

THE MAXIMUM EXPERIMENTAL SAFE GAP: THE EFFECTS OF OXYGEN ENRICHMENT AND THE INFLUENCE OF REACTION KINETICS

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Summary

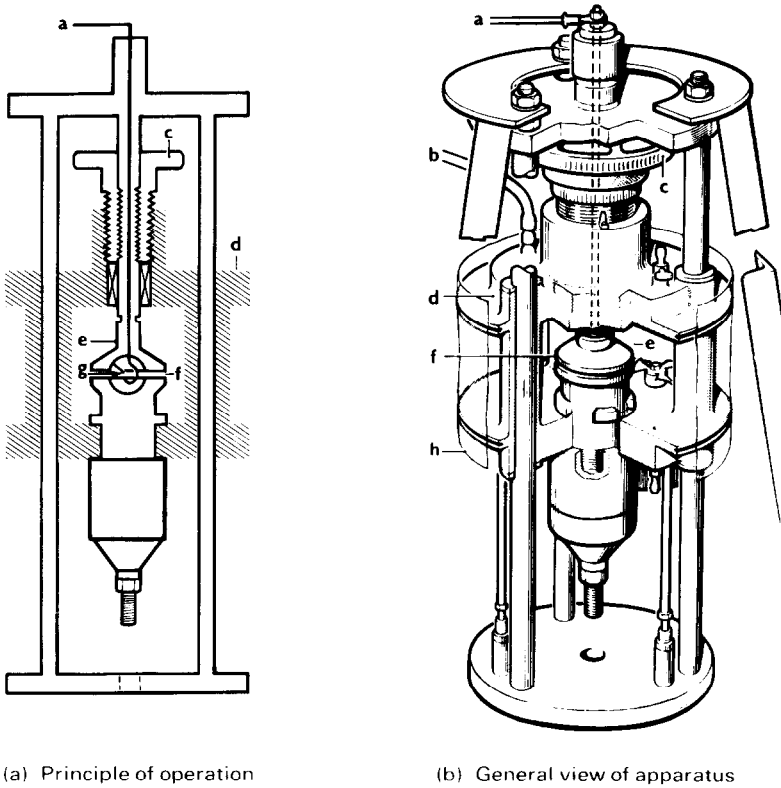
Measurements of the Maximum Experimental Safe Gaps (MESGs) for several flammable gases with oxygen-enriched air are reported. The MESGs for mixtures in air of carbon monoxide and methane and carbon monoxide and water have been measured also. The 20-cm³ apparatus was used throughout.

The results demonstrate that oxygen enrichment has a marked effect on the value of the MESG, which decreases as the oxygen enrichment increases. At high levels of oxygen enrichment very low values of MESG are obtained when the flow of the jet of hot gases through the safe gap becomes sonic.

The addition of water to carbon monoxide–air mixtures decreases the MESG rapidly, and the addition of methane to carbon monoxide–air mixtures can give MESGs with values less than those of methane–air and carbon monoxide–air. These results demonstrate the influence of reaction kinetics on the MESG.

Introduction

The Maximum Experimental Safe Gap (MESG) is a familiar quantity used in the manufacture of flameproof electrical equipment, and is defined as the maximum distance between parallel surfaces that prevents flame on one side of the flame-path formed by these surfaces from igniting all flammable mixtures of air and the fuel under test on the other side. The MESG is a safety concept with similarities to the quenching distance, although the source of re-ignition is hot burnt gas passing between the surfaces rather than the flame itself. In a standard method of measurement, a flame-path of 25 mm is situated in the equatorial plane of a 20-cm³ spherical volume. Spark ignition of a flammable mixture in this volume gives a flame which approaches the flame-path. By testing for either ignition or non-ignition of an external flammable mixture, a specified procedure is used to obtain the MESG of the fuel under test. Full details of the procedure are given elsewhere [1]. Figure 1 is a diagram of the apparatus used in the Explosion and Flame Laboratory, Buxton.



(a) Principle of operation

(b) General view of apparatus

a... Electrical cable b... Gas inlet c... Equatorial gap adjustment wheel
 d... Movable frame for adjusting equatorial gap e... Fixed head
 f... Equatorial gap g... Ignition source h... Polythene envelope

Fig. 1. 20-cm³ explosion vessel for determining MESGs.

