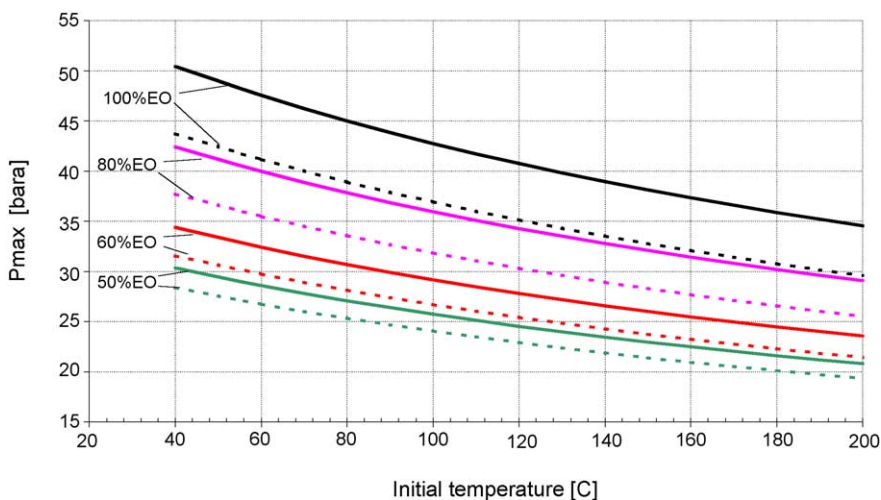

Fig. 1. Effect of initial temperature and mixture (EO–N_2) composition on the maximum equilibrium pressure. Solid line model with soot, dashed line model without soot. $P_{ini} = 4$ bar and $T_{ini} = 100$ °C.
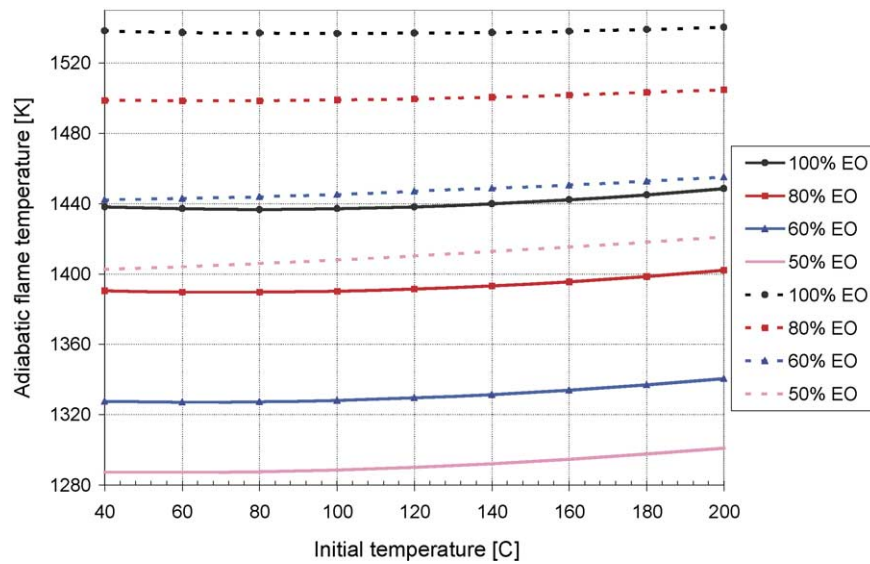
Fig. 2. Effect of initial temperature and mixture composition (EO–N_2) on the adiabatic flame temperature. Solid line model with soot, dashed line model without soot. $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.

the explosion pressure decreases with increasing temperature at constant initial pressure. Thus, the pressure ratio decreases with increasing temperature and should not be taken only as a constant value independent of changing temperature [3]. Indeed, assuming that explosion behaviour follows, at least by approximation, the perfect gas law, then it can be shown that the maximum explosion pressure decrease linearly with the reciprocal of the absolute initial temperature [38]. Such behaviour is indeed found in practice.

The equilibrium conditions of the EO–nitrogen mixture using both thermodynamic models (with and without soot present) at the initial pressure of 4 bar and temperature of

$100\,°C$ are presented in Tables 2 and 3. Only the main species at the equilibrium state (concentration above 0.01 mole%) are listed.

It can be noticed that lower values of the maximum adiabatic flame temperature are found for the thermodynamic model with soot. Equilibrium pressures, however, are higher. Since C(S) sublimates at about $3825\,°C$, it remains in the solid state and does not contribute to the gas phase volume, thus, to the explosion pressure.

For a gas mixture contained in a spherical vessel at relatively low initial pressures (e.g., below ca. 10 bar) and deflagrating this mixtures under conditions such that the flame

Table 2
Equilibrium conditions calculated with soot

Initial composition (mole%)		Equilibrium composition (mole%)							Total (%)	T_{equil} (K)	P_{equil} (bar)	No. of moles (mole)
C_2H_4O	N_2	CH_4	CO	CO_2	H_2	H_2O	N_2	Soot				
50	50	3.387	17.760	0.687	33.714	2.221	21.355	20.875	99.999	1287.26	28.27	5.28
60	40	3.562	19.645	0.604	36.683	2.102	15.304	22.097	99.998	1327.19	32.03	5.81
70	30	3.718	21.155	0.546	39.067	2.015	10.398	23.099	99.998	1360.81	35.78	6.33
80	20	3.864	22.392	0.503	41.015	1.951	6.337	23.935	99.997	1389.65	39.52	6.84
90	10	4.001	23.426	0.471	42.633	1.904	2.919	24.641	99.996	1414.77	43.26	7.36
100	0	4.132	24.305	0.447	43.994	1.871	0.000	25.247	99.995	1436.93	47.00	7.87

Table 3
Equilibrium conditions calculated without soot

Initial composition (mole%)		Equilibrium composition (mole%)								Total (%)	T_{equil} (K)	P_{equil} (bar)	No. of moles (mole)
C_2H_4O	N_2	CH_4	CO	C_2H_4	C_2H_6	H_2	C_2H_2	C_3H_6	N_2				
50	50	22.794	31.511	2.586	0.126	9.919	1.330	0.203	31.517	99.986	1404.61	26.44	4.53
60	40	24.480	34.974	2.994	0.143	12.093	1.744	0.234	23.321	99.983	1443.25	29.37	4.90
70	30	25.913	37.948	3.339	0.158	13.983	2.110	0.263	16.267	99.979	1473.62	32.24	5.26
80	20	27.154	40.531	3.634	0.172	15.630	2.430	0.289	10.135	99.976	1498.46	35.08	5.63
90	10	28.244	42.799	3.892	0.186	17.072	2.709	0.313	4.757	99.972	1519.36	37.89	6.00
100	0	29.212	44.808	4.120	0.199	18.342	2.953	0.336	0.000	99.969	1537.31	40.69	6.37

speed is well below sonic velocity (thus, precluding gas dynamic pressure effects) the explosion pressure can be estimated using the perfect gas law:

$$\frac{P_{exp}}{P_{ini}} = \left(\frac{n_{exp}}{n_{ini}}\right)\left(\frac{T_{exp}}{T_{ini}}\right)$$

The maximum explosion pressure reached depends on two ratio-terms. The first of these terms relates to the number of moles of gaseous species present relative to the number of gaseous species initially present. The second term gives the ratio of the absolute explosion temperature in the system to the initial absolute temperature [38].

The results shown in Tables 2 and 3 would seem to indicate that the first term is not negligible. In other words, a higher maximum pressure can be obtained at a lower adiabatic flame temperature due to the larger number of gaseous products formed.

