THE FLAMMABILITY OF MISTS AND SPRAYS

By J. H. BURGOYNE, D.Sc., Ph.D., F.R.I.C.*

SYNOPSIS

After a brief review of the literature, measurements of the effect of drop size on the lower flammability and nitrogen dilution limits for tetralin-in-air suspensions are reported. The concept of " concentration " of the fuel is discussed in this context, and conclusions are drawn regarding the practical explosion hazard connected with mists and sprays of combustible liquids in air.

Introduction

Suspensions of finely-divided liquids in air commonly arise in practice through the processes either of condensation of the saturated vapour or of atomisation of the liquid. Since condensation is essentially a growth process, whilst atomisation is one of size reduction, the drop size is characteristically less in the former than it is in the latter. Where these processes occur in an uncontrolled manner, the " mist " formed by condensation is unlikely to contain many drops of diameter greater than 0·02 mm, whilst the " spray " formed by dispersion will contain few drops as small as this. If control is exerted it is of course possible to cause the size ranges to overlap almost as much as may be desired.

If the suspended liquid is combustible, the suspension will be capable of propagating flame from a suitable source of ignition, provided that the concentration of drops is great enough, having regard to the size of the drops present. The suspension will then be capable of giving rise to an " explosion" if it is ignited within the confines of plant or building. This is true even though the liquid is so involatile at the prevailing temperature that no appreciable concentration of vapour can be present. The purpose of this paper is to discuss what is known regarding the interrelation between the concentration of a suspension of an involatile combustible liquid in air necessary to permit explosion on ignition, and its drop size characteristics—in other words, the relation between the lower limit of flammability and the drop size. Consideration will also be given to the related question of the amount of a diluent gas, such as nitrogen, that must be added to the air in order to make the formation of a flammable or explosive suspension impossible whatever the concentration of suspended matter.

It is to be assumed that any flammable suspension will have an upper limit of flammability as well as a lower limit. Little satisfactory information is available on this subject, however, and the matter will not be pursued in this paper. The difficulty about the experimental measurement of upper limits in suspensions is that any lack of uniformity of concentration near the limit permits flame to propagate through the region of lower concentration, whilst leaving the region of greater concentration unaffected. Since such lack of uniformity is extremely difficult to avoid at the high concentrations concerned, an extended range of average concentrations is experienced over which partial flame propagations

* Department of Chemical Engineering and Chemical Technology, Imperial College, London, S.W.7.

occur and so the upper limit concentration cannot be defined with any precision. As the same kind of situation will arise in practice, it may be thought that the definition of an actual upper limit concentration, even if this could be achieved, would not serve a particularly useful purpose.

Measurements of the Lower Limit of Flammability of Condensed Mists

Haber and Wolff[1] measured the lower limits of condensed mists of three organic liquids using a vertical cylindrical explosion vessel 3 in. diameter and 20 in. long. Ignition was by pilot flame at the lower end and the upper end was open at the instant of firing. The following values were obtained, including in each case the small proportion of vapour associated with the liquid suspension:

Petroleum fraction	0·044 oz/ft³
Tetralin	0·041 oz/ft³
Quinoline	0·066 oz/ft³

It was pointed out that the values were closely similar to those obtainable for the corresponding vapours at the higher temperatures necessary to achieve the requisite vapour pressure.

Burgoyne and Richardson[2] measured the lower limits for condensed mists of a number of mineral and other oils, using a long 1·9 in. diameter vertical tube with pilot-flame ignition at the lower, open end. Values ranging from 0·042 to 0·056 oz/ft³ were obtained. Burgoyne, Newitt, and Thomas,[3] using a similar 2 in. tube, obtained a value of 0·049 oz/ft³ for a mineral lubricating oil.