The MESGs of a wide variety of industrial gases and vapours have been published [2]. In regulations for the construction of flameproof equipment, gases are classified according to MESG as follows:

- Class I:* Firedamp (CH₄) only: MESG = 1.14 mm
- Class IIA:* MESG ≥ 0.9 mm
- Class IIB:* 0.9 > MESG ≥ 0.5 mm
- Class IIC:* MESG < 0.5 mm

Flameproof equipment must be assessed by a certifying authority and is subject to close scrutiny for structural integrity and several other tests before certification is granted. These tests use gas mixtures with known MESGs so that the suitability of electrical equipment for a particular class can be as-

sessed. In order to achieve a margin of safety, test gases are chosen with associated MESGs narrower than those of the gases or vapours for which the flameproof apparatus is designed. A method of achieving this is to use oxygen-enriched test gases.

The work described here aims to establish the effects of oxygen enrichment on MESGs for a range of flammable gas—air mixtures. Apart from the relevance to testing, these effects are of practical importance if electrical equipment is to be used in oxygen-enriched atmospheres. Measurements are reported also which assess the effects on the MESG of adding methane and water separately to mixtures of carbon monoxide and air. These effects are investigated by using a perfectly-stirred reactor analysis.

Experimental

The MESGs have been measured for the following series of mixtures, and are shown in Figs. 2–4.

- (a) Methane and oxygen in stoichiometric proportions diluted by nitrogen.
- (b) Propane and oxygen in stoichiometric proportions diluted by nitrogen.
- (c) Ethylene and oxygen in stoichiometric proportions diluted by nitrogen.
- (d) Hydrogen and oxygen in stoichiometric proportions diluted by nitrogen.
- (e) Acetylene and oxygen in stoichiometric proportions diluted by nitrogen.
- (f) Carbon monoxide and air in stoichiometric proportions with added water vapour.
- (g) Air in stoichiometric proportion with mixtures of methane and carbon monoxide.

Commercially available cylinder gases were used in all cases. Water vapour concentrations were obtained by using a MESG apparatus heated above ambient. Methods of carrying out the MESG measurements have previously been described [1].

The MESG measurements have been standardised to conditions of 20°C and 100 kPa, by application of the following empirical equations [1]:

Pressure correction:

$$\text{Pressure-standardised MESG (100 kPa)} = \frac{\text{Measured MESG}}{0.35 + (0.0065 \times p)}$$

where p is the measured pressure in kPa.

Temperature correction:

$$\text{Standard MESG (20°C)} = \frac{\text{Pressure-standardised MESG (kPa)}}{1.0161 - (0.00081 \times T)}$$

where T is the measured temperature in °C.

Results and discussion

Oxygenated mixtures

The fuel—nitrogen MESGs are plotted against nitrogen concentration in Fig. 2. All the curves are of similar shape, showing low values of MESG — in the range of 0.02–0.04 mm — at low nitrogen concentrations (highly reactive mixtures). As the reactivity of the gas mixture decreases, the MESG increases at an increasing rate. At nitrogen concentrations of 70–80%, high values of MESG are measured and the rate of increase of MESG with increasing nitrogen content is rapid. The curves for the different fuels are not always arranged in the order that would be expected from the reactivity of the fuel—air mixtures and their MESGs, i.e., methane < propane < ethylene < acetylene < hydrogen. Although methane is substantially less reactive than the other fuels over the whole curve, hydrogen appears less reactive than both ethylene and acetylene, and, over some portions of the curve, less reactive than propane. The values of fuel—air MESGs are a function not only of the fuel reactivity but also of the nitrogen concentrations in the near-stoichiometric fuel—air mixtures at which the usual tabulated MESGs are measured. All the curves show a break-point, at various nitrogen concentrations, where the gradient changes. This discontinuity lies at the junction of the curves drawn through the measurements for each fuel, as demonstrated in Fig. 2.

