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Ignition of combustible/air mixtures by small radiatively heated surfaces ¹

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Abstract

Optical radiation as an ignition source in potentially explosive atmospheres was investigated for a number of explosive mixtures with respect to the most important case occurring in practice, i.e., absorption of the radiation by a solid target. Iron oxide was used as the target material. The combustibles were selected in compliance with the well-known temperature classes and apparatus groups to allow a useful graduation of the power limits to be applied. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical radiation may become an ignition source in potentially explosive atmospheres if the radiated power or energy is sufficiently high. Optical radiation must, therefore, be taken into account as a potential ignition source in compliance with the European Directive 94/9/EC [1] that contains a list of ignition sources including optical radiation. The basic standard EN 1127-1 [2] on explosion prevention and protection also requires the consideration of this ignition source but gives no information about quantitative limits of radiated power or energy. Mainly three ignition mechanisms can play a role here. Either the radiation is absorbed by the explosive mixture itself (and

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Table 1

Minimum radiant ignition powers ($\lambda = 1064$ nm) for iron oxide targets (absorptivity of 0.82 at 1064 nm). Minimum ignition energies, auto-ignition temperatures and maximum experimental safe gaps are taken from Ref. [18]

Group according to EN 50014	Combustible in brackets: increased mixture temperature	Minimum ignition energy (MIE) [mJ]	Auto-ignition temperature (AIT) [°C]	Maximum experimental safe gap (MESG) [mm]	Concentration of combustible at minimum ignition power [vol.%]	Minimum ignition power (400-µm fibre) [mW]	Minimum ignition power (62.5-µm fibre) [mW]
IIA	methane	0.28	595	1.14	5.0	1125	304
	isopropyl alcohol		425	0.99	4.5	660	273
	<i>n</i> -pentane	0.28	260	0.93	3.0	847	315
	propane	0.25	470	0.92	5.0	842	250
	<i>n</i> -heptane (110°C)	0.24	220	0.91	3.0	502	-
	methane/hydrogen		595 ^a	0.90 ^b	6.0	848	259
IIB	diethyl ether/ <i>n</i> -heptane (110°C)		200^{a}	0.90 ^b	4.0	658	-
	tetra-hydrofurane		230	0.87	6.0	-	267
	diethyl ether	0.19	175	0.87	12.0	127	89
	propanal (110°C)		190	0.84	2.0	617	-
	ethene	0.082	425	0.65	7.0	494	202
	methane/hydrogen		565 ^a	0.50 ^b	7.0	401	163
IIC	carbon disulphide	0.009	95	0.37	1.5	149	50
	ethine	0.019	305	0.37	25.0	167	110
	hydrogen	0.016	560	0.29	10.0	331	140

^aAuto-ignition temperature calculated through IGNITEMP [20]. ^bMaximum experimental safe gap calculated according to Ref. [19].

there leads to a local temperature increase or photochemical processes with subsequent ignition) or focused laser radiation leads to the formation of a plasma capable of causing ignition. As far as continuous-wave (CW) radiation is concerned, the most important case in practice is absorption of the radiation by a solid target, resulting in the target's heated surface becoming an ignition source [3-8]. In view of this mechanism, limiting values for continuous-wave radiation sources intended for use in potentially explosive atmospheres have been determined within the framework of a European cooperative project [9]. Project work concerned above all radiation sources with small diameters, such as optical fibres. Various radiation sources, target materials and explosive mixtures were investigated to obtain minimum values for the radiant power and irradiance capable of causing ignition. For continuous-wave radiation sources in the visible and near infrared region, 50 mW has been found to be the lowest igniting radiant power, including explosive mixtures with very low minimum ignition energies and auto-ignition temperatures. Several publications [9–16] have reported on this project.

However, the project did not result in a sufficiently differentiated classification of the explosive mixtures with regard to this ignition source. It seems reasonable to correlate this hot surface ignition phenomena to the well-known auto-ignition temperatures of the combustibles. Additional investigations were performed to check whether such a correlation is also applicable to ignition by very small, hot bodies. In combination with the ignition temperature, the influence of flame propagation (expressed by the groups IIA, IIB and IIC according to EN 50014 [17]; see Table 1) on the radiant ignition powers was taken into account.

2. Experimental

The experimental set-up has been described in detail in *PTB-Bericht* W-67 [15]. The ignition vessel outlined therein was replaced by a glass cylinder of 50 cm in height and 15 cm in diameter (see Fig. 1). Most of the experiments were carried out in a quiescent mixture at ambient pressure and at a temperature of $(52 \pm 2)^{\circ}$ C, some of them at 110°C with liquids with lower vapour pressure (see Table 1). These temperatures were chosen



Fig. 1. Experimental set-up for gas/vapour ignition tests with optical fibre delivering radiated power.