4. Experimental apparatus

The test equipment used is a strengthened 20-l sphere (Fig. 3). The strengthened sphere is a reinforced and upgraded version of the standard, commercially available 20-l explosion sphere. In comparison with the standard 20-l sphere [39,40], it can handle a wider range of operating conditions. The dimensions of the equipment are identical to the standard 20-l sphere. With the strengthened 20-l sphere, it is possible to conduct experiments at process conditions, like high initial pressures, up to 35 bar, and high initial temperatures, up to 300 °C. The explosion chamber is connected to a storage canister through a duct. A fast acting valve opens and closes the borehole of the duct within an adjustable time, called the injection time. Both the explosion chamber and
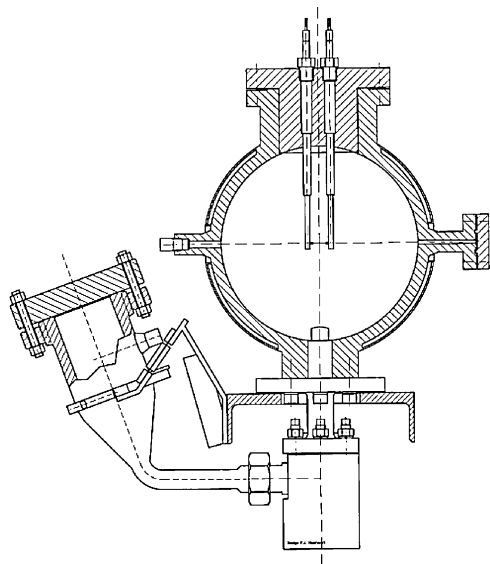

Fig. 3. Cross-section of the strengthened 20-l sphere with the storage canister on the left.

storage canister 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. It is also possible to heat or cool the vessels to temperatures different from one another. The temperature of the vessels is monitored by thermocouples. Two piezo-electrical pressure transducers trace the development of the explosion in the explosion chamber independently.

5. Decomposition experiments of stagnant EO vapour and EO–nitrogen mixtures

Quiescent explosion experiments were performed for pure ethylene oxide and ethylene oxide diluted with nitrogen.

5.1. Experimental procedure

The experimental procedure consists of three main steps. In the first step, the explosion sphere is closed and nitrogen is used to replace air in the explosion sphere. The explosion sphere is evacuated to 0.3 bar, and subsequently nitrogen is added up to 4 bar. This operation is repeated three times ensuring that the oxygen concentration remaining is not higher than 0.0088% (v/v), i.e., 0.5 cm^3 at the end of the third repetition. In the second step, the necessary amount of ethylene oxide is added. In the third step, the required amount of nitrogen is added. Its addition is initially rapid to facilitate the mixing process. The mixture is left undisturbed for 5 min. Since the density ratio between EO and N$_2$ is small, i.e., equal to 1.38, the two compounds can be mixed well by means of diffusion within the allowed time.

For experiments with pure EO, only the first step remains unchanged. In the second, final step, EO is added up to 4 bar and released to atmospheric pressure. This procedure is performed three times, ensuring low nitrogen content.

In all quiescent experiments the mixture is left undisturbed for at least 2 min so that remaining turbulent gas motions decay. Then the mixture is ignited, and pressure signals are recorded.

5.2. Experimental results

Table 4 summarises the experimental decomposition results of EO–nitrogen mixtures, and Table 5 shows the effect of ignition energy variation on the decomposition of pure EO vapour. The explosion time is defined as the time interval between the moment the mixture is ignited and the moment the maximum pressure value is reached. Every experiment was performed at least twice. The results are reproducible. The biggest reproducibility discrepancy was observed for the 60% EO–nitrogen mixture. In all experiments with an EO concentration above 60%, fluffy soot was formed in small quantities in the post decomposition mixture. The amount of

Table 4
Effect of nitrogen content on the explosion severity indices of ethylene oxide

Experiment no.	Composition EO/N$_2$ (EO%)	Ignition energy (J)	(dP/dt)$_{max}$ (bar/s)			P_{max} (bar)			K_d (bar m/s)	Experimental time (s)	Remarks
			Sensor 1	Sensor 2	Average	Sensor 1	Sensor 2	Average			
2	60	180	37.36	37.20	37.28	20.42	20.18	20.30	10.12	1.30	
3	60	180	33.69	35.95	34.82	19.48	20.70	20.09	9.45	1.72	
4	60	180	23.09	22.93	23.01	17.59	17.49	17.54	6.25	1.73	
5	60	180	29.56	30.06	29.81	18.72	18.76	18.74	8.09	1.51	
6	60	180	16.40	15.84	16.12	17.31	17.13	17.22	4.38	3.48	
7	60	180	20.95	19.53	20.24	17.28	17.41	17.35	5.49	2.77	
8	80	180	33.96	31.93	32.95	25.72	25.12	25.42	8.94	1.28	Soot is present
9	80	180	40.01	42.15	41.08	26.07	25.12	25.60	11.15	1.19	Soot is present
10	80	180	53.23	48.83	51.03	27.63	26.73	27.18	13.85	0.99	Soot is present
21	80	180	44.16	41.46	42.81	26.15	25.73	25.94	11.62	1.22	Soot is present
18	100	180	75.21	77.07	76.14	33.92	33.01	33.47	20.67	0.72	Soot is present
19	100	180	78.85	79.59	79.22	33.98	33.47	33.73	21.50	0.74	Soot is present
27	100	180	80.13	81.28	80.71	33.92	33.05	33.49	21.91	0.72	Soot is present

Table 5
Effect of ignition strength on the explosion severity indices of pure ethylene oxide

Experiment no.	Ignition energy (J)	(dP/dt)$_{max}$ (bar/s)			P_{max} (bar)			K_d (bar m/s)	Experimental time (s)	Remarks
		Sensor 1	Sensor 2	Average	Sensor 1	Sensor 2	Average			
23	0.71	40.01	40.17	40.09	31.86	31.64	31.75	10.88	1.34	Soot is present
25	0.72	40.36	43.05	41.71	31.88	31.84	31.86	11.32	1.33	Soot is present
18	180	75.21	77.07	76.14	33.92	33.01	33.47	20.67	0.72	Soot is present
19	180	78.85	79.59	79.22	33.98	33.47	33.73	21.50	0.74	Soot is present
27	180	80.13	81.28	80.71	33.92	33.05	33.49	21.91	0.72	Soot is present
28	540	166.57	176.85	171.71	36.54	36.1	36.32	46.61	0.42	Soot is present
29	540	175.28	171.80	173.54	36.8	36.03	36.42	47.11	0.41	Soot is present

soot increased with a higher initial concentration of EO in the mixture.

Our experimentally determined K_d value for the decomposition of quiescent pure EO vapour is very similar to the experimental data of Siwek presented by Barknecht ([2] p. 73 and 75). Siwek measured a K_d value of 26 bar m/s comparing to our value of 21 bar m/s. The difference can be easily attributed to the difference in the ignition energy used; 250 J used by Siwek and 180 J used by us. When, even higher ignition energy was used (540 J), the K_d value increased to 46.88 bar m/s, overshooting the value of Siwek. Substitution of the ignition energy used by Siwek into an equation derived from Fig. 9 yields a K_d value of 26.7 bar m/s, closely matching the results of Siwek.

Examples of a few tests for different EO–nitrogen mixtures for both sensors are presented in Fig. 4. It can be noticed that the results become less reproducible with increasing nitrogen concentration. Especially for the mixture composition with 40% nitrogen, the pressure–time curves do not overlap each other, exhibit different explosion times, and have even different shapes.

Fig. 5 shows the effect of the ignition energy on the decomposition of pure EO vapour. A clear correlation between the explosion time and the magnitude of the ignition energy is visible. The largest ignition energy applied results in the shortest explosion time and the highest maximum explosion pressure.