Three factors determine the value of the MESG: the temperature of the emerging hot jet, the relative rate of entrainment of ambient mixture into the jet and the reactivity, defined as the rate of combustion of the gas mixture [3]. The relative rate of entrainment depends on the velocity and density of the hot jet and the size of the jet orifice (the MESG), and is defined as the rate of entrainment of mass relative to the mass of the jet. As the nitrogen content of the gas mixture decreases, the reactivity of the gas mixture increases and the internal explosion pressure at which the hot jet ejects through the safe gap increases. When the nitrogen content is relatively high (above the discontinuity in the curves in Fig. 2), the flow through the safe gap is subsonic and the increase in pressure causes a higher jet velocity and an increased relative rate of entrainment; this decreases the probability of external ignition. However, both the temperature of the jet and the reactivity are higher and this increases the probability of ignition because of the effect on the combustion rate. A smaller jet orifice is necessary to increase the relative rate of entrainment so that ignition is prevented. The smaller MESG reflects this narrowing of the jet orifice.

At relatively low nitrogen content, the hot jet is ejected at high internal pressures and the flow through the safe gap is choked. Further decrease in the nitrogen content and the consequent rises in the internal explosion pressure have relatively little effect on the jet velocity, although the temperature and reactivity do continue to increase. Thus the relative rate of entrainment must be raised by relatively greater amounts than when the flow was sub-

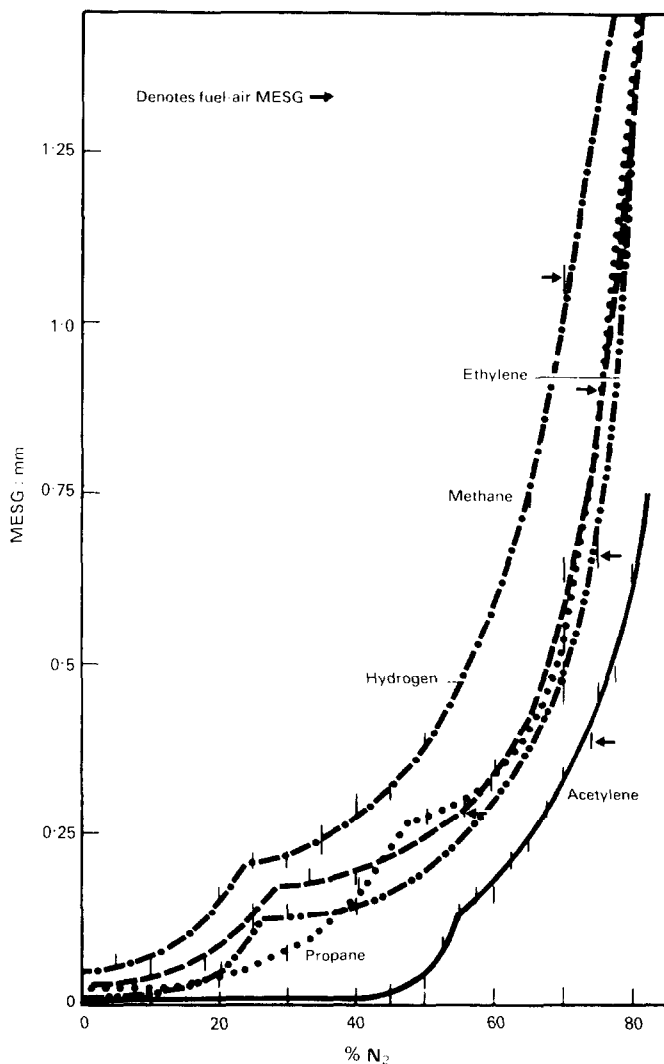


Fig. 2. MESG measurements: fuel—oxygen in stoichiometric proportions with added nitrogen.

sonic, because when the flow is choked there is no decrease in the probability of ignition resulting from an increased velocity. Thus the jet orifice must be decreased by a greater amount than previously if ignition is to be prevented. If this is so, MESGs below the values expected from extrapolation from higher nitrogen contents should be obtained once the flow of hot gas is choked. The measurements in Fig. 2 demonstrate this effect.

Since the position of the ignition source in the internal vessel and the size of the internal vessel determine when and at what pressure hot gas first ejects from the safe gap, it is probable that the nitrogen content at which the discontinuity occurs, for a given fuel, will be apparatus dependent.