Investigations of the Effect of Drop Size on the Lower Limit of Flammability

In all the foregoing investigations the suspensions were formed by largely uncontrolled condensation. Drop sizes were therefore quite small. The first attempt to correlate lower limit with drop size was made by Burgoyne and Cohen.[4] For this purpose they developed a generator for the production of pure liquid suspensions having essentially uniform and controlled drop size. The method[5] was based upon that of Sinclair and La Mer.[6] A saturated vapour was condensed under conditions of controlled cooling in nitrogen containing a controlled concentration of condensation nuclei, and oxygen added in proportion as in air. The liquid employed was tetralin and lower limit measurements were made in a long

2-in. vertical tube with pilot flame ignition at the lower, open end. The concentration of liquid in a suspension at the limit of flammability was measured with the aid of a device that suddenly enclosed a known length (i.e. volume) of the tube through which the unburnt mixture was flowing slowly downwards, and collecting and weighing the total amount of liquid suspended therein. In this way a number of measurements were made of limit values corresponding to mean drop diameters up to 0·055 mm. The values given in Table I are

TABLE I.—*Lower Limiting Concentrations for drops of Tetralin to Give Flammable Suspensions*

Drop diameter (mm)	Limiting concentration (oz/ft²)
0·010	0·045
0·020	0·037
0·030	0·026
0·040	0·019
0·050	0·018

taken from the smoothed relationship. These results were extended by Burgoyne and Taylor.[7] As a result of a careful study of the effects of controls on the operation of the generator and with scrupulous attention to cleanliness, it was possible to extend considerably the range of drop diameters, while maintaining substantially uniform drop size in each suspension. Using a 2 in. flammability tube, open at the top end with pilot-flame ignition at the lower closed end, they succeeded in confirming the results of Burgoyne and Cohen for drop diameters up to 0·055 mm and obtained the further results given in Table II. The method of measuring concentration at the limit was unchanged.

TABLE II.—*Results of Burgoyne and Taylor for the Lower Limiting Concentrations for Drops of Tetralin to give Flammable Suspensions*

Drop diameter (mm)	Limiting concentration (oz/ft³)
0·077	0·012
0·087	0·0096
0·093	0·0079
0·099	0·0071
0·111	0·0060
0·115	0·0046
0·136	0·0029

Tables I and II indicate a rapid fall of the lower limit value with increasing drop diameter. Reflection shows, however, that the significance of " concentration " requires further consideration when related to a suspension in which one component (the liquid) is moving more quickly (downward) than the other (the air) and flame is travelling (upward) against both flows. Clearly, the rate of flow into the flame front of liquid relative to air, is greater than is indicated by the above " concentration " figures if the liquid is travelling the faster.

Burgoyne and Taylor devised a method of directly measuring the relative rates of flow of liquid and air into the flame front under limit conditions. This consisted in withdrawing a sample of the product gases from directly behind the limit flame travelling up the tube and finding the carbon: nitrogen ratio therein. This was done by oxidising all carbonaceous products, over copper oxide, to carbon dioxide and finding the ratio of this gas to nitrogen in the products by conventional gas analysis. From the resultant ratio of carbon to nitrogen in the products, the ratio of tetralin to air passing through the limit flame-front could be inferred directly.

At the same time, further developments in the generator permitted an extension of the range of drop diameters available up to over 0·2 mm and with the aid of a hypodermic battery, as described by Rasbash[8] drop diameters up to 1·5 mm

were achieved. The full set of flame front concentrations at the limit of flammability then obtained in relation to drop size for tetralin are given in Table III.

TABLE III.—*Flame Front Concentrations at Limit of Flammability for Drops of Tetralin*

Drop diameter (mm)	Flame front concentration at limit (oz/ft³)
0·096	0·040
0·104	0·043
0·106	0·041
0·115	0·038
0·129	0·037
0·137	0·034
0·151	0·036
0·159	0·031
0·162	0·036
0·175	0·030
0·191	0·030
0·208	0·031
0·560*	0·100
1·500*	No propagation

* *Mean drop diameters for suspensions formed with the hypodermic battery*

In the meantime, Browning, Tyler, and Krull[9] investigated the effect of particle size on the lower limit of flammability of a uniform suspension of methylene bistearamide (a solid wax), graded by elutriation into size fractions of 0·010 mm range, with mean diameters from 0·015 to 0·085 mm. The suspension was circulated in a closed loop system and ignited by electric arcs. The figures given in Table IV were obtained.