6. Observations and discussion of stagnant EO decomposition experiments

Table 6 and Fig. 6 compare explosion pressures calculated by the thermodynamic model with and without the presence of soot in the post explosion products and experimentally obtained results. As anticipated, the experimentally determined explosion pressures are lower than those theoretically calculated for the adiabatic situation. The differences between the theoretical and experimental values are possibly due to the occurrence of heat losses in the 20-l explosion sphere, partial equilibrium being attained during the explosion, and incomplete decomposition of EO. The difference between the theoretical and the experimental value increases with increasing nitrogen content in the mixture. Higher nitrogen content slows down the explosion rate. Hence, it prolongs the explosion time (Table 4), and therefore, increases the heat losses. Increased heat losses reduce the maximum temperature achieved, which, in turn, lowers the pressure and increases the amount of unconverted EO. The difference is larger for the thermodynamic model with soot present.
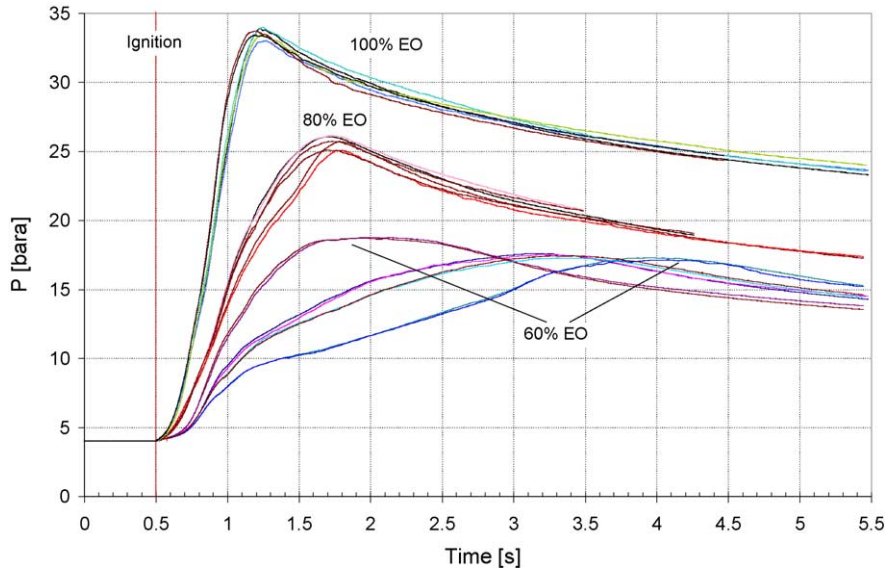
Fig. 4. Pressure–time history for EO–nitrogen mixtures of different initial composition. $P_{ini} = 4$ bar, $T_{ini} = 100\,°C$ and IE = 180 J.

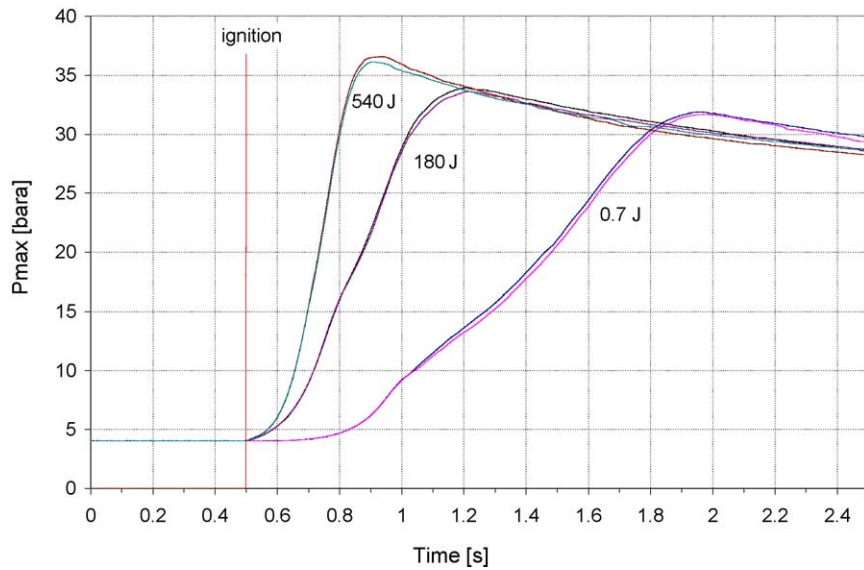

Fig. 5. Pressure time history for pure EO vapour explosions initiated by different ignition energy. $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.

Considering Tables 4 and 5, and Figs. 6–10 the following can be observed:

1. The maximum explosion pressure and the maximum rate of pressure-rise increase with increasing EO concentration

in the EO–nitrogen mixture. Within the investigated range, the dependence is linear (Figs. 6 and 7). The higher the EO concentration, the higher the measured explosion indices.

2. For pure EO, the maximum explosion pressure and the maximum rate of pressure-rise increase with increasing

Table 6
Maximum explosion pressure of pure ethylene oxide decomposition (IE = 180 J)

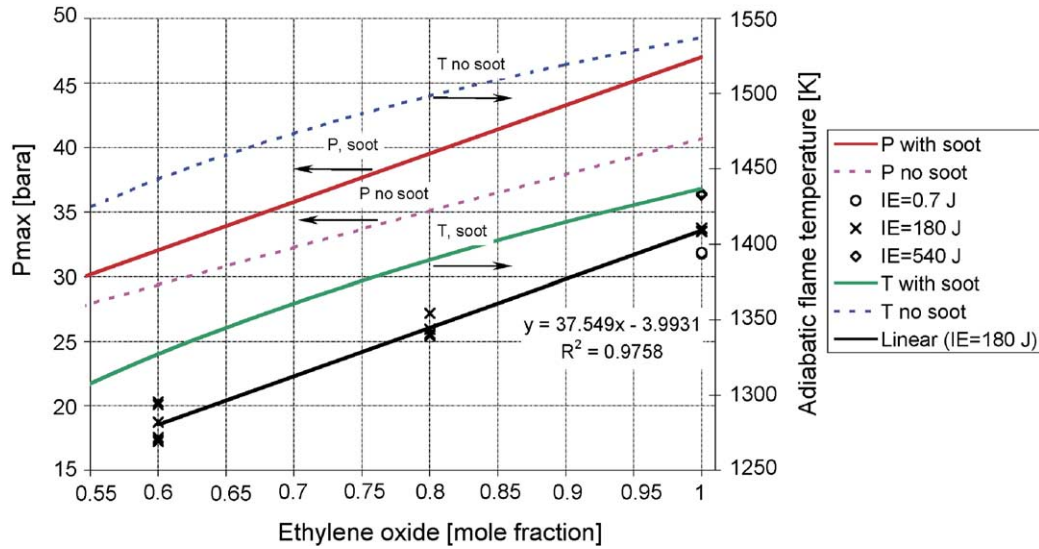| Initial composition (% EO)	P (atm)			Difference model–experiments	
	Model with soot	Model no soot	Experiment	With soot	No soot
100	43.32	37.41	33.73	9.90	3.99
80	36.43	32.27	25.94	10.39	6.23
60	29.53	27.03	20.30	10.99	8.49
50	26.07	24.35	–	–	–

Fig. 6. Effect of mixture composition on P_{max}; comparison between theoretical and experimental values. $P_{ini} = 4$ bar, $T_{ini} = 100\,°C$; lines—theoretical calculations (solid—model with soot, dashed—model without soot), points—experimental results ignited by different ignition energy.

ignition energy [37]. The higher the ignition strength, the higher the maximum explosion pressure and the maximum rate of pressure-rise. Within the investigated range, this dependence is linear (Figs. 8 and 9). A very strong correlation exists between the applied ignition energy, the mixture composition and the explosion time. The higher the ignition energy and EO concentration in the mixture, the shorter the explosion time (Fig. 10).

3. The explosion time changes significantly with changes in the EO/N$_2$ mixture composition. A mixture of 60% EO and 40% nitrogen has the longest explosion time; pure EO has the shortest.

4. The presence of soot in the post-explosion mixture is observed for experiments in which the EO concentration is 80% (v/v) or higher.

All investigated dependencies are linear relations and are given in Table 7. These can be used for explosion severity parameters prediction within the range considered in this work. The best approximation is the influence of the ignition energy on the explosion pressure ($R^2 = 0.9931$) and the worst is the influence of nitrogen dilution on the maximum rate of pressure rise ($R^2 = 0.8575$). The value of R^2 shows how well the linear approximation fits the experimental results.