Carbon monoxide MESGs

Figures 3 and 4 show the MESGs for carbon monoxide/methane and carbon monoxide/water vapour mixtures in air. The accelerating effect on carbon monoxide combustion of hydrogen-containing compounds is due to the introduction of hydrogen atoms and hydroxyl radicals into the otherwise slow reaction [4]. Both series of measurements demonstrate that small amounts of methane and water vapour can reduce the MESG substantially,

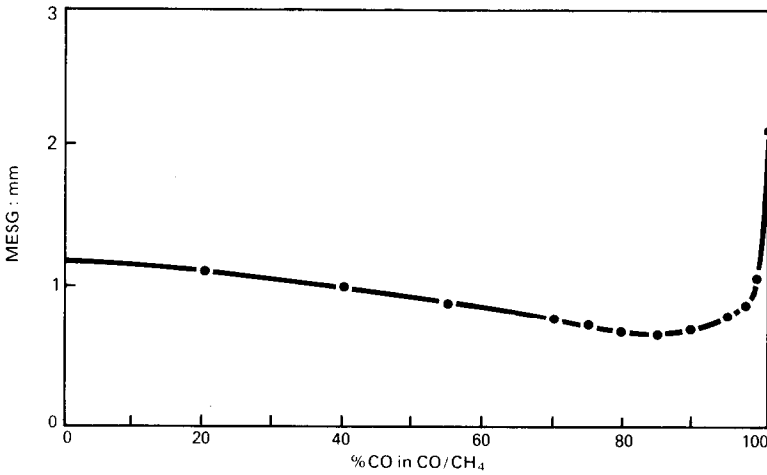


Fig. 3. MESG measurements: carbon monoxide/methane mixtures in stoichiometric proportions with air.

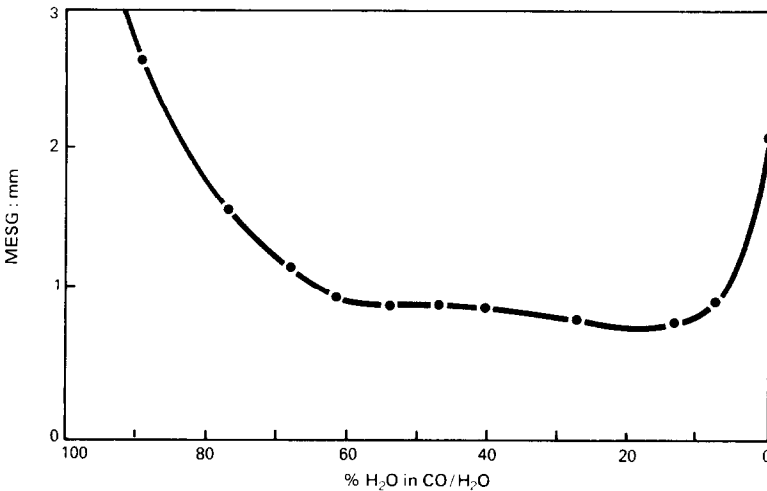


Fig. 4. MESG measurements: carbon monoxide/water mixtures in stoichiometric proportions with air.

and that the lowest value of the MESG obtained with carbon monoxide/methane mixtures is significantly less than either of the component fuels. In fact carbon monoxide/methane mixtures should be classed with IIB gases and vapours whereas methane and carbon monoxide separately are classed as IIA.

Similarly, the addition of water vapour to carbon monoxide results in MESGs below 0.9 mm and, in practice, carbon monoxide should be classed as a IIB compound.

Chemical effects

The reactions in the hot jet leading to external ignition take place in a highly turbulent, well-mixed region of hot gases and flammable mixture that can be idealised as a perfectly-stirred reactor (PSR). The "blow out" firing-rate, at which the PSR is unable to sustain itself, is a function solely of the chemical reaction. If this critical firing rate is identified with the relative rate of entrainment necessary to prevent ignition in the MESG experiments, the influence of chemical effects on the MESG should be demonstrable by calculations using a procedure for PSR analysis developed by Pratt [5].

