The Flammability of Methane-Air Mixtures in Water-Base Foams

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This investigation forms part of a programme of research into flame propagation phenomena in systems in which the gas phase is accompanied by a physically-distributed liquid phase (e.g. spray , foam or film) which plays some part, either as a fuel or as a suppressant, in the combustion process. In the present instance the object was to examine the extent to which the flammability range of a methane-air mixture is restricted by inclusion in water foams of defined properties. So far as we are aware this subject had not previously been studied, except for some preliminary experiments (as yet unpublished) carried out at the Safety in Mines Research Establishment at Buxton, England, through which the problem first came to our attention. The influence of water vapour upon the flammability range of methane in air has been studied by Coward & Gleadall[1] and by Yeaw & Shnidman[2]; and Billett[3] has examined the effect of water spray on the flammability of butane in air.

The foam properties with which correlation of the flammability range was sought were "wetness" and bubble size. "Wetness" was defined by an inverse function, the "expansion ratio", which was taken to be the ratio of the volume of a certain quantity of foam to the volume of liquid therein. An object of the experimental method of foam generation was to attain uniform bubble-size throughout any particular foam and the size was defined by a mean diameter.

Apparatus and methods.

A continuous flow system was employed to prepare methane-air mixtures and to generate foams having these mixtures as the contained gas-phase. Air and methane from compressed gas cylinders were passed through drying towers, flow control valves and orifice flow meters before mixing. The mixture then passed through a water saturator and a capillary to damp out bubbling pulsations before entering the foam generator. In this, the gas mixture bubbled through a copper gauze submerged in detergent solution to a controlled depth. The bubbles escaping from the liquid surface gave rise to a foam of reasonably uniform bubble size which ascended a perspex drainage column of controllable

height before turning into the horizontal flammability testing tube. This consisted of a perspex tube $2\frac{3}{4}$ in. internal diameter and some 4 ft. long which was continuously rotated about its axis so as to minimise drainage from the foam travelling along it. Foam emerging from the end of the tube fell into an open waste receiver.

Inflammability of the foam in the tube could be tested at any time by applying a one-inch coal gas flame to the open end and seeing whether or not flame would propagate throughout the contents of the tube. The products of propagation, if any, were swept out by the oncoming foam in readiness for another test. The rate of flow of foam along the tube did not exceed 1 cm/sec. whereas the minimum rate of flame propagation was 12 cm/sec. The flow of foam did not, therefore, interfere with flammability testing.

The foam properties were measured on samples emerging from the end of the tube. Expansion ratio was measured by allowing a known volume of foam to fall into a measuring vessel containing a layer of hexanol as separable foam breaker, and measuring the volume of the aqueous liquid formed. Bubble size was measured by allowing the foam to fall into a flat-bottomed perspex receiver containing a thin layer of the detergent solution. The foam was photographed through the bottom of this receiver, which was inscribed with a cm. scale, and after suitable enlargement of the plate, the mean diameter of some 250 bubbles was found by measurement.

The detergent solution consisted of a 1% solution in distilled water of "Perlankrol" (Lankro Chemicals Ltd., Eccles, Manchester, England) and had a surface tension of 26.3 dynes/cm. at 20°C, as measured by the capillary rise method.

The expansion ratio of the foam could be controlled by the gas flow (bubbling) rate and also by varying the height of the foam drainage column. Bubble size was primarily controlled by the mesh of the copper gauze through which bubbling took place, but was also influenced by the gas flow rate. Approximate ranges of variation available for satisfactory use were: expansion ratio 20 to 1500; bubble diameter 1 to 4.5 mm.

The method of conducting an experiment was as follows. With a gauze appropriate to the bubble size required, the air flow was adjusted to give approximately the desired expansion ratio. Methane was then added to the gas stream and its flow rate adjusted to give a limit mixture in the foam, as judged by repeated flammability tests. Samples of foam were then taken for measurement of properties and these were recorded against the limit gas mixture composition as determined from the flow meter readings.

Results.

In the absence of foam, the flammability limits of the

methane in air in the horizontal tube were 5.41 and 13.94 vol.-%. In the presence of foam these were narrowed to varying degrees. The narrowing was in general increased with decreasing bubble size. The effect of varying expansion ratio (R) was however somewhat complex. It is illustrated by a few figures in the accompanying table, but may be summarised as follows:

(1) For values of R between 1500 (the highest used) and about 300, the flammable range narrowed with decreasing R (increasing wetness), and at 300-250 reached a minimum, which for the smaller bubble sizes amounted to complete suppression.