The first and third dependency is fully in agreement with what is expected. Higher concentrations of non-reactive nitrogen increase the heat sink capacity of the explosive mixture, thus, lowering the decomposition flame temperature. The lowering of the flame temperature reduces the laminar burning velocity. The lowering of the decomposition flame speed reduces the maximum rate of pressure rise. As the du-
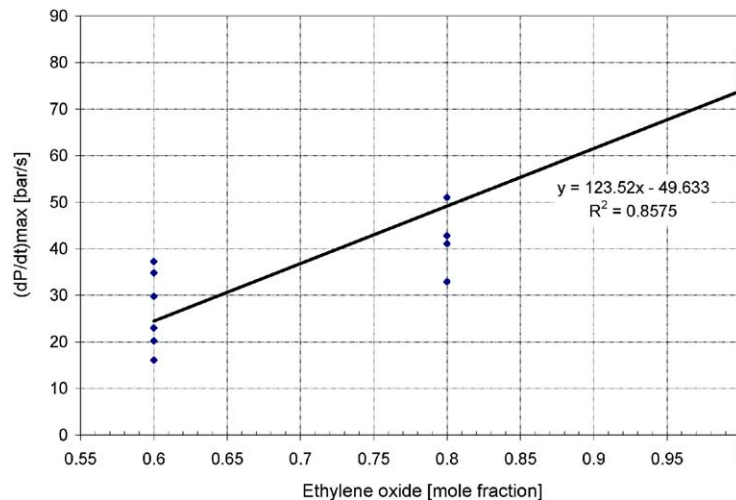

Fig. 7. Effect of the mixture composition (EO–N$_2$) on the maximum rate of pressure rise. IE = 180 J, $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.
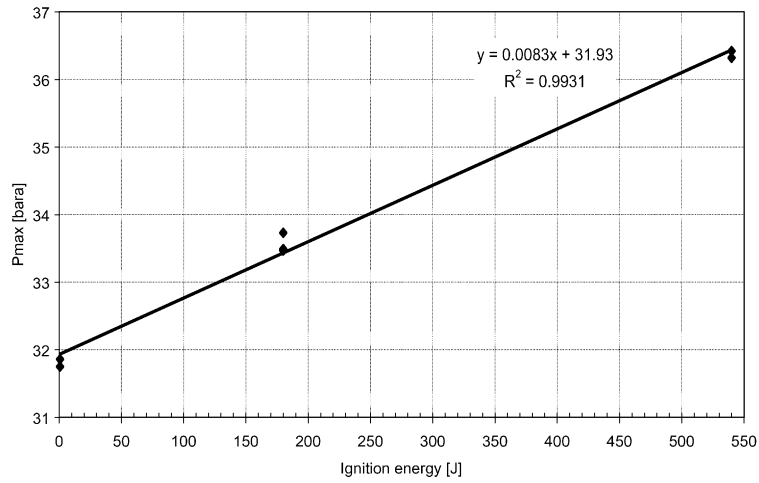
Fig. 8. Effect of the ignition energy strength on the explosion pressure. pure EO, $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.
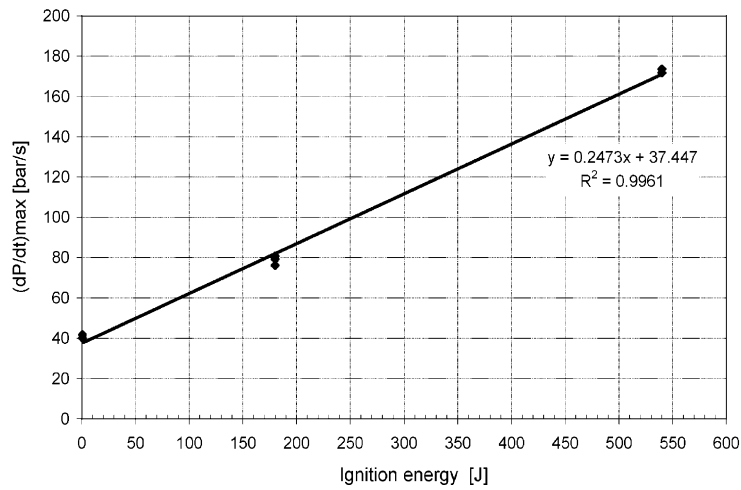

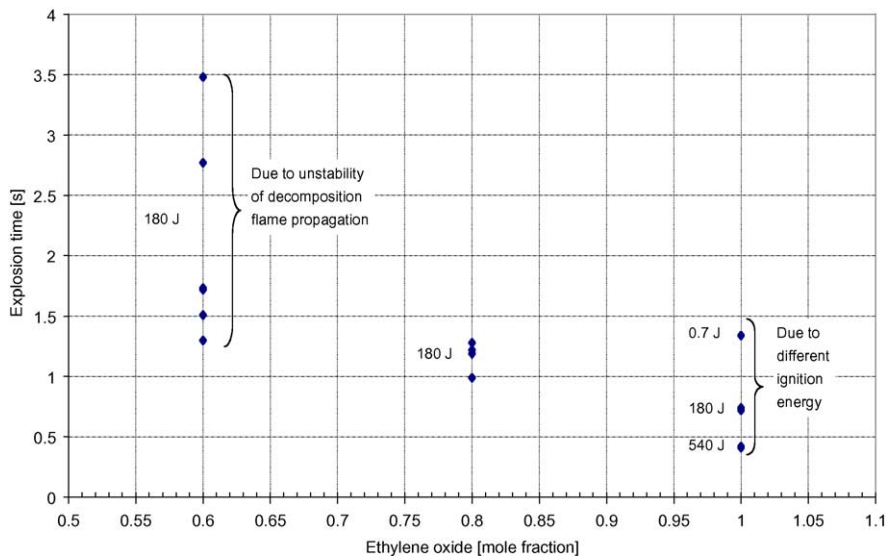Fig. 9. Effect of the ignition strength on the maximum rate of pressure rise. pure EO, $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.

Fig. 10. Effect of the mixture composition on the explosion time. EO–N_2, $P_{ini} = 4$ bar and $T_{ini} = 100°C$.

Table 7
Explosion indices dependencies for EO decomposition

Dependency	Formula	Applicability range	R^2	Figure
Influence of N_2 dilution on P_{max} (bar)	$P_{max} = 37.549 \, (Yeo) - 3.9931$	$Yeo \in \langle 0.6, 1.0 \rangle$; IE = 180 J	0.9758	6
Influence of N_2 dilution on $(dP/dt)_{max}$ (bar/s)	$(dP/dt)_{max} = 123.52 \, (Yeo) - 49.633$	$Yeo \in \langle 0.6, 1.0 \rangle$; IE = 180 J	0.8575	7
Influence of IE on P_{max} (bar)	$P_{max} = 0.0083 \, (IE) + 31.93$	IE = 0.7–540 J; Yeo = 1.0	0.9931	8
Influence of IE on $(dP/dt)_{max}$ (bar/s)	$(dP/dt)_{max} = 0.2473 \, (IE) + 37.447$	IE = 0.7–540 J; Yeo = 1.0	0.9722	9

$P_{ini} = 4 \, bar$, $T_{ini} = 100\,°C$.

ration time of the explosion becomes longer, the heat losses to the walls of the vessel increase. These increased heat losses lower the maximum explosion temperature and thus form an additional factor in reducing the maximum explosion pressure. In a similar way, the second dependency is explained. The higher the ignition strength, the higher the locally created turbulence intensity ahead of the propagating flame front in the incipient moment of propagation [36]. The turbulence enhances the instantaneous reaction area of the decomposition flame, increasing the heat release rate. As a consequence, a higher decomposition flame temperature is reached, thus, a higher maximum rate of pressure rise (fourth dependency) and maximum explosion pressure.

Dependence of the maximum explosion pressure on the ignition energy, although not noticed by Siwek and Rosenberg [32], was also observed by Britton [4]. He investigated the limiting dilution concentrations of nitrogen and propylene oxide for EO decomposition at an initial pressure of 6.5 bar and an initial temperature of 165 °C. Britton noticed a significant influence of different type of ignition sources, ignition energies and turbulence intensity on the explosion pressure. For a mixture composition of 52–52.6 mole% of nitrogen in EO, the results are presented in Table 8. The maximum explosion pressure and the maximum rate of pressure-rise increase with higher ignition energy as well as the initial turbulence intensity.