Residence times at blow-out calculated by this method using a reaction mechanism for methane combustion given in Table 1 are shown in Figs. 5 and 6 for methane—oxygen—nitrogen mixtures and methane/carbon monoxide mixtures. The Arrhenius parameters for this scheme have been obtained from various sources in the combustion literature. The shapes of the curves in these figures compare well with the equivalent MESG—concentration curves in Figs. 2 and 3, except where changes in the velocity effects have caused the discontinuity in Fig. 2. This comparison demonstrates the effects of chemistry and reaction rate on the MESG.

Conclusions

Measurements have shown that oxygen enrichment of mixtures of flammable gas and air can substantially decrease the MESG. When the reactivity of these mixtures is high, MESGs can be less than expected by extrapolation from less reactive mixtures. These results have been attributed to the effects of velocity and temperature changes in the jet of hot gas ejected through the flame-path. The discontinuity in the MESG of nitrogen content curves has been attributed to the onset of sonic flow in the flame-path.

Addition of small amounts of hydrogen-containing compounds to carbon monoxide—air mixtures decreases the MESG markedly. Certain mixtures containing carbon monoxide can fall into a lower flameproof classification than would be expected from the component fuels. These effects have been attributed to changes in the combustion reaction and an analysis of PSR "blow-out" has been used to demonstrate how chemical effects influence the MESG.

TABLE 1

Reaction mechanism and kinetic parameters: CH₄-O₂-N₂

A	+	B	→	C	+	D	AT ⁿ exp (-E/RT)		
							A	n	
M	+	CH ₄	→	CH ₃	+	H	4.00 × 10 ¹⁷	0.0	88000.0
CO	+	O	→	CO ₂			4.00 × 10 ¹³	0.0	0.0
CH ₄	+	O ₂	→	CH ₃	+	HO ₂	8.00 × 10 ¹⁴	0.0	56000.0
CH ₄	+	H	→	CH ₃	+	H ₂	4.14 × 10 ¹³	0.0	11610.0
CH ₄	+	HO ₂	→	CH ₃	+	H ₂ O ₂	2.00 × 10 ¹³	0.0	18000.0
CH ₄	+	OH	→	CH ₃	+	H ₂ O	2.10 × 10 ¹³	0.0	4860.0
CH ₃	+	O ₂	→	H ₂ CO	+	OH	12.0 × 10 ¹¹	0.0	12500.0
H ₂ CO	+	O	→	HCO	+	OH	1.00 × 10 ¹⁴	0.0	5300.0
CO	+	O ₂	→	CO ₂	+	O	1.60 × 10 ¹³	0.0	41000.0
M	+	H ₂ O ₂	→	OH	+	OH	3.20 × 10 ¹⁶	0.0	43000.0
M	+	H ₂ CO	→	HCO	+	H	1.00 × 10 ¹³	0.0	77000.0
CH ₃	+	O	→	H ₂ CO	+	H	3.44 × 10 ¹²	0.0	3200.0
H ₂ CO	+	OH	→	HCO	+	H ₂ O	3.50 × 10 ¹⁴	0.0	1500.0
HCO	+	O ₂	→	CO	+	HO ₂	1.00 × 10 ¹⁴	0.0	6800.0
M	+	HCO	→	CO	+	H	1.00 × 10 ¹⁴	0.0	28300.0
HCO	+	OH	→	CO	+	H ₂ O	5.39 × 10 ¹²	-0.5	504.0
CO	+	OH	→	CO ₂	+	H	5.60 × 10 ¹¹	0.0	1080.0
CO	+	HO ₂	→	CO ₂	+	OH	2.99 × 10 ¹⁰	0.5	0.0
CH ₄	+	O	→	CH ₃	+	OH	2.10 × 10 ¹³	0.0	4550.0
H ₂ CO	+	O ₂	→	HCO	+	HO ₂	6.12 × 10 ¹³	0.0	38900.0
H ₂ CO	+	H	→	HCO	+	H ₂	1.00 × 10 ¹⁴	0.0	4600.0
H ₂ CO	+	HO ₂	→	H ₂ O ₂	+	HCO	1.15 × 10 ¹³	0.0	10400.0
HCO	+	O	→	CO	+	OH	2.00 × 10 ¹³	0.0	0.0
HCO	+	H	→	CO	+	H ₂	6.023 × 10 ¹²	0.0	0.0
OH	+	H ₂	→	H ₂ O	+	H	2.20 × 10 ¹³	0.0	5150.0
H ₂	+	O ₂	→	OH	+	OH	1.7 × 10 ¹³	0.0	41850.0
H	+	O ₂	→	OH	+	O	2.20 × 10 ¹⁴	0.0	16800.0
O	+	H ₂	→	OH	+	H	2.20 × 10 ¹³	0.0	9450.0
H	+	O ₂	→	HO ₂	+	M	1.59 × 10 ¹⁵	0.0	-1000.0
HO ₂	+	H	→	OH	+	OH	2.5 × 10 ¹⁴	0.0	1900.0
HO ₂	+	H	→	H ₂ O	+	O	0.737 × 10 ¹³	0.0	5400.0
HO ₂	+	H	→	H ₂	+	O ₂	2.5 × 10 ¹³	0.0	700.0
HO ₂	+	OH	→	H ₂ O	+	O ₂	0.33 × 10 ¹³	0.0	5400.0
HO ₂	+	O	→	OH	+	O ₂	2.75 × 10 ¹³	0.0	5400.0
H	+	H	→	H ₂	+	M	2.20 × 10 ¹⁴	0.0	-2750.0
H	+	OH	→	H ₂ O	+	M	2.20 × 10 ²²	-2.0	0.0
H	+	O	→	OH	+	M	5.30 × 10 ¹⁵	0.0	-2780.0
OH	+	OH	→	H ₂ O	+	O	5.75 × 10 ¹³	0.0	18000.0
HO ₂	+	H ₂	→	H ₂ O ₂	+	H	1.92 × 10 ¹³	0.0	24000.0
O	+	O	→	O ₂	+	M	3.00 × 10 ¹³	0.0	0.0
H ₂	+	HO ₂	→	H ₂ O	+	OH	2.00 × 10 ¹¹	0.0	23868.0