Fig. 2. Radiant ignition power as function of the composition of the propane/air mixture. Ignition source is an iron oxide layer at the fibre end. LEL: lower explosion limit; UEL: upper explosion limit.

to avoid condensation of the vapours even in rich mixtures and most of all to be well above the upper limit of the ambient temperature range for ordinary explosion protected equipment (40°C). Ignition was triggered in the lower part of the vessel by an irradiated iron oxide coating at the end of an optical fibre, into which the radiation of a Nd:YAG laser ($\lambda = 1064$ nm) was launched. For this purpose, the laser radiation was first fed into a primary fibre of greater diameter and then, via a beam splitter with known split ratio, subdivided to two similar fibres. One of these fibres was coated with iron oxide, thus serving as the ignition source, whereas the second fibre allowed the actual power determination. The iron oxide was BASF Eisenoxid schwarz 0095 which is FeMnO₃. It was chosen due to its relatively high absorptivity of 0.82 at 1064 nm, its thermal stability even at high temperatures that are obtained during ignition experiments and due to its good adhesive properties when preparing the target. During the experiment, the power was increased by changing the position of the primary fibre in relation to the focal point of the laser radiation until ignition took place.

To reduce the experimental effort, only fibres of 62.5 μ m and 400 μ m in diameter were used since the previous project had shown that a lower igniting radiant power is not to be expected with fibres of smaller core diameters.

In order to determine the most easily ignitable mixture, concentrations of all combustibles were varied within the explosion limits during the 400 μ m fibre experiments. Fig. 2 shows propane as an example, together with 62.5 μ m fibre experiments. In the case of the other combustibles, only the most easily ignitable mixture determined in this way was ignited with the 62.5- μ m fibre.

3. Results

Table 1 shows the explosive mixtures investigated, together with their characteristic safety data. As found in the previous project, the igniting radiant power decreases with decreasing diameter of the optical fibre. On the other hand, the irradiance (and

correspondingly the target temperature) required for ignition increases with decreasing diameter. This dependence is especially pronounced in the case of simple hydrocarbons where the igniting radiant power using a 62.5-µm fibre was less than one-third of the power required with the 400-µm fibre. This is clearly demonstrated with methane as shown in Fig. 3 and Table 2. To explain the linear relationship between igniting radiant power and diameter of the ignition source, Dubaniewicz et al. [21] proposed a simplified model resulting in a correlation of

 $P_{\text{Laser}} = A + Br_0.$

In this equation P_{Laser} is the total minimum laser power for ignition of the combustible gas mixture, and r_0 is the radius of the irradiated particle. The constant parameter *A* depends on the gas thermal diffusivity and the "thermal pressure" needed to cause the combustion reactions to rapidly accelerate. *B* depends on thermal diffusivities of gas and fibre, emissivity of the particle, thermal conductivities of gas and fibre, minimum energy densities, the gas initial temperature and time to maintain the igniting temperature.

Fig. 3 indicates that in agreement with the results of the previous project, this linear relationship does not hold for very small fibre diameters ($< 100 \ \mu$ m). Fig. 4 confirms this observation for all combustibles under investigation. This is due to increasing heat loss from the hot spot to the fibre claddings, if the core diameter is very small, so that the effective ignition source dimensions are larger than the core diameter. A second reason is that below a distinct heat source diameter, which is small compared to the quenching distance, minimum igniting irradiances rise, while the corresponding minimum igniting radiant powers tend to a constant value [10].

The data in Fig. 3 show good agreement although experimental conditions in target material and mixture temperature differ. Work with coal targets are in progress to check the influence of the combustibility of the target material on the ignition.



Fig. 3. Minimum radiant ignition powers obtained with heated particles and methane/air mixtures taken from the literature. The data and experimental conditions are given in Table 2.

	Fibre diameter [µm]	Target material	Mixture concentration [vol.%]	Temperature	Optical ignition power [mW]	Optical ignition irradiance [mW/mm ²]
Zhang et al. [8]	50	40 μm appin coal	8		300	152789
This work	62.5	iron oxide	5	$(52 \pm 2)^{\circ}C$	304	99088
Zhang et al. [8]	100	40 µm appin coal	8		360	45837
Dubaniewicz et al. [21]	200	iron oxide-krytox	7		600	19099
This work	400	iron oxide	5	$(52 \pm 2)^{\circ}C$	1126	8960
Dubaniewicz et al. [21]	400	iron oxide-krytox	7		1100	8754
Dubaniewicz et al. [21]	800	iron oxide-krytox	7		2200	4377

Table 2 Minimum radiant ignition powers for methane/air mixtures in Fig. 3



Fig. 4. Minimum igniting radiant power vs. irradiated area. With regard to a safety margin 35 mW can be found as a safe level for very small areas and 5 mW mm⁻² for larger areas. Data taken from Table 1 and Ref. [15].

To demonstrate the influence of the mixture temperature on the minimum igniting radiant power, experiments were carried out with diethyl ether. The results are given in Fig. 5. For this particular combustible, the minimum igniting radiant power decreases rapidly with increasing mixture temperature. This stresses the need to perform the experiments under controlled temperature conditions and to indicate temperature conditions when defining safe limits of power or power density.



Fig. 5. Minimum igniting radiant power vs. temperature of a diethyl ether/air mixture of 12% by volume. A thin layer of black iron oxide at the end of a fibre optic cable (core diameter: 62.5μ m) was irradiated from backwards and acted as ignition source.