It can be envisaged that if a sufficient concentration of inert gas (nitrogen) is present in an EO mixture, the heat absorbed by the large heat sink capacity of this inert gas coupled with the reduction of net EO decomposition rate due to dilution is so great that the resultant flame temperature is too low to sustain stable decomposition flame propagation. Because the decomposition flame has become unstable, the decomposition flame front is easily suppressed (quenched) in colder regions of the mixture, but, of course, enhanced in hotter regions. In other words, as the decomposition flame becomes increasingly unstable, flame propagation behaviour changes

from deterministic to probabilistic. As a consequence, the explosion behaviour of mixtures rich in nitrogen (i.e., greater than 40 mole%), exhibits poorly reproducible (i.e., varying shape) pressure–time curves for the same initial conditions (Fig. 4). Additionally, variation of the explosion time is significant, i.e., from 0.68 to 3.48 s (Table 4). This mixture composition is close to the limiting nitrogen concentration for EO decomposition. The pressure rise of the 60mole%/40 mole% EO/N2 mixture exhibits the highest rate of pressure rise at the beginning of the explosion. For flammable mixtures with low laminar burning velocities, for which the explosion time is long, the buoyancy effect contributes more significantly to the explosion process than is the case for mixtures with high burning velocities. The flammable mixture is ignited in the centre of the explosion sphere. After the ignition, the density difference between the hot burned gas and the cold unburnt gas forms the buoyancy force, which causes the decomposition flame front to propagate upwards in the upper half of the explosion sphere. Therefore, the upwards-propagating decomposition flame front is the sum of the burning velocity and the buoyancy-induced velocity of the upward movement, while the buoyancy force opposes the downwards-propagating decomposition flame. Thus, the characteristic of the propagating decomposition flame is changing in the course of the explosion, showing a higher reaction rate (pressure-rise rate) at the beginning of the EO decomposition process (predominantly upwards flame propagation) and lower reaction rate at the time of the downward propagation. Especially during the downward propagation, the decomposition flame is distorted more easily compared to its upward propagation. For this reason the downward propagation is slower and is also more chaotic (i.e., less deterministic) in nature. Such a chaotic decomposition flame front is mirrored in a prolonged explosion (Fig. 11). Consequently, a greater variation in explosion pressure–time behaviour (Fig. 4), longer explosion time, and a slower rate of pressure-rise are found.

The fourth observation, the presence of soot in the post explosion EO mixture, is significant. Soot presence is not experimentally observed for EO/nitrogen mixtures of 60 mole% of EO, but for mixtures with higher EO concentrations. The theoretical calculations of Table 2 and Fig. 12 suggest the presence of soot in the entire investigated range of the EO–nitrogen mixture composition.

This observation suggests the following: (1) for the 60mole%/40 mole% EO/N2 mixture, the decomposition process is far from equilibrium conditions; in addition, it has the longest reaction (explosion) time and greatest heat losses; or
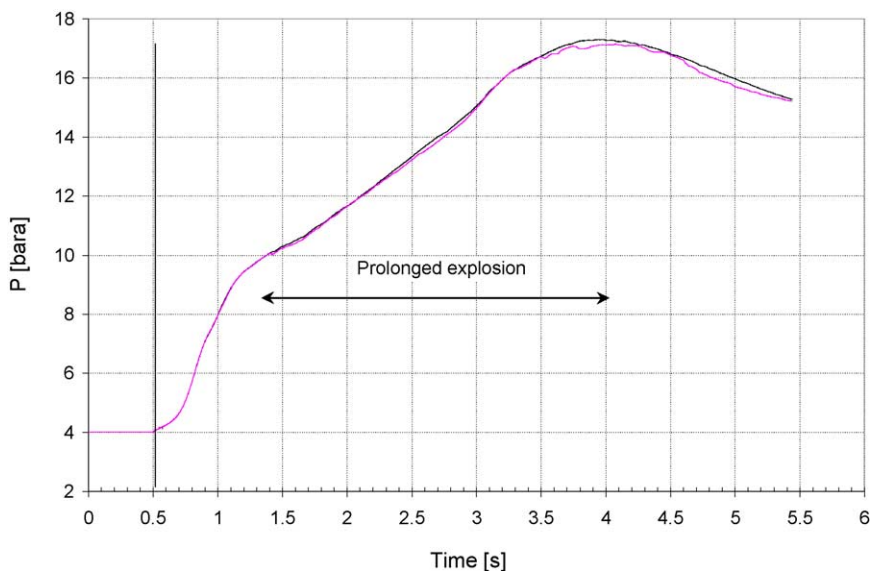
Table 8
Summary of experiment ignited by different ignition types (52–52.6 mole% EO in N_2)

Ignition type	K_d (bar m/s)	P_{max} (bar)	Mixture status
Hot wire	4	12.8	Stagnant
EO flame	9	25.9	Stagnant
Gunpowder	19	29.9	Stagnant
Gunpowder	88	33.7	Turbulent

$P_{ini} = 6.5 \, bar$, $T_{ini} = 165\,°C$ [4].

Fig. 11. Pressure development for 60mole%/40 mole% of EO/N2 mixture. $P_{ini} = 4$ bar and $T_{ini} = 100\,^{\circ}C$.

(2) changes in the initial composition of the mixture cause changes in the decomposition reaction path (i.e., cause a different reaction mechanism). The flame temperature is dependent on the initial composition of the EO–nitrogen mixture. Temperature has a strong influence on the reaction paths of a hydrocarbon–oxidiser system [27]. Therefore, the maximum temperature of the mixture is constrained by its initial composition. Since only above a certain EO concentration soot was observed in the experiments, it seems that formation of soot during the EO decomposition is sensitive to the flame temperature changes, which, in turn, changes the decomposition mechanism of EO and thus its kinetics. One may, thus, ask the following question: what is the effect of soot concentration (for the same EO mixture composition) on the measured value of the maximum explosion pressure? In order to answer this question, as an approximation, equilibrium calculations were

performed for pure EO vapour for the same initial conditions ($P_{ini} = 4$ bar and $T_{ini} = 100\,^{\circ}C$). The calculations were constrained such that the requested amount of soot was present at the equilibrium stage (forced equilibrium). The results are presented in Table 9 and in Fig. 13.

With a higher amount of soot, the adiabatic flame temperature increases. The maximum pressure also first increases, reaching its maximum at 0.45 mole fraction of soot in the mixture, and then decreases. For the unconstrained equilibrium calculation, the soot mole fraction is 0.252 and the explosion pressure is 42.7 bar. The change in the soot concentration strongly affects the maximum pressure.

With respect to our second and third observations, one may ask an additional question: What is the minimum required volume of an experimental apparatus such that heat losses can be neglected in the EO decomposition process?
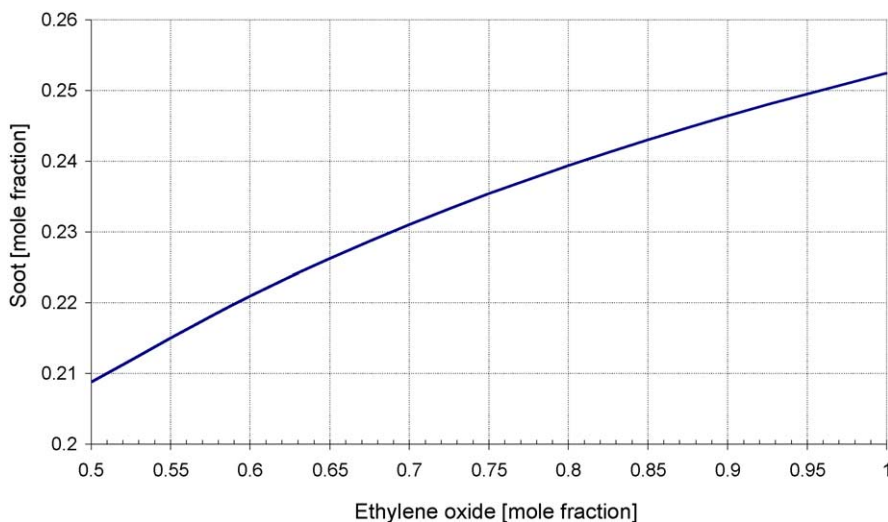

Fig. 12. Calculated mole fraction of soot presence at equilibrium state as a function of nitrogen dilution in EO mixture. $P_{ini} = 4$ bar and $T_{ini} = 100\,^{\circ}C$.