E = activation energy (cal mol⁻¹).*A* = pre-exponential factor (cm³ mol⁻¹ s⁻¹).*n* = exponent of temperature.

M = third body (shown at one side of equation only).

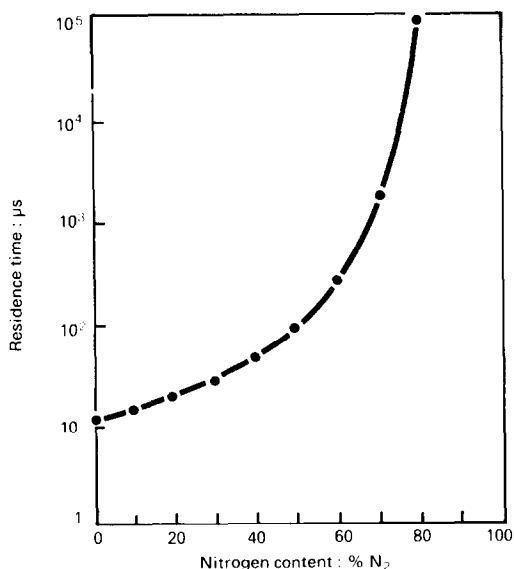
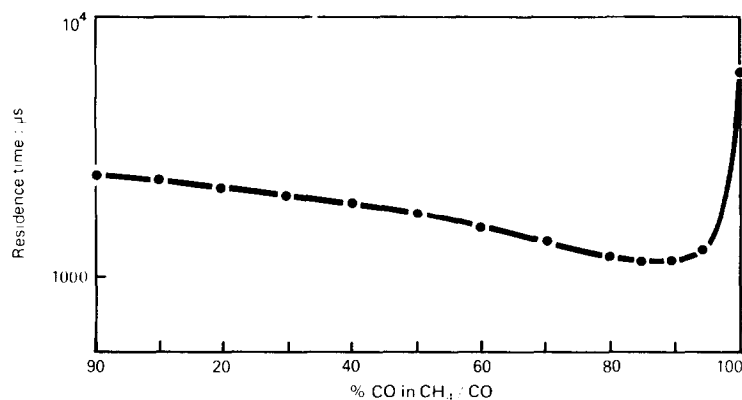


Fig. 5. Perfectly-stirred reactor "blow-out" residence times: methane—oxygen in stoichiometric proportions with added nitrogen.



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