(2) For values of R between 300 and 70, the flammable range widened again, reaching a maximum at about the latter value.

(3) For values of R below 70, the flammable range again contracted with increasing wetness and with R about 20, flame propagation creased.

In regions (1) and (2) the flame front was almost flat and vertical. With the driest foams in region (1), a definite gap appeared between the flame-front and the collapsing foam ahead. In both regions spray arising from the collapsing foam could be seen in and near the flame-front.

In region (3), the passage of the flame did not result in complete destruction of the foam. Kernels of flame travelled independently of one another, leaving behind considerable amounts of unconsumed foam.

A convincing demonstration of the existence of regions (1) and (2) could be provided by allowing an initially non-flammable foam of expansion ratio about 300, mean bubble size 1.50 mm. containing a 9% methane-air mixture, to drain for about 20 sec. by stopping the rotation of the tube, prior to ignition. The upper and lower halves of the foam could then be ignited separately and would propagate flame independently leaving unconsumed a central layer some 2 cm. thick. Due to drainage, the upper and lower layers had moved respectively into Regions (1) (dry) and (2) (wet), leaving the central layer non-flammable between the two regions.

Discussion.

The fact that the limits of flammability in foams of fixed bubble size, but varying expansion ratio, are generally symmetrical about the stoichiometic methane-air mixture, and converge upon it when convergence occurs, suggests that the principal function of the foam is to absorb the available energy in the mixture. For flame propagation to continue, some of the energy released by mixture burning in one bubble must be used to rupture the walls of the bubble and so gain access to unburnt mixture in adjacent bubbles. The heat transferred from the existing flame front towards the unburnt mixture thus released will be shared by such

liquid water as is in the area to an extent dependent upon the state of division (i.e. surface area) of the water at the time.

In Region (1) the foam is dry and bubble walls are thin. The rupture of the walls by the advancing flame gives rise to water droplets which lower the flame temperature in the course of being volatilised. Thus mixtures just able to propagate flame in the absence of foam are no longer able to do so in its presence and the limits of flammability are narrowed. With decreasing expansion ratio, the bubble walls become thicker and hence the water droplets formed become larger. So long as the droplets remain small enough to be vaporised completely during their passage through the advancing flame, this increase in size will cause increasing suppression of the limits as is observed in Region (1).

In Region (2) it appears that with increasing wetness (decrease of R) the size of droplets formed is rapidly increasing and ultimately droplet formation associated with the foam rupture ceases to be recognisable. In these circumstances the cooling effect of the foam, which is primarily exerted through droplet formation, has become much decreased and the limits are widened.

Finally, in Region (3), the energy required to break through the bubble walls, which increases continually with decreasing expansion ratio, becomes great enough to take significant toll of the energy available from the burning mixture and the limits converge to final suppression. In this region the situation is complicated a little by the fact that flame propagation does not occur uniformly through the foam. It seems likely that the flame makes its way through slightly less wet parts of the foam with the result that the remaining parts become somewhat wetter, through the relegation of foam debris, and so remain unburnt.

Throughout regions (1) and (2) in which droplet formation, or the lack of it, is the controlling factor, an effect of bubble size (d) is superimposed upon the effect of expansion ratio (R). Thus with smaller bubble size (i.e. thinner bubble walls for a given expansion ratio) smaller droplets are formed and the suppression effect is greater. In fact, if limits are plotted upon a basis of R/d in these regions the curves superimpose fairly well for the range of bubble size examined.

References.

(1) H.F. Coward and J.J. Gleadall, J.Chem. Soc. 1930, 243-8
Extinction of methane flames by water vapour.

(2) J.S. Yeaw and L. Shnidman. Proc. Am. Gas Assoc. 1938, 20, 717-45.
Extinction of gas flames by steam.

(3) H.Billett, vide B.F. Mullins & S.S. Penner. "Explosions, Detonations, Flammability and Ignition".
Pergamon Press, 1959, pp. 247-9.

TABLE

Selected values of lower and upper flammability limits (vol.-%) methane in air in foam of varying expansion ratio, but approximately constant bubble diameter = 1.5 - 1.8 mm.

Expansion ratio	Lower limit	Expansion ratio	Upper limit
38.5	7.87	37.8	11.55
53.3	7.50	49.1	11.93
82.6	7.29	79.3	11.94
130	7.44	126	11.68
189	8.24	179	10.57
217	8.77	262	9.66
279	9.43	280	9.50
321	9.35	325	9.68
438	9.04	436	9.92
598	8.72	586	10.86
692	7.56	701	11.19
878	7.48		
∞ (dry)	5.41	∞ (dry)	13.94