4. Conclusions

The measurements confirmed the finding of the previous project, i.e., the values of the minimum igniting radiant power of the combustibles under investigation did not fall below the limiting value of 50 mW [9,15,16]. For combustibles of group IIA according to EN 50014 and with auto-ignition temperatures above 200°C, ignition took place only above 200 mW as can be seen from Table 1. One should take into account that fibres coated with combustible materials such as coal may decrease or increase the minimum igniting power. When deducing safe limit values from these results by applying a safety margin, among others, the absorptivity and the combustibility of the target material as well as the mixture temperature should be considered. These safe limits will be drawn up after all results of the partners of the current project covering different experimental techniques have been combined and assessed.

In the previous project, a radiant power of 35 mW or an irradiance of 5 mW mm⁻² were recommended as safe limiting values under atmospheric conditions for the assumed ignition by a non-reactive hot surface, taking a safety margin into account. Explosive mixtures with very low minimum ignition energies and auto-ignition temperatures like carbon disulphide and diethyl ether were included as well. The measurements reported here demonstrate that for some industrially important flammable liquids and gases these limits can be relaxed. As an example, a power limit of 150 mW including a large safety margin compared to the lowest igniting power value found (see Figs. 3 and 4; Table 2) was proposed for fibre optic instrumentation to be used in mines, where explosive methane/air mixtures (and coal dust/air mixtures) may occur [22].

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References

- [1] Directive 94/9/EC on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres, Annex II, No. 1.3.1.
- [2] EN 1127:1997, Explosive atmospheres explosion prevention and protection: Part 1. Basic concepts and methodology.
- [3] G. Tortoishell, in: P. Langenbeck, H.A. McLeod (Eds.), Process optical measurements and industrial methods, Proc. SPIE, 1990, Vol. 1266, pp. 115–124.
- [4] S.R. Moore, F.J. Weinberg, Proc. R. Soc. London, Ser. A 385 (1983) 373-387.
- [5] S.R. Moore, F.J. Weinberg, Proc. R. Soc. London, Ser. A 409 (1987) 1-20.
- [6] F.B. Carleton, F.J. Weinberg, in: P. McGeehin (Ed.), Fibre Optics '90, Proc. SPIE, 1990, Vol. 1314, pp. 298–306.
- [7] P.C. Hills, P.J. Samson, I. Webster, Electr. Electron. Eng. 10 (3) (1990) 207-220.
- [8] D. Zhang, P.C. Hills, C. Zheng, T.F. Wall, P. Samson, 24th Int. Symp. Combustion, 1992, pp. 1761–1767.

- [9] P. McGeehin, Optical techniques in industrial measurement: safety in hazardous environments, EUR-Report, EC 16011 EN, Brussels, 1995.
- [10] J. Adler, F.B. Carleton, F.J. Weinberg, Proc. R. Soc. London, Ser. A 440 (1993) 443.
- [11] F.B. Carleton, F.J. Weinberg, Proc. R. Soc. London, Ser. A 447 (1994) 513-526.
- [12] C.J. Hildyard, Theoretical studies of ignition in flammable atmospheres, PhD thesis, University of Leeds, 1993.
- [13] J.D.B. Smith, Ignition hazard in flammable atmospheres, PhD thesis, University of Leeds, 1996.
- [14] H. Bothe, H.K. Cammenga, M.M. Welzel, Loss Prevention and Safety Promotion in the Process Industries, Proc. 8th Int. Symp., Antwerp, Belgium, 1995, Vol. II, pp. 327–337.
- [15] M.M. Welzel, Entzündung von explosionsfähigen Dampf/Luft- und Gas/Luft-Gemischen durch kontinuierliche optische Strahlung, PTB-Bericht W-67, Wirtschaftsverlag NW, Bremerhaven, 1996.
- [16] H. Bothe, H.K. Cammenga, M.M. Welzel, Loss Prevention and Safety Promotion in the Process Industries, Proc. 9th Int. Symp., Barcelona, Spain, 1998, Vol. 2, pp. 860–869.
- [17] EN 50014, Electrical apparatus for potentially explosive atmospheres, general requirements, 1994.
- [18] DECHEMA, PTB, BAM: ChemSafe: Sicherheitstechnische Datenbank, STN Datenbank, Karlsruhe, 1995.
- [19] E. Brandes, G. März, T. Redeker, Normspaltweiten von Mehr-Brennstoffkomponenten-Gemischen in Abhängigkeit von der Brennstoffzusammensetzung, PTB-Bericht W-69, Wirtschaftsverlag NW, Bremerhaven, 1997.
- [20] D. Oberhagemann, H. Schecker, Chem. Ing. Techn. 60 (1988) 428–429.
- [21] T.H. Dubaniewicz, L. Kenneth, L. Cashdollar, G.M. Green, R.F. Chaiken, Proc. Colloq. on gas, vapor, hybrid and fuel-air explosions, 1998, 218–236.
- [22] prEN 50303, Group I, Category M1 equipment intended to remain functional in atmospheres endangered by firedamp and/or coal dust, CEN/CENELEC final voting document, 1999.