Table 9
Forced equilibrium results of pure EO with different composition of soot at the equilibrium state

| Equilibrium composition (mole%)							Total (%)	T_{equil} (K)	P_{max} (bar)
CH_4	CO	CO_2	H	H_2	H_2O	Soot			
3.831	24.383	0.408	0.000	44.447	1.720	25.208	99.9959	1437.13	42.74
1.939	21.912	0.588	0.000	45.178	2.881	27.499	99.9986	1452.29	43.39
0.606	19.249	0.751	0.000	44.842	4.551	29.999	99.9995	1506.50	44.59
0.124	16.639	0.862	0.000	43.176	6.700	32.499	99.9997	1602.14	46.16
0.025	14.089	0.911	0.001	40.872	9.101	34.999	99.9998	1712.24	47.59
0.006	11.595	0.904	0.003	38.392	11.599	37.500	99.9998	1821.13	48.68
0.002	9.154	0.846	0.006	35.839	14.155	39.999	99.9997	1925.94	49.42
0.000	6.762	0.735	0.012	33.224	16.766	42.500	99.9993	2026.54	49.83
0.000	4.428	0.566	0.021	30.548	19.435	45.000	99.9983	2122.95	49.93
0.000	2.164	0.327	0.033	27.798	22.174	47.500	99.9961	2215.26	49.73
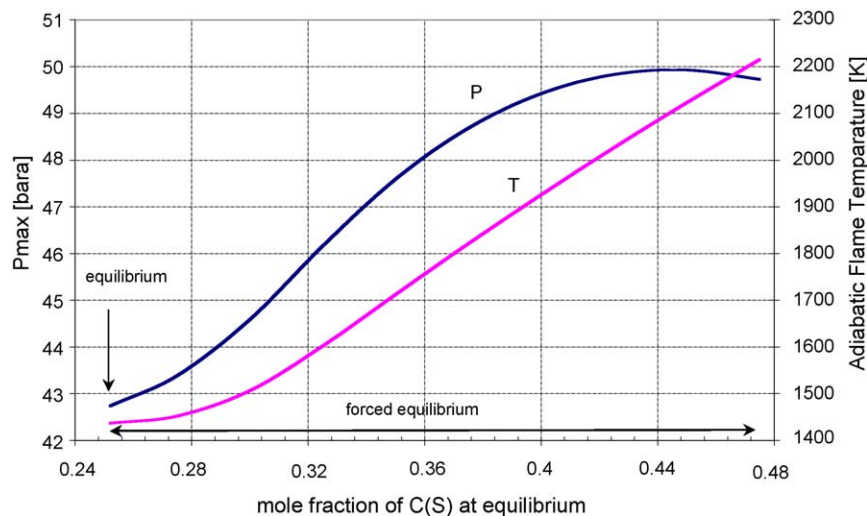
Fig. 13. Equilibrium pressure and adiabatic flame temperature as a function of soot concentration in the constrained equilibrium. $P_{ini} = 4$ bar and $T_{ini} = 100\,°C$.

The volume of Britton's experimental apparatus was 30 times larger than the 20-l explosion sphere. Nevertheless, the maximum explosion pressures were far below the theoretically calculated values and the explosion time varied significantly. Based on all the available experimental evidence it can be stated that if the reactivity of an investigated mixture is low, there will always be significant internal heat losses irrespective of even higher volumes of the experimental vessels. This is because the buoyancy force that is always induced by an ignition source. If the mixture is barely reactive, the buoyancy force is the dominating force causing the upward flame propagation. The barely propagating flame propagates to the top of the vessel and is quenched due to heat losses, consequently only a fraction of the flammable mixture is converted. In such situations, the scaling up of experiments to even larger volumes (i.e., greater than 600 l) does not cause combustion to occur in a more adiabatic way, as it does for highly reactive mixtures. For the case of a very slow, barely propagating flame experiments in larger vessels will therefore not change the nature of the flame propagation, as heat losses to the top parts of the vessel will always remain. However, combustion studies in larger vessels do offer interesting possibilities. These relate to studying the effects of accumu-lation of the reacting gas in the upper parts of the vessel and consequent heating of the unburned mixture due to radiation, convection, conduction and compression. All of these in turn relate to the moment that the flame reverses direction and propagates downwardly.

7. Decomposition of turbulent EO

The decomposition of stagnant EO vapour is a clear function of ignition energy, as can be seen in Figs. 8 and 9. As concluded in [36], the energy liberated by a pyrotechnic ignitor disturbs the quiescent gas layers in the neighbourhood of the ignitor in the unburned mixture ahead of the propagating flame. The turbulence intensity that is created is proportional to the amount of energy released by the ignitor. Therefore, the found dependence of the maximum rate of pressure rise on the ignition strength might suggest that the turbulence intensity influence the EO decomposition. This would be in agreement with the results obtained by Britton [4]. He reported on the influence of the ignition energy, and ignitor type on EO decomposition. Additionally, he reported on the influence of turbulence induced by stirring prior to ignition

on the explosion pressure and the maximum rate of pressure rise (see Table 8). However, both Siwek and Rosenberg [32] and Barknecht [2] disregarded the effect of turbulence on EO decomposition. To resolve the disagreement, it was decided that in the current work significantly high turbulence intensity would be created prior to ignition.

8. Theoretical calculations

Britton [4] obtained interesting results for turbulently decomposing ethylene oxide. His experimentally determined explosion pressures are higher than the theoretically calculated values for adiabatic conditions. If both these theoretical and experimental results are correct, they suggest that at certain experimental conditions (due to turbulence) the explosion pressure is increased by some undefined means that is not considered in the adiabatic thermochemical equilibrium approach. If true, this would be a very significant finding.

The thermochemical equilibrium model assumes adiabatic behaviour and formation of equilibrium-defined concentrations of post explosion compounds and their expansion due to the temperature rise caused by the liberated heat. This approach reproduces deflagrations (dynamic effects are neglected) in closed systems well and gives the highest possible attainable explosion pressure. Turbulent conditions could lower the heat losses such that the experimental system becomes more adiabatic, but the theoretical values should not be exceeded. Exceeding the theoretical values would suggest that there is either an unknown energy source that causes a higher explosion pressure, or an error, either in the experimental procedure or in the theoretically calculated equilibrium values.

Therefore, the equilibrium calculations of Britton were re-calculated to check their validity. The theoretical values so obtained are higher than the values of Britton (see Fig. 14). The difference between Britton's and our theoretically calcu-lated equilibrium pressures most likely originates from either differences in the chemical species considered or the thermo-dynamic values used for the calculations.

9. Experimental observations and discussion

The experimental procedure was largely identical as described in Section 5.1, but with one exception. The conditions of high turbulence were created by a rapid injection of a small amount (5%, v/v) of nitrogen into the stagnant EO vapour present in the explosion sphere prior to ignition. The rapid injection creates a turbulence level that starts to decay after the completion of the injection. In this specific case, the nitrogen injection caused the ethylene oxide present in the duct between the storage canister and the explosion sphere to decompose. This was done to boost the turbulence level in the explosion sphere. A pyrotechnic ignitor of 180 J was used as the ignition source.

It is realized that turbulence intensity induced by such injection method cannot be quantified. However, for the pur-poses here, such quantification, while desirable, is not strictly necessary. This is because the goal was to investigate whether the hypothesis of Siwek and Bartknecht, i.e., that turbulence does not affect the decomposition of EO, could be validated or not. For this purpose, achieving a significant level of turbu-lence is necessary and sufficient, and this was accomplished by the injection method used.