TABLE IV.—*Effect of Particle Size on Limit of Flammability of Methylene Bistearamide (due to Browning, Tyler, and Krall)*

Particle diameter (mm)	Limiting concentration (oz/ft³)
0·015	0·047
0·025	0·043
0·035	0·035
0·045	0·031
0·055	0·025
0·065	0·022
0·075	0·039
0·085	0·043

Downward Flame Propagation

Burgoyne and Cohen were able to obtain downward propagation of flame only with the smallest drop sizes. With 0·009 mm drops, the limit for downward propagation was 0·052 oz/ft³ compared with 0·046 oz/ft³ for upward propagation. With 0·021 and 0·036 mm drops only partial downward propagations could be obtained with the limited range of concentrations available. With 0·110 mm drops, Burgoyne and Taylor could observe no tendency to downward propagation at all. The indication is that downward propagation becomes more difficult with increasing drop size, although the difficulty of getting higher concentrations of the larger-drop suspensions has limited the investigation of this point.

Suppression of Flammability by the Addition of Diluent Gases

The progressive addition of incombustible gas to the air supporting a liquid drop suspension raises the lower limit of flammability, slowly at first, but with increasing rapidity later. Finally, at a certain proportion of added gas it becomes impossible to form a flammable suspension. Burgoyne,

Newitt, and Thomas found that with a condensed lubricating oil mist (drop diameter mainly below 0·01 mm) the requisite addition of carbon dioxide for suppression of flammability was 28·3 vol % which is similar to the figures generally obtained for hydrocarbon vapours of various kinds. Burgoyne and Cohen showed that with 0·010 mm and smaller drops of tetralin, the limiting addition of nitrogen was about 40 vol % which is again near to typical figures for hydrocarbon vapours generally. With larger drops, however (up to 0·045 mm), the requisite proportion of added nitrogen increased somewhat.

Burgoyne and Taylor confirmed and extended these observations, and obtained the results given in Table IV with mono-disperse tetralin–air suspensions.

TABLE IV.—*The Suppression of Flammability of Air–tetralin Suspensions*

Drop diameter (mm)	Nitrogen in air to suppress flammability (vol %)
0·009	38
0·017	57
0·052	57
0·110	47
0·150	47
0·190	38
0·208	28

Discussion and Application of Results

Several of the investigations mentioned have indicated that, for suspensions in which the drop diameter is of the order of 0·010 mm or less, both the lower limit of flammability and the dilution limit (proportion of diluent gas required to suppress flammability) have values that would be expected to apply to the *vapour* of the liquid concerned. Burgoyne and Cohen showed, in fact, that in suspensions of drop diameter less than 0·014 mm the drops have time to vaporise completely, due to heat transmission to them, before becoming engulfed by the oncoming flame. In these circumstances, therefore, the flame does in fact propagate into a vapour–air mixture, and it is not surprising that the suspension exhibits the flammability characteristics of the corresponding vapour–air system.

The drop size range to which these remarks apply is that which characterises mists formed by uncontrolled condensation. It follows therefore that the mistwise condensation of the vapour of a combustible liquid produces no change in flammability characteristics. In other words, the condensation of a flammable vapour–air mixture is likely to produce a flammable mist, unless and until deposition of some of the condensed liquid occurs.

The relative constancy of the lower limit of flammability of the condensed mists of various hydrocarbon materials mentioned in this review draws attention to the uniformity of values found for lower limits of hydrocarbons generally, when such limits are expressed in terms of weight of fuel per unit volume of air. Similar uniformity is experienced with saturated hydrocarbons generally, but the limit value rises with increasing proportions of oxygen, nitrogen, or halogen in the molecule, and decreases with unsaturation. This is illustrated by Table V, which indicates lower limit values for a wide range of organic vapours in air. From the conclusions of the present review it follows that these values hold also for the lower limits of mists formed by uncontrolled condensation.

Burgoyne and Cohen showed that with drop diameter increasing above the range of 0·01–0·02 mm the mechanism of flame propagation in a suspension changes. No longer do the drops have time to vaporise completely before becoming involved in the advancing flame front. Therefore, to an increasing degree as the drop size increases, the liquid burns in a diffusion flame associated with each drop, rather than as a communal vapour–air mixture. When the drop diameter has reached about 0·04 mm dropwise burning is the principal mechanism of combustion and it appears that the flame propagates by the communication of " fire " from one drop to another.

As the drop diameter rises above about 0·02 mm another change occurs. The rate of sedimentation of the drops, *i.e.* their rate of fall relative to the supporting air, becomes comparable with, and ultimately greater than, the rate of upward propagation of the slowest (*i.e.* the limit) flame. In these circumstances, the " concentration " of the fuel in the air, as measured in the usual terms of weight per unit volume, gives a misleading idea of the relative rates of flow of fuel and air into the propagating flame front. The matter may be put rather simply as follows.

Let C_s represent the concentration of suspended liquid, in weight per unit volume of air, measured by the method of enclosing a known volume of suspension and finding the weight of liquid drops therein. We will call this the " static " concentration. Let V_s be the sedimentation velocity of the drops, *i.e.* their downward velocity relative to the air; and let V_f be the upward velocity of the flame front relative to the air. Then the velocity of the drops relative to the flame is $V_s + V_f$ and the rate of flow of liquid into the flame front, relative to the rate of flow of air, *i.e.* the " flame front concentration " is given by:

$$C_s \left(\frac{V_s + V_f}{V_f} \right).$$

Let us call this the " kinetic " concentration and denote it by C_k. Then:

$$\frac{C_k}{C_s} = \frac{V_f + V_s}{V_f}.$$

When the drops are sufficiently small, V_s is small compared with V_f and $C_k = C_s$, but the difference between C_k and C_s increases as progressively greater drop sizes are considered.

For the downward propagation of flame through a suspension in which the air is stationary, V_f as defined above becomes negative.

TABLE V.—*Lower Limits of Flammability of Organic Gases and Vapours in Air*

|	(oz/ft³)
Paraffin hydrocarbons	0·044–0·054
Cyclo-paraffins	0·046–0·055
Benzene	0·049
Ethylene	0·039
Propylene	0·046
Butylene	0·051
Butadiene	0·052
Acetylene	0·030
Dimethyl ether	0·073
Higher aliphatic ethers	0·065–0·069
Ethylene oxide	0·074
Propylene oxide	0·078
Aliphatic aldehydes	0·078–0·082
Acetone	0·080
Methyl alcohol	0·113
Ethyl alcohol	0·092
Higher aliphatic alcohols	0·061–0·065
Methyl formate	0·168
Ethyl formate	0·092
Ethyl acetate	0·103
Propyl acetate	0·095
Butyl acetate	0·090
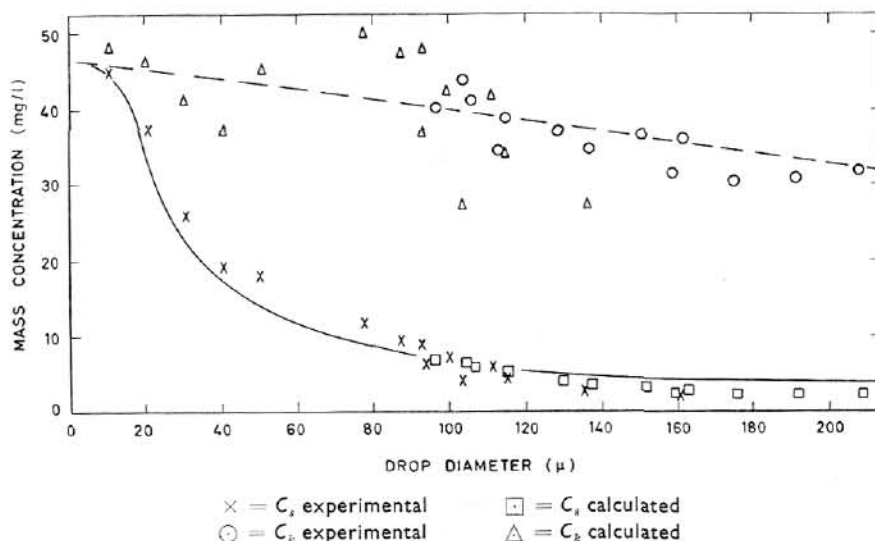
Fig. 1.—Correlation of " static " and " kinetic " concentrations at the lower limit of flammability of tetralin–air suspensions with varying drop diameter