The measured explosion pressure, in the 20-l explosion sphere of the turbulent pure ethylene oxide equalled 58 bar. About 20 times more soot was formed, in the post explo-sion mixture, in case of turbulent EO decomposition com-pared to quiescent EO decomposition. Comparisons of the EO decomposition explosion indices at quiescent and turbu-lent conditions (average values) are presented in Table 10. A significant change can be observed for the maximum rate of pressure rise and consequently the K_d value (factor 33).
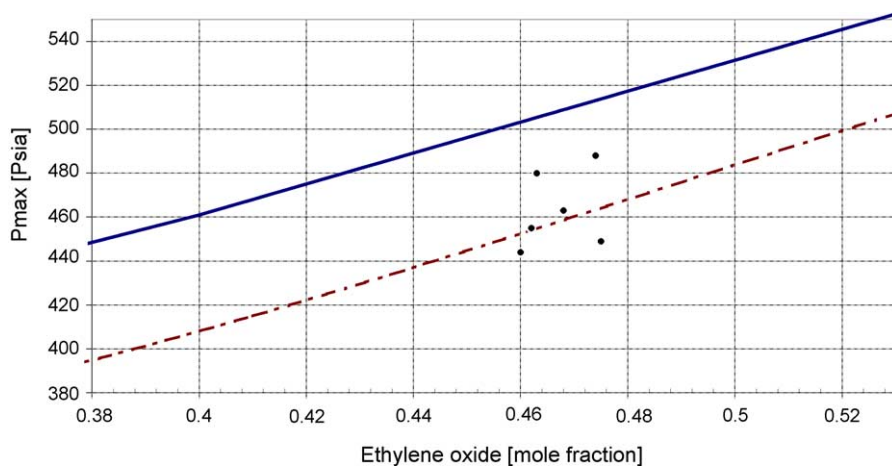

Fig. 14. Comparison of the turbulent experimental data (EO–nitrogen) and theoretically calculated values, as found by Britton (dashed line) and TUD (solid line); points show experimental results of Britton. $P_{ini} = 6.5$ bar and $T_{ini} = 165\,^\circ$C.

Table 10
Explosion severity data for EO decomposition

Mixture status	P_{max} (bar)	$(dP/dt)_{max}$ (bar/s)	K_d (bar m/s)
Quiescent (pure EO)	33.56	78.69	21.36
Turbulent (5% N_2)	58	2581.06	700.61

$P = 4$ bar, $T = 100\,^{\circ}$C and IE $= 180$ J.

Contrary to conclusions presented in the work of Siwek and Rosenberg [32] and Bartknecht [2], that the initial turbulence level is insignificant for EO decomposition, it was found that turbulence does indeed strongly affect the explosive decomposition of pure EO vapour, more specifically the maximum rate of pressure rise and the explosion pressure. This finding is in agreement with work of Britton [4].

The maximum explosion pressure is affected considerably by the state of the mixture: 33.56 and 58 bar for quiescent and turbulent decomposition, respectively. The highest attainable explosion pressure for EO decomposition, initially at 4 bar, is 49.93 bar, irrespective of the soot concentration in the post explosion mixture (see Fig. 13 and Table 9). The formation of a larger amount of soot under turbulent conditions increases the calculated explosion pressure but not to the value of 58 bar. A plausible explanation of the high explosion pressure can be attributed to fact that the high turbulence level, created in the explosion sphere by decomposing the ethylene oxide in the duct, increased the initial pressure of the mixture prior to ignition. The initial pressure was 5.7 bar and not 4 bar. The hot decomposition products emanating from the duct increased the initial pressure but did not ignite the ethylene oxide vapour in the explosion sphere.

In order to confirm the experimentally measured explosion pressure value, two extreme calculation approaches were considered at the initial pressure of 5.7 bar. In the first approach, the decomposition products of EO were assumed to be inert and are represented by nitrogen. In the second approach, it was assumed that a small and non-significant fraction of EO decomposed causing the increase of the initial pressure inside the explosion vessel prior to the ignition. Hence, the mixture inside the explosion sphere consist of nitrogen an ethylene oxide. The amount of injected nitrogen is known (5% at an initial pressure of 4 bar corresponds to a value of 3.51% at an initial pressure of 5.7 bar). In both approaches it was assumed that soot was either present or absent in the system. The calculation results are presented in Table 11.

Table 11
Maximum explosion pressure calculations for turbulent EO decomposition by two approaches

	Approach 1		Approach 2	
	Without soot	With soot	Without soot	With soot
P_{max} (bar)	43.67	47.25	55.62	62.05
T_{equil} (K)	1417.1	1370.4	1497.3	1410.0

As can be seen, the experimentally determined explosion pressure lies between the two calculated scenarios giving the credibility to the experimental value. It may be concluded that the higher initial pressure (5.7 bar), due to decomposition of ethylene oxide in the duct, is responsible for the higher than initially calculated value of 49.93 bar, which is based on an initial pressure of 4 bar. A significant effect of the turbulence level on the maximum rate of pressure rise and hence on K_d cannot be explained by a small difference (factor 1.43) in the initial pressure. The K_d value obtained for quiescently decomposing EO vapour is 22 bar m/s and for turbulently decomposing EO vapour 701 bar m/s (factor 33). This pressure difference appeared as an undesired effect of the chosen experimental method for the high turbulence level creation and does not have a significant effect on the main investigated hypothesis.

The discrepancies between results of Siwek and obtained in this work possibly could be explained by the method Siwek used to create turbulence prior to ignition. If too low pre-injection pressure difference between the storage canister and the explosion vessel was used the resulting turbulence level would be too low to observe a noticeable differences between turbulent and quiescent EO decomposition. Since Siwek injected only 5% (v/v) of nitrogen to the 20-l explosion sphere, this explanation is very plausible. The difficulty in creation of turbulence of significant intensity prior to ignition would especially apply to large-volume vessels where a higher amount of injection gas is needed. After completion of the nitrogen blast to explosion vessel created turbulence intensity decays over time. The moment a flammable mixture is ignited with respect to the moment the nitrogen blast enters the explosion vessel is called the ignition delay time. The ignition delay time corresponds the turbulence decay after the injection. Therefore, another possibility is that the ignition delay time was not chosen correctly (i.e., was too long) hence the mixture under investigation might be almost stagnant at the moment of ignition. In both cases of the explanation attempts of the results of Siwek, the effect is the same: non-significant turbulence intensity at the moment of ignition. However, the experimental results of Siwek presented by Bartknecht (Table 1) clearly show a difference between stagnant and turbulent EO decomposition. It is, thus, recommended to perform a systematic study on the effect of initial turbulence level on the explosive decomposition of EO vapour.

10. Conclusions for stagnant and turbulent EO decomposition

In this work, explosive decomposition of ethylene oxide in the 20-l explosion sphere was studied. Pure ethylene oxide or diluted with nitrogen was ignited in the centre of the explosion sphere by means of fused wire and pyrotechnic ignitiors. For pure, stagnant ethylene oxide vapour the ignition energy was varied from 0.71 to 580 J. The main points of the work may be summarised as follows:

(1) Explosion severity parameters (P_{max}, $(\mathrm{d}P/\mathrm{d}t)_{max}$ and K_d) have been determined for pure EO.

(2) The effect of nitrogen on reducing the explosion parameters of ethylene oxide vapour diluted with nitrogen has been quantified. This knowledge is useful for designing proper protection measures for use in equipment handling EO in which the concentration of nitrogen is lower than the limiting nitrogen concentration.

(3) The influence of the ignition energy and nitrogen dilution on the explosion severity indices for EO vapour has been established and quantified. The quantified dependencies found, may be used for predicting explosion severity parameters, but only within the investigated range of this work.

(4) Turbulence affects the explosion pressure and strongly affects the maximum rate of pressure rise hence the K_d value. Relative to the values of the quiescent mixture, turbulence increased the maximum rate of pressure rise by a factor of almost 33.

(5) A comparison between themochemical models with or without soot presence on the maximum explosion pressure and the adiabatic flame temperature was theoretically studied. Soot presence yields higher explosion pressures and lower adiabatic flame temperatures compared to the thermodynamic model without soot presence.

(6) Different amounts of soot were found in the post explosion mixtures, these depend on ethylene oxide concentrations in nitrogen and turbulence. Calculations of constrained equilibrium, i.e., with imposed soot concentration at the equilibrium state, show that explosion pressures increase with increasing soot formation, reaching a maximum value, and then decreasing at even higher soot concentrations.

(7) Experiments with 60 mole% EO resulted in no soot formation. Above that value, soot formation was always found. These results would seem to indicate a change in the decomposition reaction mechanism of ethylene oxide at higher EO concentrations due to different values of the flame temperature.

(8) Based on experimental results, we doubt the utility of scale up experiments to larger vessels containing barely reactive mixtures, e.g., mixtures close to the limiting nitrogen concentration. We base this doubt on our belief that for these mixtures the dominating post-ignition influence is the buoyancy effect and not phenomena related to the combustion process itself, such as the burning velocity or flame speed.

Acknowledgements

References

[1] R.R. Baldwin, A. Keen, R.W. Walker, Studies of the decomposition of oxirane and of its addition to slowly reacting mixtures of hydrogen and oxygen at 480 °C, J. Chem. Soc. Faraday Trans. 180 (2) (1984) 435.

[2] W. Bartknecht, Explosionsschutz: Grundlagen und Anwendung, Springer–Verlag, 1993, pp. 72, 321.

[3] M. Braithwaite, B. Dobson, C.A. Potter, A.A. Pekalski, J.F. Zevenbergen, B. Scarlett, Explosion safety engineering in ethoxylation reactors, in: Proceedings of the 3rd International Seminar on Fire and Explosion Hazards, Lake Windermere, England, 10–14 April, 2000.

[4] L.G. Britton, Use of propylene oxide versus nitrogen as an ethylene oxide diluent, Process Safety Prog. 19 (4) (2000) 199.

[5] L.G. Britton, Thermal stability and deflagration of ethylene oxide, Plant/Operations Prog. 9 (1990) 75.

[6] J.L. Brockwell, Prediction of decomposition limits for ethylene oxide-nitrogen vapor mixtures, Plant/Operations Prog. 9 (1990) 98.

[7] F.A. Burden, J.H. Burgoyne, Proc. R. Soc. London A 199 (1949) 328.

[8] J.H. Burgoyne, E. Belt, R. Muir, Explosive decomposition of ethylene oxide vapor under pressure, in: Proceedings of the Symposium on Chemical Process Hazards, Spec. Reference Plant Design, Manchcster, 1960, pp. 30–36, CAN 59:21589 AN 1963:421589.

[9] P. Canu, R. Rota, S. Carra, Application to ethylene oxide deflagrations of a general model for vented explosions, La Rivista dei Combustibili 45 (1991) 89.

[10] P. Cardillo, N. Mazzei, A. Lunghi, Ethylene oxide and its reactions: thermodynamic and safety aspects, La Rivista dei Combustibili 52 (3) (1998) 115.

[11] L.D. Chen, G.M. Faeth, Initiation and properties of decomposition waves in liquid ethylene oxide, Combustion Flame 40 (1981) 13.

[12] Explosion at the BASF Antwerp Ethylene Oxide/Glycol plant, Loss Prevention Bulletin 1000, August 1991, 1 p.

[13] R. Friedman, E. Burke, A study of the ethylene oxide decomposition flame, in: Proceedings of the 5th International Symposium on Combustion, 1954.

[14] M. Glor, R. Siwek, Proceedings of the Seventh International Symposium on Loss Prevention and Safety Promotion in the Process Industries S May 1992 No. 78, Taormina, Italy, 1992.

[15] H. Grosse-Wortman, Explosive decomposition of ethylene oxide and ethylene oxide–nitrogen mixtures, Chem. Ing. Tech. 42 (2) (1970) 85.

[16] J.L. Gustin, Proceedings of the 10th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Stockholm, Sweden, June, 2001, p. 427.

[17] L.G. Hess, V.V. Tilton, Ethylene oxide—hazards and methods of handling, Ind. Eng. Chem. 42 (6) (1950) 1251.

[18] G. Hostache, W. Ebner, Spontaneous decomposition of ethylene oxide. Influence of inerting and vessel size on the final pressure. Energies of ignition, Chem. Ing. Tech. 63 (1991) 1262.

[19] R.K. June, R.F. Dye, Explosive decomposition of ethylene oxide, Plant/Operations Prog. 9 (1990) 67.

[21] A. Lifshitz, H.B. Hamou, Thermal reactions of cyclic ethers at high temperatures. 1. Pyrolysis of ethylene oxide behind reflected shocks, J. Phys. Chem. 87 (10) (1983) 1782.

[22] B.E. Melin, Loss Prevention Bulletin 1000 (1991) 13.

[23] F.A. Meskens, Methods for the preparation of acetals from alcohols or oxiranes and carbonyl compounds, Synthesis 7 (1981) 501.

[24] K.H. Mueller, W.D. Walters, The thermal decomposition of ethylene oxide, J. Am. Chem. Soc. 73 (1951) 1458.

[25] T. Ogawa, A. Miyake, H. Matsuo, Proceedings of the 7th International Symposium on Loss Prevention and Safety Promotion, vol. 1, 1992, pp. 14.1–14.13.

[26] G. Ondrey, Chem. Eng. 99 (3) (1992) 37.

[27] A.A. Pekalski, J.F. Zevenbergen, H.J. Pasman, S.M. Lemkowitz, A.E. Dahoe, B. Scarlett, The relation of cool flames and auto-ignition

phenomena to process safety at elevated pressure and temperature, J. Hazard Mater. 93 (2002) 93.

[28] B. Pesetsky, J.N. Cawse, W.T. Vyn, Liquid phase decomposition of ethylene oxide, Loss Prev. 13 (1980) 123.

[29] B. Pesetsky, R.D. Best, Methane diluent requirements for ethylene oxide storage and handling, Loss Prev. 13 (1980) 132.

[30] E.G. Plett, Flammability of gaseous mixtures of ethylene oxide, nitrogen, and air, Plant/Operation Prog. 3 (3) (1984) 190.

[31] V. Schliephake, H. Giesbrecht, U. Loffler, Proceedings of the 7th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Taormina, Italy, No. 8, May, 1992.

[32] R. Siwek, E. Rosenberg, Proceedings of the 6th International Symposium on Loss Prevention and Safety Promotion, 1989, pp. 52.1–52.15.

[33] P. Thibault, L.G. Britton, F. Zhang, Deflagration and detonation of ethylene oxide vapor in pipelines, Process Safety Prog. 19 (3) (2000) 125.

[34] J.E. Troyan, R.Y. Levine, Ethylene oxide explosion at Doe Run, Loss Prev. 2 (1968) 125.

[35] G.A. Viera, L.L. Simpson, B.C. Ream, Chem. Eng. Progress (August) (1993) 66.

[36] G. Zhen, W. Leuckel, Effects of ignitors and turbulence on dust explosions, J. Loss Prev. Process Ind. 10 (1997) 317.

[37] J.F. Zevenbergen, A.A. Pekalski, S. van den Ban, B. Dobson, M. Braithwaite, S.M. Lemkowitz, H.J. Pasman, B Scarlett, Test methods for determining explosion characteristics re-examined, in: Proceedings of the Mary Kay O'Connor Process Safety Center Symposium, College Station, Texas, USA, 2000.

[38] S.M. Lemkowitz, R.M. Schotte, Explosion theory, NPT Process Technol. 2 (March–April) (1999) 19.

[39] ASTM E1226-94, Standard test method for pressure and rate of pressure rise for combustible dusts.

[40] ISO 6184-2:1985 Explosion Protection Systems—Part 2. Determination of Explosion Indices of Combustible Gases in Air.

[41] http://www.reactiondesign.com.