Thus:

$$\left(\frac{C_k}{C_s}\right)_{\text{downward}} = \frac{V_f - V_s}{V_f}$$

If we make the somewhat arbitrary assumptions that, at the limit, V_f is numerically the same for downward as for upward propagation, and that C_k is also the same in the two cases, we have:

$$(C_s)_{\text{up}}\left(\frac{V_f + V_s}{V_f}\right) = (C_s)_{\text{down}}\left(\frac{V_f - V_s}{V_f}\right).$$

For 0·009 mm drops, for which $V_s = 0·3$ cm/s, Burgoyne and Cohen found $(C_s)_{\text{up}} = 45·7$ oz/ft³ and $(C_s)_{\text{down}} = 52·1$ oz/ft³.

Hence:

$$45·7\left(1 + \frac{0·3}{V_f}\right) = 52·1\left(1 - \frac{0·3}{V_f}\right)$$

and:

$$V_f = \frac{97·8 \times 0·3}{6·4} = 4·6 \text{ cm/s.}$$

On the assumption that the limit is reached when the relative flame velocity has this value, the measurements of C_s and C_k at the limit for tetralin–air suspensions may be correlated with the aid of the equation:

$$\frac{C_k}{C_s} = \frac{V_f + V_s}{V_f}$$

using sedimentation velocities calculated from the drop size by the modified form of Stokes Law given by Davies.[10] Fig. 1 shows this correlation, using all the results available. Limit C_k values are calculated from C_s values, and *vice versa*. The result encourages the belief that sedimentation of the drops is the main factor determining the difference between C_s and C_k and that the simple relation given above embodies most of the truth.

The results as a whole show that the flame front concentration at the limit, represented by C_k, decreases significantly as the drop size increases and the " vapour " mechanism of flame propagation gives way to the dropwise spread of flame. The author noticed several years ago[11] that the lower limit concentrations for dust suspensions often appear to be lower than one has reason to expect; and suggested that the explanation of this may lie in the fact that with particles, flame propagation owes a good deal to heat transfer by radiation. Since gases are transparent to radiation, particle-to-particle ignition can occur without raising the temperature of the intervening air to the same extent as in a purely gaseous mixture, where the fuel and air are uniformly mixed. The effect may be enhanced with sedimenting drops or particles since these burn with an elongated " tail " of flame, which grows longer as the size, and so the sedimentation velocity, increases. This gives rise to an extended source of heat transfer for dropwise propagation. Similar reasons help to explain why abnormally large proportions of diluent gas are necessary to suppress inflammability in the size range where dropwise flame propagation occurs.

To sum up, the following practical conclusions may be drawn:

(1) For suspensions formed by uncontrolled condensation of the saturated vapour, the drop size is small and the lower limit of flammability, measured as weight of liquid per unit volume of air, is essentially the same as that for the vapour. For saturated hydrocarbons this is of the order of 0·045 oz/ft³ (or g/l.): for unsaturated hydrocarbons it is less and for oxygenated compounds it is more. Such concentrations of finely divided drops are of considerable optical density and may be conveniently monitored by light extinction methods. (See Brown.[12])

(2) For suspensions formed mechanically, the drop size is characteristically larger and in specifying lower limit concentrations account must be taken of the conceptions of " static " and " kinetic " concentrations which recognise the effect of sedimentation of the drops. If a filtration method of estimating " concentration " is used, the suspension should be drawn *downward* into the filter at a relative air velocity of about 5 cm/s. In this way the filter simulates the rising limit flame and a value corresponding to the " kinetic " concentration is obtained.

(3) For mechanically-formed sprays with drop diameters in the characteristic range of 0·020 to 0·200 mm the requirement of diluent gas for flame suppression is abnormally high. In the condensed mist range (below 0·020 mm) the requirement is similar to that for the vapour.

(4) In very coarse sprays, with drop diameters somewhere between 0·6 and 1·5 mm, normal flame propagation becomes impossible although burning drops could carry flame downwards. The presence of smaller drops in such a suspension may, depending on their concentration, make upward flame propagation possible. Further, the entry of a fast-moving explosion flame (*e.g.* from a pipe run) into a chamber containing a suspension that is normally noninflammable due to large drop size is likely to lead to flame propagation, through the shattering effect on the drops of the pressure waves preceding the explosion flame.

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